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Reverse Thermo-Remanent Magnetism in the $FeTiO_3$-Fe_2O_3 System

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Reverse thermo-remanent magnetization (reverse T.R.M.) in a synthesized solid solution of $x\mathrm{FeTiO_3}$-$(1-x)\mathrm{Fe_2O_3}$ has been investigated for specimens with x near 0.5. It has been confirmed that the reverse T.R.M. is closely related to the order-disorder transformation which exists in this system; the reverse T.R.M. is observed only in a state of metastable equilibrium, and not in specimens either completely ordered or completely disordered. The reverse T.R.M. is found to be the result of antiparallel coupling between the magnetic moments of the order phase and an Fe-rich metastable phase through a superexchange interaction. The origin of the metastable phase has been investigated in detail and a model which can explain consistently the experimental results is presented.

Introduction

Reverse thermo-remanent magnetism (reverse T.R.M.) is the phenomenon whereby a specimen is cooled through the Curie point in a magnetic field, and the remanent magnetization is in a direction opposite to that of the field originally applied. This phenomenon was first discovered by the Nagata group in certain minerals contained in Haruna volcanic rocks[1] and it attracted great attention throughout the world in the fields of both rock magnetism and palaeomagnetism. Since then, Uyeda has made detailed investigations, the results of which may be summarized as follows[2]:

1. The reverse T.R.M. is an intrinsic property of the ilmenite-hematite system, $x\mathrm{FeTiO_3}$-$(1-x)\mathrm{Fe_2O_3}$.
2. Among these solid solutions, only those with $0.7>x>0.4$ show the reverse T.R.M., which is, therefore, considered to be characteristic of specimens with an order-disorder transformation[3].
3. Reverse T. R. M. is expected to be the result of antiparallel coupling between the magnetic moments of the ordered and disordered phases through an exchange interaction.

Uyeda's model of the exchange coupling of two phases was supported by Meiklejohn, who observed a slight shift of the hysteresis loop of $0.6\mathrm{FeTiO_3}$-$0.4\mathrm{Fe_2O_3}$ at 300°K after magnetic annealing[4]. In both Uyeda's and Meiklejohn's experiments, however, there were some difficulties in obtaining reproducible results on the reverse T. R. M., which made their results very complicated and the detailed mechanism of this phenomenon has remained uncertain.

We have investigated in detail the relation between the order-disorder transformation and the reverse T. R. M., and have found that if the state of order of the specimen is controlled strictly, reproducible results can be obtained. In this paper we present some of our results, together with our model which explains reverse T.R.M. of the Haruna type consistently.

Experimental Results

Three specimens with $x=0.56$, 0.51 and 0.465, which show the most prominent order-disorder transformation, were used in our experiments. They were prepared by the same method as previously reported[5] and were confirmed to be single-phase through x-ray analysis. Each specimen was sealed carefully into an evacuated silica tube in order to avoid oxidation or reduction during heat treatments at high temperature, and measurements were carried out with the specimens still sealed. The temperature

variation in the long range order of these specimens is shown in Fig. 1, which was obtained by the same procedure as described in the previous paper[3]. The ordinate is the magnetization at room temperature, which

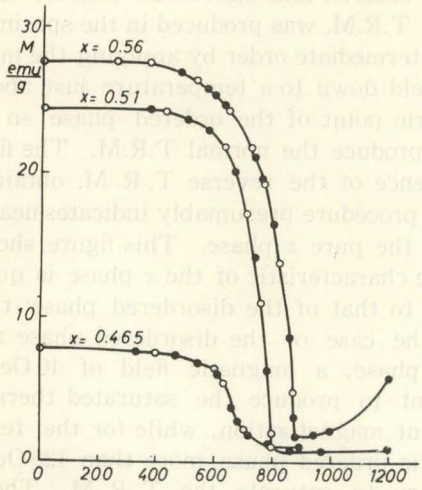

Fig. 1. Magnetization at room temperature vs. the quenching temperature for three compositions. x=mol. % $FeTiO_3$.

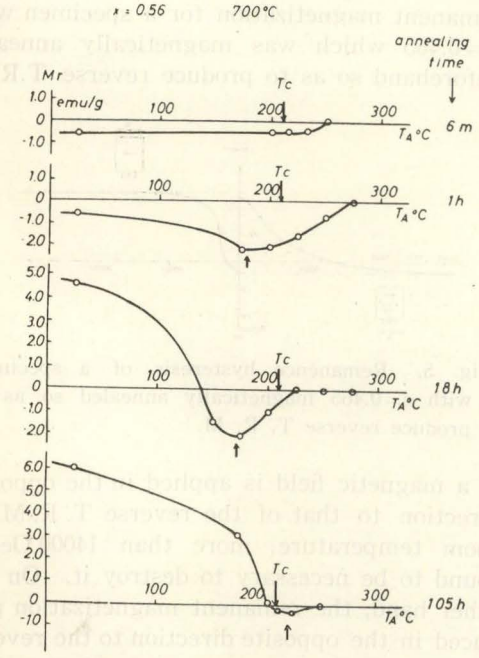

Fig. 2. Thermo-remanent magnetizations of a specimen with x=0.56, annealed at 700°C for various times. The abscissa is the temperature down to which a magnetic field was applied in the cooling process.

