

Cluster-glass behaviour of the substituted molybdenum ferrite: a magnetic and Mössbauer study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 9963

(<http://iopscience.iop.org/0953-8984/12/48/312>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 07:03

Please note that [terms and conditions apply](#).

Cluster-glass behaviour of the substituted molybdenum ferrite: a magnetic and Mössbauer study

L Wang^{†||}, J Ding[‡], A Roy[§], J Ghose[§], Y Li[‡] and Y P Feng[†]

[†] Physics Department, National University of Singapore, Lower Kent Ridge Road 119260, Singapore

[‡] Material Sciences Department, National University of Singapore, Lower Kent Ridge Road 119260, Singapore

[§] Chemistry Department, India Institute of Technology, Kharagpur 721 302, India

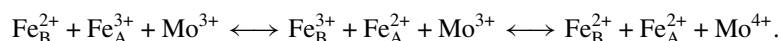
E-mail: scip8038@nus.edu.sg (L Wang)

Received 16 June 2000, in final form 12 September 2000

Abstract. Magnetic and Mössbauer spectroscopy studies have been carried out to investigate the ferrite $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$. Zero-field-cooled (ZFC) and field-cooled (FC) data, hysteresis loops, coercivity measurements, Mössbauer analysis and magnetic relaxation measurements show the presence of a cluster-glass behaviour. All of the results indicate that the ferrite may consist of two components: ferrimagnetic clusters and an antiferromagnetic matrix. The ferrimagnetic cluster may be Mo rich and has a compensation temperature, and its Curie temperature is higher than that of the antiferromagnetic matrix.

1. Introduction

The iron-based oxide system comprises a number of crystal structures. Fe_2MoO_4 is a cubic spinel compound, which has unusual magnetic properties and has been investigated by many researchers (Ghose *et al* 1974, Gupta *et al* 1979, Ramdani *et al* 1985, Abe *et al* 1971, 1973). It has been shown that the cations at the tetrahedral and octahedral sites (denoted as A and B sites) of the spinel lattice are Fe^{2+} , Fe^{3+} , Mo^{3+} and Mo^{2+} . The electric charge can be transferred among different cations. The formal valence assignment can be represented by the equilibrium reactions



Recently, Roy *et al* (1997, 2000) studied the magnetic and room temperature Mössbauer properties of titanium-substituted $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples. Their work has shown that titanium ions dominantly replace the A-site Fe^{3+} ions. This leads to many changes in the magnetic and electric transport properties of the molybdenum–titanium ferrite sample.

Spin-glass (SG) states have been found in a wide variety of systems including magnetic insulators and amorphous alloys with the following common features: (1) freezing of magnetic moments below some freezing temperature (T_f), (2) lack of periodic long-range magnetic order; (3) remanence and magnetic relaxation over macroscopic timescales below T_f when there are changes of magnetic field. A modified version of the SG system, termed a ‘cluster glass’ (CG), can be considered to be a set of clusters, formed due to short-range ordering in some

|| Lan Wang: author to whom any correspondence should be addressed.

temperature range. Recently, a CG state has been found in many amorphous alloys, thin magnetic films and oxide compounds (Wang *et al* 2000, Pogorelov *et al* 1999, Nam *et al* 1999, Li *et al* 1999, Dimitrov *et al* 1999, Mukherjee *et al* 1996).

In this work, magnetic and Mössbauer studies on $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ were done at various temperatures. Our study has shown that ferrimagnetic clusters and antiferromagnetic matrix may exist in this system.

2. Experimental techniques

A spinel of the composition $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ was prepared by mixing stoichiometric amounts of Fe_2O_3 (Specpure, Johnson-Matthey), Fe (electrolytic grade, Sarabhai Chemicals), MoO_2 (reduced from Specpure MoO_3) and TiO_2 (analytical grade, SD Fine Chemicals), and thoroughly grinding in an agate mortar for several hours. The pellet form of the sample was placed inside a quartz tube, which was then degassed under vacuum and sealed. The sealed tubes were heated to 1443 K for two hours and then quenched in liquid nitrogen.

