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Experimental Study on Parasitic Ferromagnetism of αFe_2O_3

AKIRA TASAKI, KIITI SIRATORI AND SHŪICHI IIDA
Department of Physics, Faculty of Science
University of Tokyo

In order to determine the origin of the parasitic ferromagnetism of αFe_2O_3 (hematite), oxidation and impurity effects on this weak ferromagnetism of polycrystalline αFe_2O_3 were studied. It was found that only the isotropic part of the parasitic ferromagnetism was changed easily by oxidation or reduction, whereas the anisotropic part was almost uninfluenced.

A large synthetic single crystal, weighed about 50 mg, was grown by the flux method. In this single crystal, it was found that a weak ferromagnetic moment appeared only when the spin lay in the (111) plane, as was expected from Dzyaloshinsky's mechanism.

Recovery of residual magnetization after cooling-heating cycles was also studied for both the polycrystalline specimens and the single crystal. It was found for the polycrystals that the recovery is almost 100% except after the first one cooling-heating cycle without influenced by the terrestrial magnetic field. While, for the single crystal, the direction of the residual magnetization was very sensitive to the direction of terrestrial field at the transition temperature and the amount of recovery was changed easily by the direction of the terrestrial field.

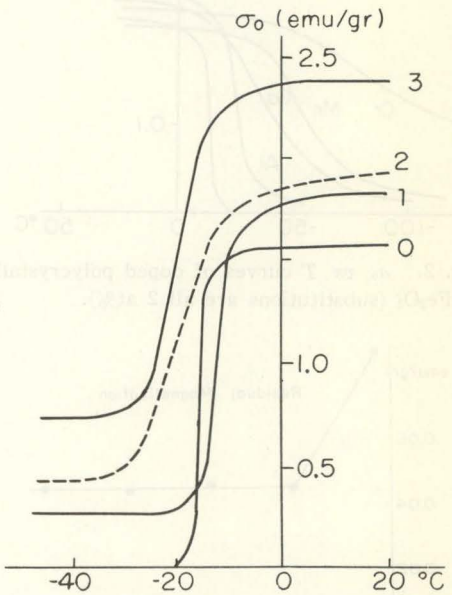
1. Introduction

αFe_2O_3 (hematite) has a small spontaneous magnetization in the (111) plane at room temperature, which disappears (or decreases) abruptly at the transition temperature (−15°C) on cooling. Above this temperature, the spin axis of this antiferromagnet lies in the (111) plane, and below this along the [111] axis. The origin of this parasitic ferromagnetism has been interpreted by Dzyaloshinsky[1] to be due to the presence of a peculiar symmetry of this crystal. However, there are still several unelucidated points in the detailed magnetic properties of this crystal. This paper deals with the following problems; 1) the role of imperfections[2),3)], recovery of residual magnetization after cooling-heating cycle (memory phenomenon)[4)] and 3) fine measurements for a good synthetic single crystal.

2. Experimental procedure and results

Polycrystals

Polycrystalline specimens were synthesized by the usual ceramic "wet" method. It is known that the magnetization of αFe_2O_3 is expressed by $\sigma=\sigma_0+\chi H$. To obtain σ_0 (parasitic ferromagnetic moment) and χ (susceptibility), the measurement of σ (magnetization) was performed at three different field-strengths (H) with magnetic balance. Fig. 1 shows σ_0 *vs* T curves with oxygen pressures[2)] applied in the heat treatment as a parameter. Fig. 2 shows the effects of substitution of iron ion with foreign trivalent cations.[3)] All the specimens were prefired at 1000°C for 3 hours, except the one shown in curve 3 in Fig. 1, which was made from iron-oxalate



Fig, 1. σ_0 *vs* T curves of polycrystalline αFe_2O_3. Heat treatments of the samples are as follows: Annealed at 1000°C, 3 hrs. in air (0), Oxidized at 500°C, 70 hrs. in 100 (1) and 1000 (3) Kg/cm² oxygen. Reduced at 1000°C, 3 hrs. in 10^{-3} mmHg (2).

directly by a chemical reaction at 450°C at 1000 kg/cm² pressure of oxygen. It was found that the "isotropic part" (after Néel) in σ_0 changes with the change in the degree of oxidation whereas the anisotropic part is almost unchanged. However, as shown in Fig. 2, when the foreign atoms are added in a form of solid solution, the isotropic part in σ_0 does not appear, but the transition temperature decreases and the transition becomes gradual.

