

The Magnetization of Solid Solutions of Ilmenite in Hematite

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Ilmenite, FeTiO_3 , and hematite, $\alpha\text{Fe}_2\text{O}_3$, will form hexagonal crystal in all proportions, but as the temperature falls below 1000°C the crystals exsolve into two phases, one rich in ilmenite (hemoilmenite) and the other rich in hematite (ilmenhematite). Uyeda (1958) has studied synthetic mixtures of these minerals and has found that a composition close to 50% ilmenite-50% hematite would spontaneously reverse its magnetic polarity on cooling. In the present investigation the large single crystals of hemoilmenite from the deposits in the Allard Lake region of Quebec have been used.

The Allard Lake hemoilmenite has an overall composition of 70% ilmenite-30% hematite with a well developed exsolution structure. The hemoilmenite phase forms the groundmass in which the ilmenhematite phase is present as discontinuous lamellae that have exsolved in the basal plane. The lamellae fall into two distinct size ranges. The large lamellae, which are irregular in outline, vary from 1 to 10 mm in length and from 0.005 to 0.02 mm in thickness. The small lamellae have a pronounced elongation in one direction. They are roughly 5 to 10 microns long, 1 micron wide and 0.2 microns thick. They tend to have their long axis aligned along one of the trigonal symmetry directions in the basal plane. These directions can be determined from parting cracks visible in the large ilmenhematite lamellae in polished section. The composition of the large lamellae is 13% ilmenite in hematite while that of the small lamellae is 7 to 10% (Carmichael 1961).

The natural remanence of the crystals is due to the small ilmenhematite lamellae. They have a coercive force of 1500 Oersteds and a strong anisotropy causing magnetization in the basal plane only. Within the basal plane there is a weaker anisotropy that defines an easy direction of magnetization. The large lamellae have a coercive force of about 100 Oersteds but are not magnetized in

the natural state. The hemoilmenite phase has a Curie point at about 0°C and is not magnetic at ordinary temperatures. Curves of the change with temperature of both the natural remanence, J_N , and the thermoremanence produced in 0.5 Oersteds, $J_T(0.5)$, are shown in Fig. 1. Both show an increase in intensity upon heating which resembles that found by Uyeda for synthetic specimens of similar composition. In contrast to most magnetic rocks, J_N is almost twice as great as $J_T(0.5)$ which suggests that magnetization mechanism in the natural state is not simply

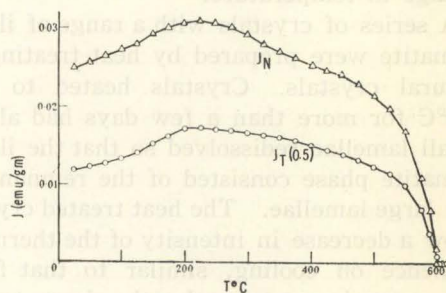
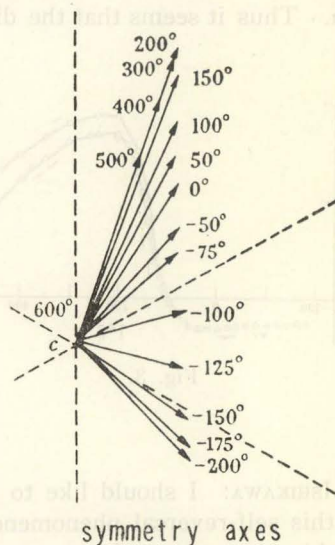


Fig. 1.



symmetry axes

Fig. 2.

cooling in the earth's field.

The intensity and direction of both J_N and J_T for single crystals were measured in zero field over a temperature range from about 75° below the Curie point down to -196°C . Both remanent magnetizations rotate within the basal plane from about 200°C downward. Fig. 2 is a polar plot of the remanent vector in the basal plane for a typical crystal cooled in 0.8 Oersteds to 500°C and then in zero field to -196°C . The rotation of the vector in the basal plane is not a true rotation but an apparent one due to the growth of a new magnetic moment, opposite in sense to the remanence, but directed along one of the crystal symmetry directions. The symmetry directions are parallel to lines of Fe atoms in the crystal but are also parallel to the preferred directions of the long axes of the small lamellae. The growth and decay of the new moment is completely reversible with change in temperature.