X-ray diffraction analysis of the sample was carried out in a Philips x-ray diffraction unit (Model PW1710) using $\text{Co K}\alpha$ ($\lambda = 1.7989 \text{ \AA}$) with a Ni filter. X-ray diffraction analysis of the polycrystalline sample shows the presence of a single-phase cubic spinel.

The magnetization measurements were carried out under magnetic fields of up to 90 kOe in the temperature range from 5 to 300 K, using a vibrating-sample magnetometer. In the zero-field-cooled (ZFC) measurements, samples were cooled to 4.2 K in zero applied field and then a constant field was applied during the increase in temperature. For the field-cooled (FC) measurements, the sample was cooled down to 4.2 K under an applied field and then magnetization versus temperature was measured in a constant field. The dc magnetic relaxation experiments were done at 80 K.

The Mössbauer spectra were recorded with a Ranger Mössbauer spectroscope in the temperature range of 4.2–295 K.

3. Results and discussion

Figure 1 shows the Mössbauer spectra at various temperatures. The room temperature spectrum (295 K) comprises a broad doublet which has been shown to be due to the presence of Fe^{2+} and Fe^{3+} ions at the A and B sites of the spinel lattice (Roy *et al* 2000). The spectra show magnetic splitting below 250 K, indicating that the ferrite becomes magnetically ordered below a transition temperature of ~ 250 K. This is very close to the T_C -value (225 K) found from the magnetic measurements on $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ (Roy *et al* 1997). All the spectra below 250 K clearly show that there are several magnetic sextets present in this ferrite. This is expected, as there are Fe^{2+} and Fe^{3+} ions distributed between the two sites of the spinel lattice. If the distribution of the ions is non-uniform or random for each type of site, then there is a likelihood of spin-glass or cluster-glass formation. We tried to fit the low-temperature spectra with four sextets; however, a doublet was required to obtain good fitting in addition to the four sextets, and the site population of the doublet also increased with increasing temperature over a large temperature range as shown in figure 2. The magnetically split component coexists with its collapsed component which grows at the expense of the sextet with increasing temperature. Such a superparamagnetic behaviour is characteristic of variable spin clusters as discussed earlier (Chechersky *et al* 1993, Nath *et al* 1994). The sextets are very broad (the average halfwidth is about $0.7\text{--}0.8 \text{ mm s}^{-1}$), which may be due to the random distribution of the ions and the fluctuation of spin clusters or spins. The main features of our fitting—the

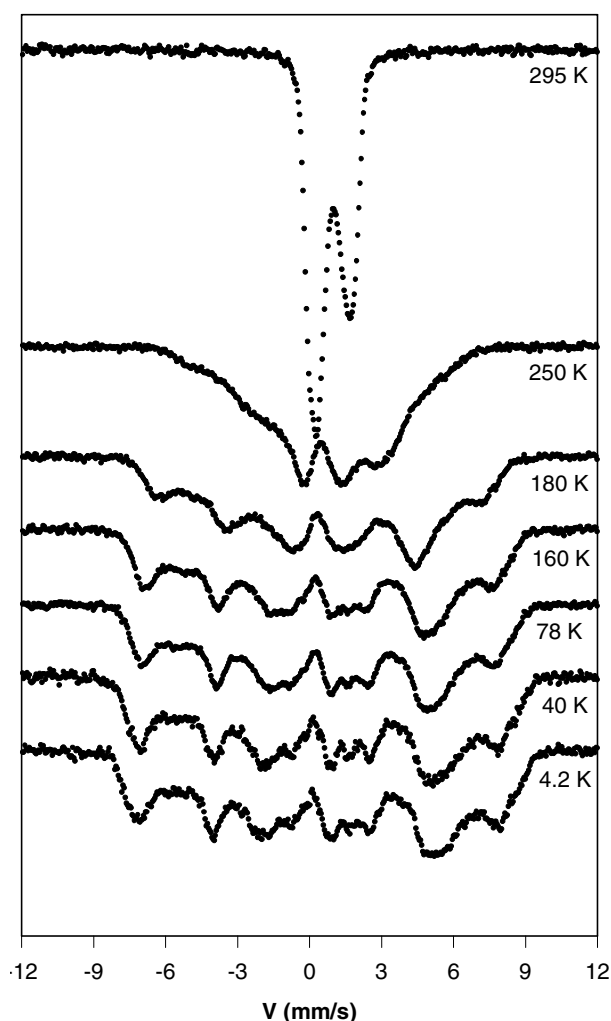


Figure 1. The Mössbauer spectra for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ at various temperatures.