Residual magnetization σ_r was measured by using an astatic magnetometer. In Fig. 3 is shown the change of σ_r of the polycrystalline αFe_2O_3 after repetition of cooling-heating treatments.[5] It was found that σ_r decreased by about one-half after the first cooling-heating cycle, but remained constant in subsequent repetition of the treatment. This is a result with a sharp contrast to that of single crystals mentioned below.

Synthetic single crystal

Fortunately, we have succeeded in making single crystals of about 50 to 80 mg weight.

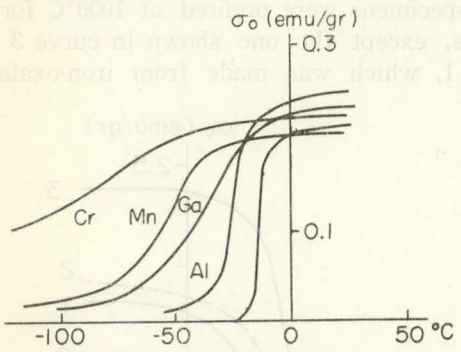
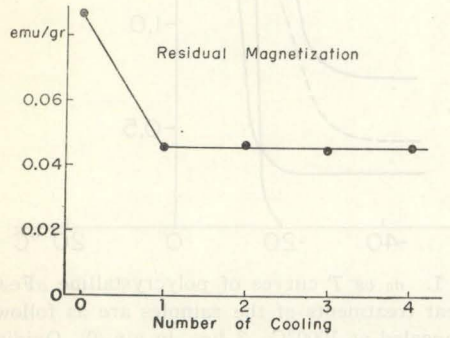


Fig. 2. σ_0 *vs* T curves of doped polycrystalline αFe_2O_3 (substitutions are all 2 at%).



Fig, 3. Residual magnetization of polycrystalline αFe_2O_3 *vs* number of cooling-heating cycle repeated.

The χ and σ_0 *vs* T curve in (111) plane are shown in Fig. 4. The magnetization along the [111] axis, however, could not be measured with so high an accuracy as in the (111) plane, since our magnetic balance has no special attachment to prevent rotation of the suspended specimen. Therefore, we measured the torque within a $\{1\bar{1}0\}$ plane (that includes [111] direction) and the result is shown in Fig. 5. The discontinuity in the torque curve[6] is caused by the abrupt change of the direction of parasitic ferromagnetic moment. From this discontinuity, we can calculate the weak ferromagnetic moment. This is 0.34 emu/gr, showing a good agreement with the value of 0.36 that is obtained from magnetization measurement. It is added that $(\chi_\perp - \chi_{//}) = 9.8 \times 10^{-6}$ emu/gr is obtained from the field dependence of low temperature torque curves. A very important result is that there is no discontinuity in torque curves below the transition temperature, *i.e.*, there is no magnetization in (111) plane and also along

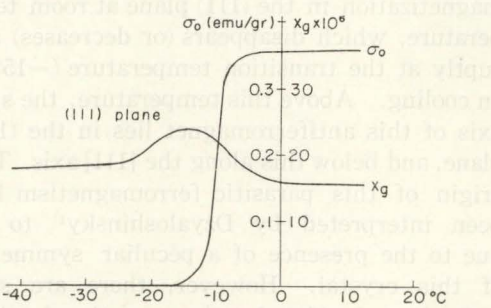


Fig. 4. χ_g and σ_0 *vs* T curves of a synthetic single crystal of αFe_2O_3.