is known to be approximately proportional to the long range order parameter. The numerals attached to the curves indicate the mole percentage of ilmenite in the specimens. The transition temperatures of these specimens agree quite well with those previously reported[3]. The disordered specimens, obtained by quenching from above the critical temperature, were annealed for a certain time at a constant temperature of 700°C to develop order, and were then quenched to room temperature to detect the state of order developed in the annealing process. Thermo-remanent magnetization in the annealed specimens was produced by applying a magnetic field of 100 Oe from 450°C to a temperature T_A during the process of cooling. Such a magnetic annealing treatment has been found not to disturb the arrangement of ions[3]. In Fig. 2, the thermo-remanent magnetizations thus produced for the 56 mole % $FeTiO_3$ sample are plotted against T_A. Each curve corresponds to the result obtained for a different annealing time at 700°C. The Curie point of the thermo-remanent magnetization T_c, which corresponds to that of the ordered phase, was determined by measuring the temperature at which the thermo-remanent magnetization disappeared. As is indicated in the figure, no appreciable change of the Curie point of the ordered phase was observed in the process of development of order at 700°C. From these figures we see that the reverse T.R.M. is produced even if the magnetic field is applied only down to a temperature appreciably above the Curie point. This fact suggests that another phase (or phases) exists with a range of Curie points higher than that of the ordered phase. This unknown phase is designated hereafter as the "x phase." As the Curie point of the disordered phase is lower than that of the ordered phase of the same composition, the x phase must be an Fe-rich region as compared with both the ordered and disordered phases. The reverse T.R.M. is the result of antiparallel coupling between the magnetic moment of the ordered phase and that of the x phase which was locked in the direction of the field applied during the magnetic annealing process. The Curie points of the x phase, which are distributed over a range of temperature change with the development of order.

When the specimen was cooled in a magnetic field through the Curie point of the ordered phase, a normal T.R.M. was superimposed on the reverse T.R.M. This effect was more pronounced if the specimen is annealed for long times.

The maximum values of the reverse T.R.M. obtained for a specimen with $x = 0.56$ are plotted in Fig. 3 as a function of the annealing time at 700°C. The upper line in the figure indicates the long range order parameter developed in the annealing process, while the lower line is the maximum reverse T.R.M. of the specimen. The striking result is that the reverse T.R.M. exists only in the intermediate state, and is not found in either the fully ordered state or in the disordered state. These facts indicate clearly that the x phase which is responsible for the reverse T.R.M. is only a metastable phase; that is, it is created in the process of the formation

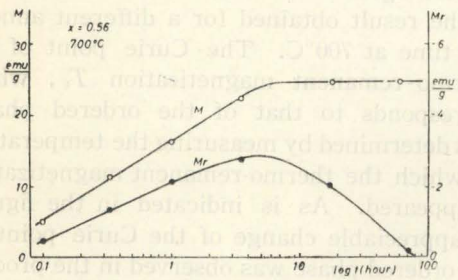

Fig. 3. ○ ···Magnetization at room temperature vs. annealing time at 700°C. $x=0.56$.

● ···Maximum reverse T. R. M. vs. annealing time at 700°C. $x=0.56$.

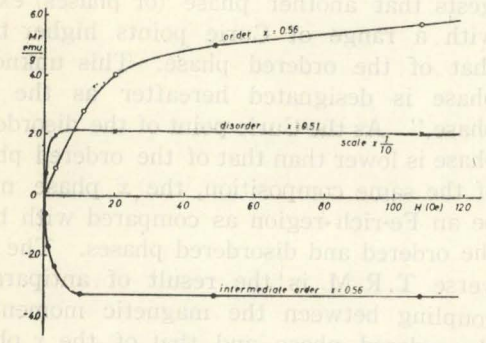

Fig. 4. Field dependence of the remanent magnetization. Reverse T. R. M. was produced in a specimen with intermediate order by applying a magnetic field down to a temperature just above the Curie point of the ordered phase.

of order and disappears if the crystal reaches equilibrium. The same kind of behavior is observed for specimens with other compositions. In Fig. 4, the field dependence of the reverse T.R.M. is shown, together with the field dependence of the normal T. R. M. for the ordered and disordered phases. The reverse T.R.M. was produced in the specimen with intermediate order by applying the magnetic field down to a temperature just above the Curie point of the ordered phase so as not to produce the normal T.R.M. The field dependence of the reverse T. R. M. obtained by this procedure presumably indicates nearly that of the pure x phase. This figure shows that the characteristic of the x phase is quite similar to that of the disordered phase; that is, in the case of the disordered phase and the x phase, a magnetic field of 10 Oe is sufficient to produce the saturated thermoremanent magnetization, while for the ferrimagnetic ordered phase, more than 120 Oe is necessary to saturate the T. R. M. The x phase is, therefore, supposed to be nearly in the disordered state so that the magnetic moment of the x phase must be very weak. Fig. 5 shows the hysteresis curve of the remanent magnetization for a specimen with $x=0.465$ which was magnetically annealed beforehand so as to produce reverse T.R.M.

