J. Geophys. 42, 351 – 359, 1977

Journal of Geophysics

Pseudo-Single-Domain Effects and Single-Domain Multidomain Transition in Natural Pyrrhotite Deduced from Domain Structure Observations

H. Soffel

Institut für Allgemeine und Angewandte Geophysik der Universität München, D-8000 München 2, Theresienstraße 41, Federal Republic of Germany

Abstract. The domain configuration of primary pyrrhotite in a Devonian diabase was studied using the Bitter pattern technique. Due to the uniaxial symmetry the multidomain grains have a rather simple domain structure. The single-domain – multidomain transition occurs at an average particle diameter of 1.6 μm. In the multidomain grains clusters of inclusions seem to produce pseudo-single-domain effects with complicated domain configurations. Such pseudo-single-domain effects are necessary for the interpretation of the magnetically hard component of remanence which cannot be explained by the observed abundance of true single-domain particles alone.

Key words: Rock magnetism – Domain structure – Pyrrhotite – Diabase – Palaeomagnetism.

1. Introduction

The remanent magnetization of rocks can in general be interpreted by a mixture of multidomain and single-domain behaviour. The multidomain behaviour is restricted to the remanence components with coercive forces smaller than say 16 kA/m (=200 Oe) depending on the material and grain size of the ferrimagnetic ore phase. Single-domain particles are believed to be responsible for the remanence components with large coercive forces, say larger than 24 kA/m (=300 Oe), depending on the shape and nature of the ore fraction. In many cases it is not possible to explain the actually observed intensity of remanence of rocks with coercive forces larger than several hundred Oe with the observed abundance of true single-domain grains, although such attempts have been successful in some cases (Soffel, 1968; 1969). Stacey (1962; 1963) introduced the idea of pseudo-single-domain effects by assuming zones within or at the edges of large multi-domain grains with single-domain properties. Clusters of lattice imperfections and small inclusions, exsolution features, cracks and very irregular shapes of the ore grains can lead to such pseudo-single-domain effects.

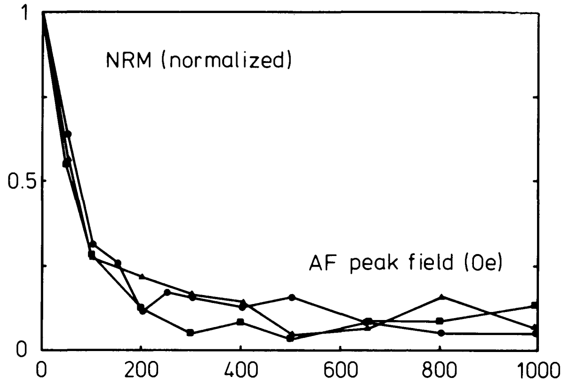


Fig. 1. AF-demagnetization of 3 pilot samples

Experimental proof for the existence of pseudo-single-domain grains has been established for instance from the study of alternating field demagnetization curves, and dependence of thermoremanent magnetization (TRM) upon grain size and external field strength. The experimental and theoretical results have recently be summarized by Stacey and Banerjee (1974).

This paper adds further experimental proof of the presence of pseudo-single-domain effects from the study of domain configurations and other rock magnetic parameters of primary pyrrhotite in a Devonian diabase from Northern Bavaria/Germany.

2. Palaeomagnetic and Rock Magnetic Properties of the Devonian Diabase

The Devonian diabase of Bad Berneck (Northern Bavaria, $\lambda = 11.7$ °E, $\varphi = 50.1$ °N) has an average natural remanent magnetization of about 0.5 A/m (= 500 µG) which is typical of a basic rock of that age. The mean direction of NRM is: $D = 286°$, $I = +72°$. AF-demagnetization of 3 pilot samples (Fig. 1) reveals the presence of components of remanence with different stabilities. Firstly a component carrying most of the NRM with low stability which can be removed by AF-fields up to about 8 kA/m (100 Oe). Secondly, a magnetically hard component which maintains more or less its intensity in AF-fields up to 80 kA/m (1000 Oe). The average intensity of this stable component (after AF-treatment in a peak field of 16 kA/m) is 0.082 A/m (= 82 µG), that is 16% of NRM. The mean direction is only slightly changed ($D = 260°$, $I = 46°$). Thirdly a transition zone between 8 kA/m (100 Oe) and 24 kA/m (300 Oe) with intermediate stability. Within this transition zone the intensity of remanence drops only by a factor of about two. The entire change of remanence direction occurs at demagnetizing fields smaller than 8 kA/m (100 Oe).

Thermal cleaning at 290 °C also produced only a slight change of remanence direction ($D = 280°$, $I = 36°$). Bedding correction was not possible due to very uncertain tectonic conditions. However other diabase bodies nearby with reliable tectonic data yielded typical paleozoic pole positions.