temperature-dependent evolution of the average hyperfine field and the site population of the doublet (figure 2)—indicate the existence of spin clusters.

Figure 3 shows the magnetization loops taken at various temperatures. Each of the magnetization loops can be considered as composed of two parts. At low fields, magnetization increases rapidly with magnetic field and changes sign at zero field, indicating the presence of a ferrimagnetic component or weak magnetism. At higher fields, magnetization increases almost linearly with magnetic field. This behaviour is typical for paramagnetism and antiferromagnetism. The relatively high slope (magnetic susceptibility) is probably associated with canting in antiferromagnetism, which has been found in Fe_2TiO_4 and other oxide compounds (Ishikawa *et al* 1971, Lago *et al* 2000, Rouco *et al* 1994). It is to be noted that no ferrimagnetism or ferromagnetism was evident in our Mössbauer spectrum taken at 295 K; thus the rapid change in magnetization at low fields signifies the presence of a superferromagnetic component. This result indicates the existence of magnetic clusters in our sample.

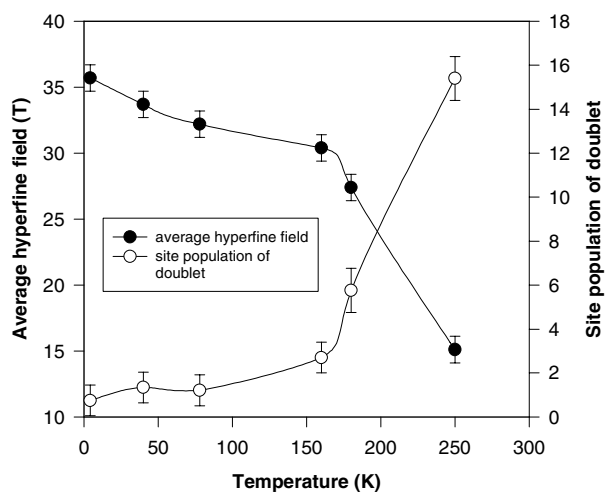


Figure 2. The temperature dependence of the average hyperfine field and the site population of the doublet.