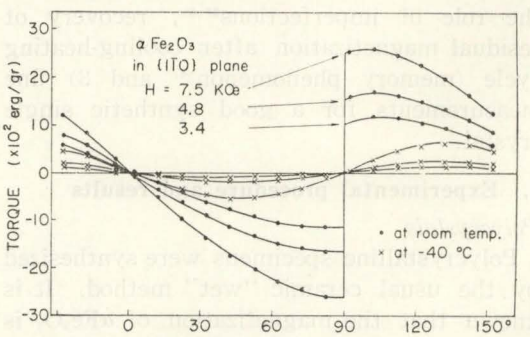


Fig. 5. The torque curves in $\{1\bar{1}0\}$ plane of synthetic single crystal of αFe_2O_3 at room temperature (●) and at -40°C (×). The discontintinuities which appear at room temperature show the weak ferromagnetic moment of this crystal.

[111] direction below the transition temperature.

The recovery phenomenon of σ_r was studied again in this single crystal.[7] The results are shown in Fig. 6. Here, the reading of the torque of a lower magnet (5 mm length) of the astatic magnetometer is plotted directly against the angle of the specimen in (111) plane. Curve 0 is the initial curve and point A indicates the location of the magnetizing field with + direction. Curves 1, 2 and 3 show the result after adding one, two and three cooling-heating cycles with terrestrial magnetic field along [111] (for curves 1 and 2) and then along the reverse direction B to the initial magnetizing field direction in the (111) plane (for curve 3). In curve 0, the direction of σ_r coincides exactly with the direction of the magnetizing field A, but, in curves 1 and 2, the magnitude and the direction of σ_r change considerably. In curve 3, the location changes completely so as to coincide with the direction of the terrestrial field B which was applied during heating.

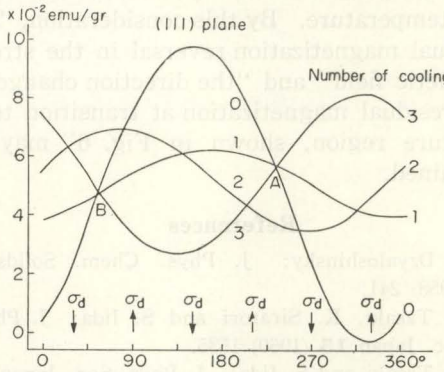


Fig. 6. Torque due to residual magnetization of synthetic single crystal αFe_2O_3 at room temperature curves. 0 illustrates result after magnetized along A, curve 1 and 2 results after adding one and two cooling-heating cycles with terrestrial magnetic field along [111], and curve 3 that after cooling-heating cycle with terrestrial field along B.

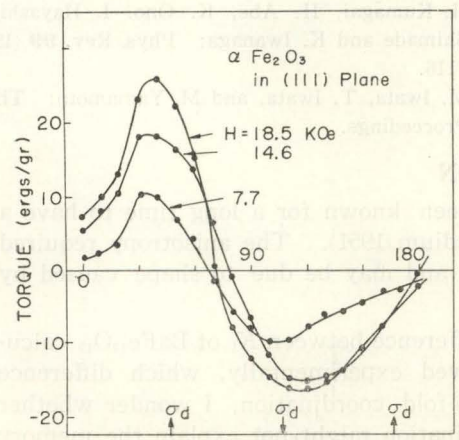


Fig. 7. Torque curves in (111) plane of synthetic single crystal of αFe_2O_3.

Fig. 7 shows torque curves in (111) plane of our synthetic single crystal. In natural crystals, we also found uniaxial-type anisotropy before.