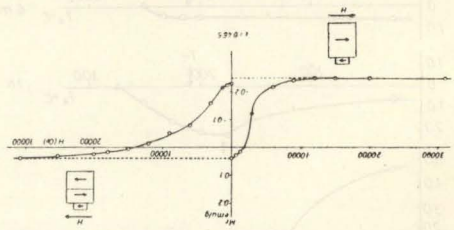

Fig. 5. Remanence hysteresis of a specimen with $x=0.465$ magnetically annealed so as to produce reverse T. R. M.

If a magnetic field is applied in the opposite direction to that of the reverse T. R. M. at room temperature, more than 14000 Oe is found to be necessary to destroy it. On the other hand, the remanent magnetization produced in the opposite direction to the reverse T. R. M. at room temperature by a field strength of 30000 Oe can easily be destroyed by a field of 1000 Oe applied in the direction of the reverse T.R.M. Such an asymmetric hysteresis suggests that the magnetic moment

of the x phase which was fixed in the direction of the applied field during magnetic annealing process did not change its direction even if an external field as strong as 30000 Oe was applied in the opposite direction, as is schematically shown in the figure. This behavior is the most clear evidence that the magnetic moments of the ordered phase and x phase are coupled antiferromagnetically through the superexchange interaction. A similar asymmetric remanence hysteresis was observed in magnetic fields of 30000 Oe for specimens of other composition, although the remanence coercivity is decreased to 3400 Oe and 760 Oe for $x=0.51$ and $x=0.56$ respectively.

Discussion

We have confirmed that the reverse T.R.M. is the result of antiparallel coupling between the magnetic moments of the ordered phase and an Fe-rich matastable phase. Moreover the x phase must be atomically antiphase with respect to the ordered phase in order that the resultant magnetic moment of the two phases can be aligned antiparallel through a superexchange interaction. The possibility of the existence of such a metastable phase was examined by following graphically the development of the ordered phase in a disordered matrix. Fig. 6 (a) is a two dimensional representation of disordered 0.5 $FeTiO_3$-0.5 Fe_2O_3. The positions of Ti ions, indicated by black circles in the figure, were chosen by means of a table of random digits. Then, an ordered phase was developed in the disordered matrix by rearranging the metal ions as shown by the arrows in the figure. Here we have assumed that diffusion of ions take place more easily within the same layer than between the layers. Fig. 6 (b) indicates schematically the ordered phase thus produced, on the boundary of which we find the Fe-rich metastable regions. These regions may correspond to the "x phase", although the boundary can not clearly be determined. As the Ti ions rejected from the Fe layers in the ordered phase displace to the same layers in the metastable phase, the x phase is always antiphase to the ordered phase. Therefore the superexchange interaction acting between the neighbouring layers can align the resultant magnetic moments of the two phases antiparallel. Of course, Ti rich metastable regions are also created on the boundary. However, they do not affect the reverse T.R.M., because the Curie point of this phase is lower than that of the ordered phase.

Thus, graphical studies show that our two phase model is fairly promising, and we believe that the phenomenon of the reverse T.R.M. of the Haruna type is completely explained by our model.

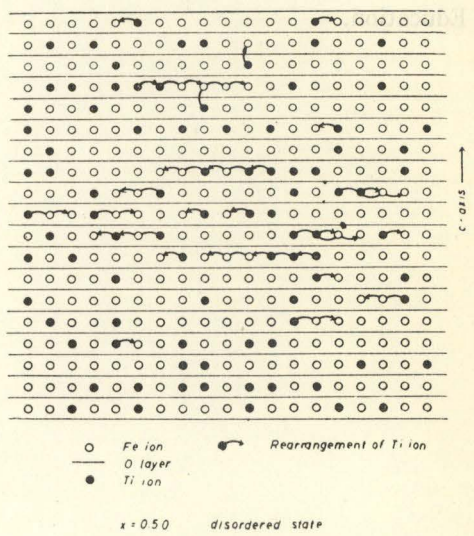

Fig. 6 (a). Two dimensional representation of disordered 0.5$FeTiO_3$-0.5Fe_2O_3.

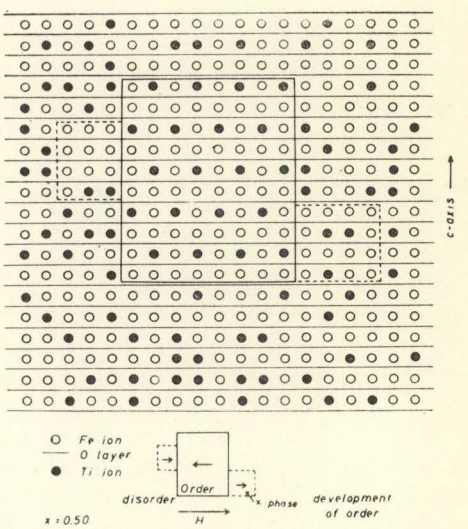

Fig. 6 (b). Ordered phase and x phase developed in the disordered matrix. The boundary of x phase, which is expected not to be definite in the actual crystal, is written schematically in the figure.

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