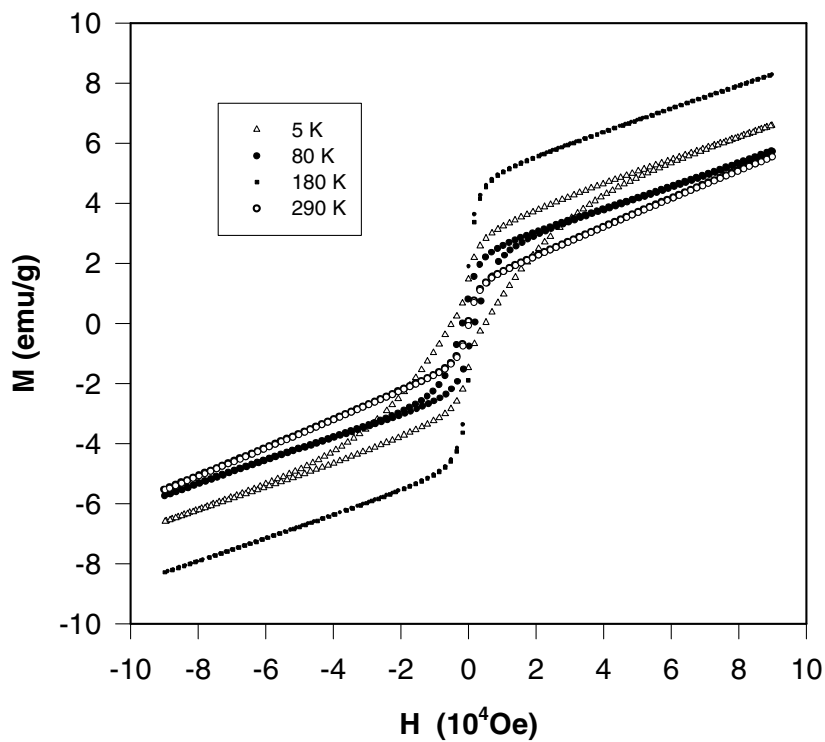


Figure 3. The magnetization loops for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ at various temperatures.

Figure 4 shows the $\partial M/\partial H$ slope at high fields (magnetic susceptibility $\chi(T)$) as a function of temperature T . The magnetic susceptibility has a maximum in the temperature range of 250–270 K indicating the Néel temperature of an antiferromagnetic phase. The magnetic

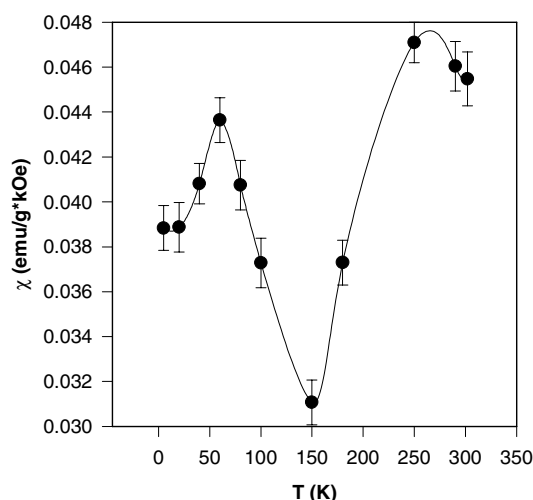


Figure 4. The susceptibility of the antiferromagnetic clusters ($\chi(T)$) versus temperature curve for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$.

phase transformation in this temperature range was confirmed in the Mössbauer measurement (figure 1). Another maximum is observed at ~ 70 K which is near the compensation temperature of the ferrimagnetic phase as shown in the FC measurement. In some ferrimagnetic material, the total contribution of the antiparallel magnetic sublattices may cancel out at a temperature called the compensation temperature (Kahn 1999). This result indicates a mixture of two components (ferrimagnetic clusters and an antiferromagnetic matrix). The minimum separating the two maxima appears to be the temperature region below which the exchange interaction between clusters and the matrix is large, giving rise to hysteresis loops and a cluster-glass phase (figure 3, and, later, figure 6 and figure 7).

In order to determine the magnetization of the ferrimagnetic component, we assume that the total magnetization $M(H, T)$ can be described with the following formula:

$$M(H, T) = M_s(T) + \chi(T)H$$

where $M_s(T)$ is the magnetization of the ferrimagnetic component and $\chi(T)H$ is the contribution of the antiferromagnetic matrix. $M_s(T)$ can be obtained by extrapolating the high-field linear part of the hysteresis loop to zero field.

Figure 5 plots the $M_s(T)$ versus T curve. Below the Néel temperature (around 265 K), M_s increases rapidly to a maximum, which appears at around 170 K. It is to be noted that the position of the maximum of M_s is almost at the same temperature as the minimum for $\chi(T)$ in figure 3, where the interaction between clusters and the matrix is large, giving rise to a hysteresis loop. When temperature is higher than ~ 170 K, M_s decreases with increasing temperature because of the thermal movement of spin clusters. M_s decreases with decreasing temperature when temperature is lower than ~ 170 K, because the magnetization of clusters decreases with decreasing temperature due to the compensation effect of the sublattice of the ferrimagnetic clusters. M_s has a minimum at around 50 K, indicating the compensation temperature. M_s increases again when temperature is lower than the compensation temperature. The minimum of M_s (the compensation point) appears at the same temperature as a maximum of $\chi(T)$ (figure 3). This result shows that the magnetization M_s , which corresponds to the ferrimagnetic component, is strongly correlated with $\chi(T)$, which describes the antiferromagnetic matrix. The total physical picture of the $\chi(T)$ curve is formed: from 300 K to 150 K, the susceptibility