3. Discussion

The first result of the polycrystalline studies is that the isotropic part in σ_0 is easily changed by the heat treatments whereas the anisotropic part is almost unchanged. This fact shows that the anisotropic part is, as is expected from Dzyaloshinsky's mechanism, an intrinsic property of αFe_2O_3 crystal but the isotropic part is easily produced by the presence of imperfections in the crystal. Presence of Fe^{2+} or magnetite is quite probable in the case of reducing treatment, since we have found the reduction of about 0.7 at.% oxygen in this specimen[2]. However, in the case of oxidizing treatment we could not find any appreciable increase in the amount of oxygen (less than 0.5 at.% in the case of 1000 Kg/cm² oxygen pressure treatment). It was also found that this isotropic part appears easily when the specimen was made from impure iron[3] (*e.g.*, carbonyl iron in a commercial grade). Considering these facts, we are led to think that the isotropic part is due to the presence of ferromagnetic impurity precipitates in the specimen, and not due to the presence of Fe^{4+} in the crystal. The solubility limit of these impurities may be dependent on the pressure of oxygen in heat treatment. Both studies of oxidization and impurity effect for the polycrystalline specimens, seem to support the Dzyaloshinsky's mechanism. The wide transition region which was observed in a natural crystal by S.T. Lin[7] may be explained by the existence of soluble impurity the concentration of which has a distribution within the crystal. The presence of weak ferromagnetism along [111] axis is also explained if these impurity atoms prefer to occupy alternate layers along C

axis. The result that the transition temperature decreases generally when the foreign atoms are added in a form of solid solution, can not be explained easily, since a simple theory that is based on the change in balance between the (*puseudo*) dipole-dipole interaction and one ion anisotropy, predicts an increase of transition temperature. It may be that the one ion anisotropy is strongly dependent on crystal parameters.

Considering crystal symmetry, we had rather expected a six fold torque curve in (111) plane. However, as shown in Fig. 7, we only found two fold torque curves which have no relation to the crystal symmetry. We think that this uniaxial torque may be due to the presence of some secondary structures of the crystal, since we have found a beautiful "dendrite structure" in synthesized single crystal flakes. However, we can not find the reason why six fold anisotropy that was found by the resonance measurement ($\sim$70 Oe)[8], is so small as it can not be detected by this torque measurement.

For the memory phenomenon of αFe_2O_3, following facts should be emphasized: 1) In polycrystal αFe_2O_3, memory is almost 100% except first one cooling-heating cycle and the direction of residual magnetization is maintained. 2) In polycrystal, the memory amount does not depend on the impurity concentration nor on the oxidation treatment. 3) In the case of synthetic single crystal, different from the case of polycrystalline specimens, the residual magnetization is very sensitive to the magnetic field at the transition temperature.

Fact 1) is explained by us assuming the presence of an extra uniaxial anisotropy in (111) plane. It seems that this extra anisotropy is not present in good single crystals. A new interesting result is found by T. Iwata and others[9] that the direction of the residual magnetization of polycrystals can be changed by applying a strong magnetic field (more than 80 kOe) at liquid nitrogen temperature. It seems that the uniaxial anisotropy assumed should relate to this phenomenon. One possible assumption is that the anisotropy relates to the presence of exchange coupled ferromagnetic impurities that magnetization direction may be changed by the application of strong magnetic field. Another considered mechanism is that, instead of the uniaxial anisotropy, we assume the antiferromagnetic domains in which the direction of the residual magnetization is memorized below the transition temperature. By this consideration, "the residual magnetization reversal in the strong magnetic field" and "the direction change of the residual magnetization at transition temperature region, shown in Fig. 6" may be explained.

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DISCUSSION

E. P. WOHLFARTH: Hematite powders have been known for a long time to have a high coercive force (*e.g.* Thellier, J. Phys. Radium 1951). The anisotropy required to explain this does not seem to be crystalline, and may be due to shape caused by local regions of relative high magnetization.

E. W. GORTER: In view of the very large difference between K_1 of $BaFe_{12}O_{19}$ calculated from dipole-dipole interaction and observed experimentally, which difference must be due to the presence of Fe^{3+} in 3 (or 5)-fold coordination, I wonder whether the presence of some Fe^{3+} ions in such a coordination might not explain the memory effect, in view of the hysteresis in the torque curves of $BaFe_{9.8}Co_{1.1}O_{19}$ at low temperatures observed by Smit, Lotgering and Enz.