A series of crystals with a range of ilmenhematite were prepared by heat treating the natural crystals. Crystals heated to over 600°C for more than a few days had all the small lamellae redissolved so that the ilmenhematite phase consisted of the remnants of the large lamellae. The heat treated crystals show a decrease in intensity of the thermoremanence on cooling, similar to that found for natural crystals. In the heat treated specimens the new moment is antiparallel to the remanence rather than along a symmetry direction. Thus it seems that the directional

control of the new moment in natural crystals is connected with a shape or crystalline anisotropy of the small lamellae in the symmetry directions. For crystals containing ilmenhematite with 25 to 18% ilmenite in hematite the antiparallel moment causes a reversal of the magnetic vector above room temperature. Fig. 3 shows the variation of the thermoremanence with change in temperature for a crystal that had been heated for 100 days at 900°C . The magnetic constituent is the remnants of the large lamellae which contain 20% ilmenite in hematite.

This reversing range of composition of ilmenhematite is distinct from that found by Uyeda. The growth and decay of the antiparallel moment with change in temperature suggests an order-disorder mechanism. Ishikawa and Akimoto (1958) have found that the Ti^{4+} ions remain disordered on cooling for any composition containing less than 45% ilmenite so that ordering of titanium cannot cause the antiparallel moment in this range of composition. In contrast to the Ti ions, the ordering of Fe ions does not require migration of atoms through the lattice. Fe^{2+} ions could be ordered onto *A* sites by electron transfer from Fe^{2+} ions on *B* sites to Fe^{3+} ions on *A* sites. Each such transfer would cause a net increase of 2 Bohr magnetons in the antiparallel moment. The tendency to cause this ordering at low temperature could be the lower energy of the ilmenite arrangement of Fe^{2+} ions, which would be counteracted at high temperature by the increased entropy of the disordered state.

A demonstration of spontaneous reversal will be given using a heat-treated Allard Lake crystal having a magnetic constituent with a composition of 20% ilmenite in hematite.

References

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3. Y. Ishikawa and S. Akimoto: J. Phys. Soc. Japan **13** (1958) 1298.

DISCUSSION

Y. ISHIKAWA: I should like to comment to Dr. Carmichael that, in order to interpret this self-reversal phenomenon, you must take into account the important fact that this phenomenon is not observed in either a completely exsolved specimen or a fully mixed specimen, but is observed in an imperfectly mixed state. This fact sug-

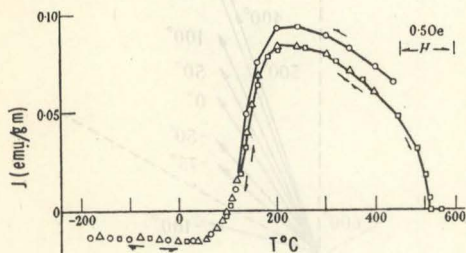


Fig. 3.

gests that this phenomenon is also characteristic of the inhomogeneous specimen. In this point, the situation is quite similar to the self-reverse T.R.M. of Haruna type. If this phenomenon is really attributed to the ordering of Fe^{2+} and Fe^{3+} , the reversal phenomenon must be observed even in the homogeneous specimen. Several years ago, we measured electrical conductivity of the synthesized solid solution of ilmenite and hematite and did not find any anomalies over the wide range of temperature. Therefore this self-reversal phenomenon may be attributed to other mechanisms.

C. M. CARMICHAEL: I agree with Dr. Ishikawa that the total crystal is not homogeneous but have assumed that this crystal which was heated for 100 days at 900°C has reached equilibrium in the regions of each phase. These are the remnants of the large lamellae for the hematite-rich phase and the groundmass for the ilmenite-rich phase. This leaves only the boundary regions of the hematite-rich lamellae for intermediate compositions and the amount must be below that detectable by Curie point, x-ray or polished section analysis. Further, in the case of the specimen reversing slightly above liquid N_2 temperature there could be no phase present with so low a Curie point.

S. UYEDA: In order to check the plausibility of Dr. Carmichael's hypothesis, we have measured the electrical resistivity *vs.* temperature characteristics of Dr. Carmichael's heat treated specimen (1150° , 8 days). We found an anomalous decrease in the electrical resistivity at about the temperature one would expect.

loop at $0.05\text{FeTiO}_3\text{-}0.15\text{Fe}_2\text{O}_3$ at 300°K after magnetic annealing. In both Uyeda's and Maki'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 $x = 0.05$, 0.1 and 0.15 , which show the most prominent order-disorder transformation, were used in our experiments. They were prepared by the same method as previously reported, 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 temperatures, and measurements were carried out with the specimens still sealed. The temperature

Reverse thermo-remanent magnetization (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, and it attracted great attention throughout the world in the fields of both rock magnetism and paleomagnetism. Since then, Uyeda has made detailed investigations the results of which may be summarized as follows:

1. The reverse T.R.M. is an intrinsic property of the ilmenite-hematite system, $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$.
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. 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 Maki, who observed a slight shift of the hysteresis