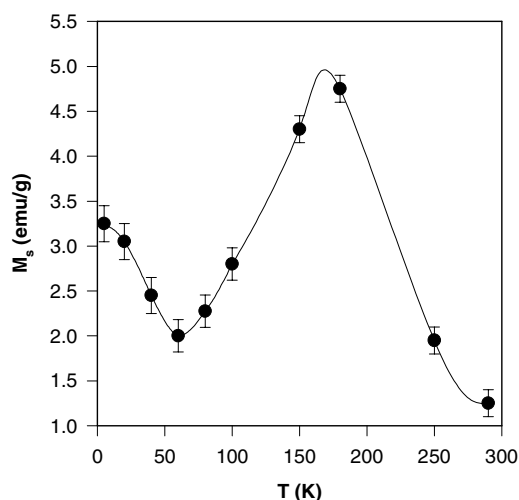


Figure 5. The saturation magnetization of the ferrimagnetic clusters (M_s) versus temperature curve for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$.

of the antiferromagnetic matrix shows the normal character of antiferromagnetic material with a Néel temperature at about 250 K; from 150 K to 4.2 K, because of the strong interaction between the ferrimagnetic clusters and the antiferromagnetic matrix, and the compensation effect of the ferrimagnetic clusters, the matrix susceptibility increases at first, then decreases after getting to the maximum at the compensation point.

Figure 6 shows the curve of the coercivity H_c versus temperature T . Coercivity decreases with increasing temperature from 5 K to 300 K except for a step around the compensation temperature. The onset of the coercivity is closely related to formation of the cluster-glass phase (as discussed below). The decrease of coercivity with the increase of temperature is determined

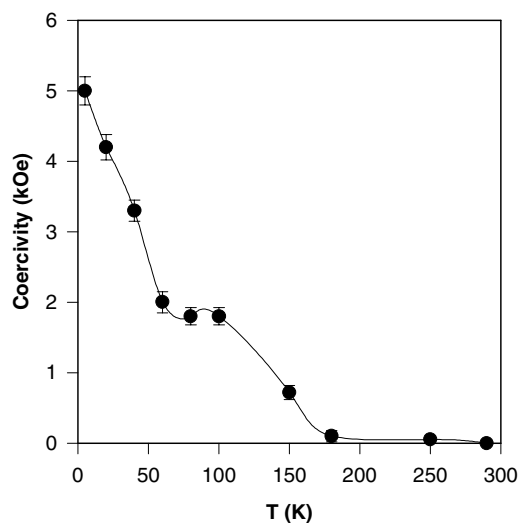


Figure 6. The change of coercivity for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ with temperature.

by the ratio of the thermal agitation energy to the energy of interaction between ferrimagnetic clusters and the antiferromagnetic matrix. The step around the compensation point could be explained by the magnetization being weak near the compensation point. Because the strong interaction between the ferrimagnetic clusters persists, while the magnetization is very small, the torque caused by the field is small; thus it is difficult to change the cluster direction with the magnetic field.

As is well known, magnetization versus temperature curves obtained during magnetic field cooling (FC) or zero-field cooling (ZFC) can be used to study spin-glass and cluster-glass behaviour (Rouco *et al* 1994, Li *et al* 1999). To determine the region of irreversibility, samples were cooled to 4.2 K in zero applied field (the ZFC process). Then a constant field was applied during the temperature increase, and the ZFC magnetization $M_{ZFC}(H)$ was measured from 4.2 to 300 K. For field-cooling magnetization ($M_{FC}(H)$), the sample was cooled down to 4.2 K under a constant field.

Figure 7 shows the ZFC and FC curves under magnetic fields of 298 Oe, 1998 Oe and 34 998 Oe respectively for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$. The maximum position T_f of M_{ZFC} marks the refreezing of the CG. Above T_f , the system gradually approaches the ferrimagnetic (FM) state. The merging point T_m for $M_{ZFC}(T)$ and $M_{FC}(T)$ implies that the system is in the same FM state for ZFC and FC processes above that temperature.

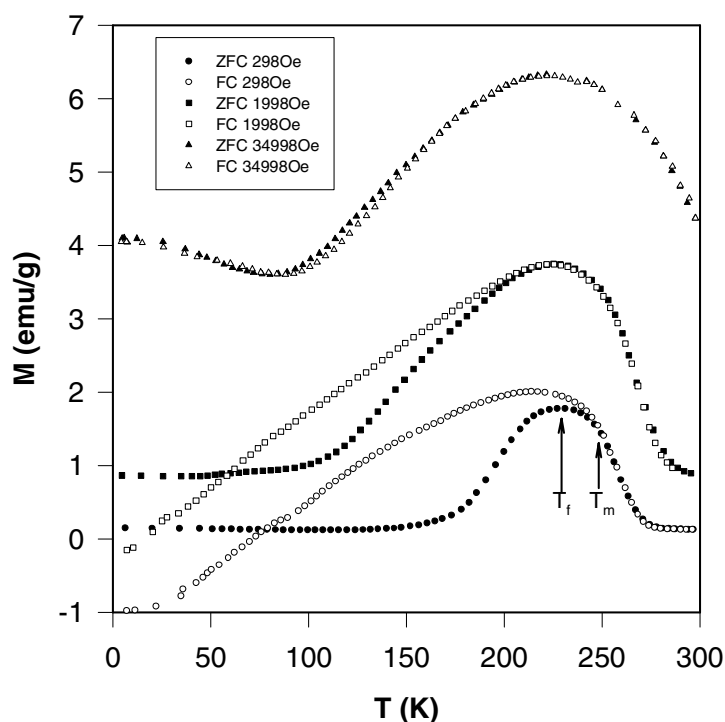


Figure 7. The ZFC and FC curves for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ at various applied fields.

At a low field (here 298 Oe), T_f and T_m were not found at the same temperature, indicating the presence of a mixed (CG and FM) state at low applied field. The mixed state disappears at higher fields (e.g., 1998 Oe). T_f and T_m are almost the same at this applied field. The difference between the FC and ZFC curves almost disappears at the higher applied field of 34 998 Oe. This demonstrates that the system is always in a FM state if the magnetic field is sufficiently

high. This is also demonstrated by the magnetic relaxation measurement. The relaxation is very weak at -30 kOe.

From the FC and ZFC curves in a magnetic field of 298 Oe, the Néel temperature T_N of the antiferromagnetic matrix can be estimated as ~ 265 K. The ferrimagnetic clusters may have a much higher Curie temperature (>300 K), since superparamagnetism was observed at room temperature (figure 1 and figure 3).

The FC curves for low magnetic field showed relatively strong negative magnetization at low temperatures (below the compensation temperature of around 75 K). This phenomenon has been reported for molecular-based ferrimagnets (Ohkoshi *et al* 1997, Mathoniere *et al* 1994, 1996). This is certainly due to the direction change of the magnetization of the ferrimagnetic component at the compensation temperature. When a field is applied at high temperature, because the interaction between the ferrimagnetic cluster and antiferromagnetic matrix is very weak, the ferrimagnetic cluster will rotate and point in the field direction. Then the temperature is decreased to a very low temperature where the interaction between clusters and the matrix is much stronger and the magnetic field cannot rotate the ferrimagnetic clusters. Because of the compensation effect, the magnetization of the ferrimagnetic cluster now points in the opposite direction to the magnetic field; then the negative signals appear. The ferrimagnetic clusters are oriented by the magnetic field at high temperature and are maintained by the strong interaction at low temperature.

The low applied field (298 Oe) is not sufficiently high to overcome the interaction between ferrimagnetic clusters and the antiferromagnetic matrix and rotate the negative magnetization to the positive direction at low temperature. The ferrimagnetic cluster will rotate in a higher applied magnetic field, as no negative magnetization is shown in the ZFC and FC curves under magnetization fields of 1998 and 34 998 Oe, respectively. The irreversibility of the FC and ZFC curves is related to the hysteresis in the magnetization loops taken at different temperatures.

If clusters exist in a system, strong relaxation phenomena should appear at temperatures below T_f . In this work, a dc magnetic relaxation experiment was performed at 80 K. The sample was first saturated with a positive field of 60 kOe. The applied magnetic field was then brought to the desired level at a ramping rate of 20 kOe min^{-1} . The sample was held at the constant field for 1800 s, during which time the change in magnetization was recorded.

Figure 8 shows the relaxation measurement results at different holding fields. As expected, M shows a strong relaxation effect at 80 K at relatively low fields (-5 and -15 kOe, as shown in figure 7(a) and 7(b)). The relaxation effect is very weak at higher fields (-30 kOe, as shown in figure 7(c)). $M(t)$ has a linear relationship with $\log(t)$, which is expected for a glass or interacting-cluster system (Tholence and Tournier 1974, Tournier and Ishikawa 1964).

From the above studies, the $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ compound probably consists of two components (ferrimagnetic clusters and an antiferromagnetic matrix). Since Fe_2MoO_4 is ferrimagnetic with a Curie temperature of 345 K and a compensation temperature of 160 K, and Fe_2TiO_4 is antiferromagnetic (or weakly magnetic because of canting) with a Néel temperature of 120 K, the ferrimagnetic clusters may be rich in Mo. The $\text{Fe}_A\text{-O-Fe}_B$ interactions in Fe_2MoO_4 are between Fe^{3+} (strong) and Fe^{2+} (weak), while the interactions are between Fe^{2+} ions only in Fe_2TiO_4 . When the Mo^{4+} is replaced by Ti^{4+} , the number of Fe^{3+} ions is reduced and hence the $\text{Fe}_A\text{-O-Fe}_B$ interactions become weaker, which is manifest in the lowering of the Curie temperature. The B-B interactions are stronger than the A-B interactions in Mo-rich samples, which is the condition under which a compensation temperature can occur (Ramdani *et al* 1985, Roy *et al* 2000, 1997). The above discussion indicates that the distribution of Mo and Ti ions may not be uniform. The ferrimagnetic Mo-rich clusters show a high Curie temperature and exhibit superparamagnetic behaviour at room temperature (above the magnetic ordering temperature of 265 K).

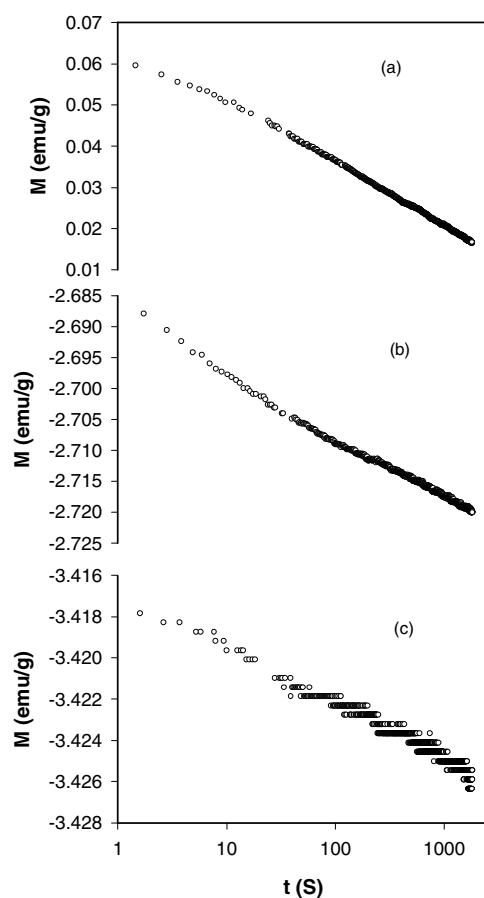


Figure 8. The M versus time curve for $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ at various holding fields.

4. Conclusions

Magnetic and Mössbauer measurements on $\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$ are reported in this paper. In the Mössbauer spectra, magnetic splitting occurs below 250 K but the ferrite remains superparamagnetic well above this temperature. The temperature dependence of the site population of the doublet and the average hyperfine-field distribution of the magnetic splitting indicate the existence of spin clusters. The magnetic loops taken at different temperatures suggest a mixture of ferrimagnetic clusters and an antiferromagnetic matrix. Cluster-glass behaviour was also confirmed by the magnetic relaxation measurements and ZFC and FC measurements. The ferrimagnetic cluster may be rich in Mo and possess a Curie temperature higher than the Néel temperature of the antiferromagnetic matrix.

References

- Abe M, Kawachi M and Nomura S 1971 *J. Phys. Soc. Japan* **31** 940
 Abe M, Kawachi M and Nomura S 1973 *J. Phys. Soc. Japan* **34** 565
 Chechersky V, Kopelev N S, Larkin B-h O M I, Peng, J L, Markert J T, Greene R L and Nath A 1993 *Phys. Rev. Lett.* **70** 3355

- Dimitrov D V, Unruh K, Hadjipanayis G C, Papaefthymiou V and Simopoulos A 1999 *Phys. Rev. B* **59** 14 499
- Ghose J, Greenwood N N, Halam A C and Read D A 1974 *J. Solid State Chem.* **11** 239
- Gupta M P, Kanetkar S M, Date S K, Nigavkar A S and Sinha A P B 1979 *J. Phys. C: Solid State Phys.* **12** 2401
- Ishikawa Y, Sato S and Syono Y 1971 *J. Phys. Soc. Japan* **31** 452
- Kahn O 1999 *Nature* **399** 21
- Lago J, Battle P D and Rosseinsky M J 2000 *J. Phys.: Condens. Matter* **12** 2505
- Li X G, Fan X J, Ji G, Wu W B, Wong K H, Choy C L and Ku H C 1999 *J. Appl. Phys.* **85** 1663
- Mathoniere C, Nuttal C J, Carling S G and Day P 1994 *J. Chem. Soc. Chem. Commun.* 1551
- Mathoniere C, Nuttal C J, Carling S G and Day P 1996 *Inorg. Chem.* **35** 1201
- Mukherjee S, Ranganathan R, Anilkumar P S and Joy P A 1996 *Phys. Rev. B* **54** 9267
- Nam D N H, Jonason K, Norblad P, Khiem N V and Phuc N X 1999 *Phys. Rev. B* **59** 4189
- Nath A, Kopelev S, Chechersky V, Peng J L, Greene R L, Larkin B-h O M I and Markert J T 1994 *Science* **265** 73
- Ohkoshi S, Yorozu S, Sato O, Lyoda T, Fujishima A and Hashimoto K 1997 *Appl. Phys. Lett.* **70** 1040
- Pogorelov Y G, Kakazei G N, Sousa J B, Kravets A F, Lesnik N A, de Azevedo M M P, Malinowska M and Panissod P 1999 *Phys. Rev. B* **60** 12 200
- Ramdani A, Gleitzer C, Gavaille G, Cheetham A K and Goodenough J B 1985 *J. Solid State Chem.* **60** 269
- Rouco A, Obradors X, Tovar M, Perez F, Chateigner D and Bordet P 1994 *Phys. Rev. B* **50** 9924
- Roy A, Ghose J, Ray A and Ranganathan R 1997 *Solid State Commun.* **103** 269
- Roy A, Kumar S, Banerjee D and Ghose J 2000 *Solid State Commun.* **114** 143
- Tholence J L and Tournier R 1974 *J. Physique Coll.* **35** C4 229
- Tournier R and Ishikawa Y 1964 *Phys. Lett.* **11** 280
- Wang L, Ding J, Li Y, Kong H Z, Feng Y P and Wang X Z 2000 *J. Phys.: Condens. Matter* **12** 4253