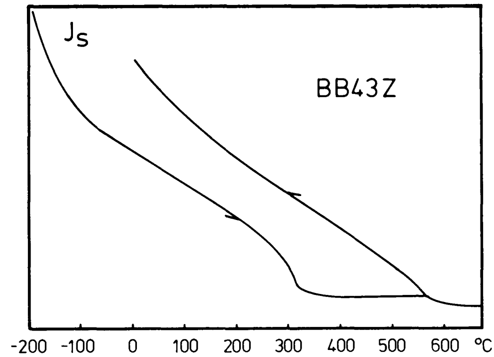


Fig. 2. Saturation magnetization J_s versus temperature of a natural diabase sample. Heating and cooling cycle are indicated by arrows

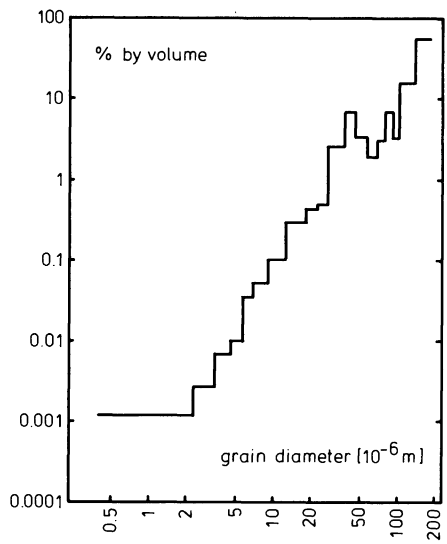


Fig. 3. Histogram of grain size versus their contribution in percent by volume to the total ore content

The saturation magnetization J_s (in a field of 800 kA/m) versus temperature from -200 °C up to 700 °C is shown in Figure 2. A Curie temperature T_c of 320 °C is observed in the heating curve. This phase is destroyed by heating up to 700 °C and completely replaced by magnetite ($T_c = 580$ °C) with increased saturation magnetization as can be seen from the cooling curve of Figure 2. J_s/T-curves of basic rocks showing similar features are usually interpreted in terms of a nonstoichiometric titanomagnetite phase with a T_c of 320 °C being exsolved into a phase close to magnetite plus a phase rich in Titanium close to Ilmenite upon further heating. Polished section studies revealed the presence of idiomorphic primary pyrrhotite which has a T_c of 320 °C and for which an oxidation to magnetite takes place after heating to 700 °C. No indications of other primary ore phases like Titanomagnetite, Hematite, Magnetite or Chromites could be found by the polished section studies. Only primary pyrite occurs occasionally as separate grains or as intergrowths with pyrrhotite. The average total ore content of the diabase is about 0.5 % by volume.

The grain sizes vary between 300 μm and about 1 μm. Most of the grains have a diameter of around 50 μm. Figure 3 shows a histogram of the grain sizes versus their abundance in percent by volume. It has been obtained from the study of several representative polished sections. Almost the entire ore content (99.7 %) is contained in the grains with diameters larger than 20 μm with true multi-domain behaviour. A little less than 0.3 % are in the range between 2 and 20 μm, that is in the transition stage between the multidomain and single-domain state. Only about 0.001 % of the ore content is concentrated in grains smaller than 2 μm which are believed to be in the single-domain state as will be shown in the next section.

3. Domain Structure Studies of Pyrrhotite

The domain structure was studied with the Bitter pattern technique. Technical details can be taken from Bitter (1931) and Elmore (1938). Instead of the magnetite colloid proposed by Elmore (1938), a suspension called "Ferrofluid" was used. The advantages of the Ferrofluid are better resolution of the domain structures and the possibility for experiments at various temperatures.

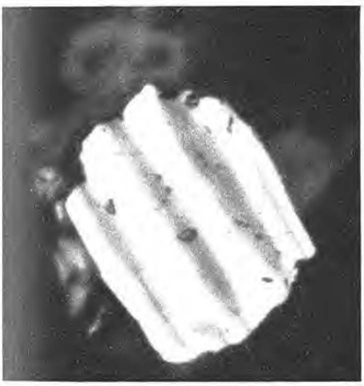
In contrast to magnetite and titanomagnetites, where special techniques for the preparation of strainfree surfaces are necessary (Soffel, 1963; Hanss, 1964; Soffel, 1968; Soffel and Petersen, 1971; Soffel, 1971) this is not the case for the pyrrhotite which has been studied here. Carefull polishing with very fine grained diamond paste was sufficient. Ionic etching (Soffel, 1968) showed no effect of further improvement of the domain configuration.

Pyrrhotite has an orthohexagonal structure which is slightly monoclinic. At room temperature the plane (001) is one of easy magnetization, the direction [001] is that of very difficult magnetization. According to Bin and Pauthenet (1963), crystal anisotropy is very large. The values for room temperature are: $K_1 = 0.35 \times 10^6$ erg/cm^3; K_2 = nearly zero; $K_3 = 1.18 \times 10^6$ erg/cm^3; $K_4 = 32.2 \times 10^6$ erg/cm^3; saturation magnetization J_s at room temperature is about 96 kA/m (96 Gauss). J_s is therefore of about the same amount as for Ti-rich Titanomagnetites with T_c at about 150 °C, while the crystal anisotropy at room temperature is by about two orders of magnitude larger (Syono, 1965). The value for the magnetostrictive constant is estimated in Section 5.

Due to the uniaxial crystal symmetry, low saturation magnetization and large crystal anisotropy a quite simple domain configuration with parallel lamellae without closure domains at the margins of the crystals can be expected. This is indeed the case as shown in Figure 4. Smaller grains have increasingly simpler domain configurations. Figure 5 shows a four domain grain. The larger grain in Figure 6 with a more complicated domain configuration is accompanied by a two domain and a single-domain particle.

Figure 7 shows a plot of number of lamellae shaped domains versus grain diameter. From this an extrapolation can be made for the determination of the single-domain-multidomain transition which seems to take place at a critical diameter $d = 1.6$ μm for this material. From this value the specific wall energy


4


5

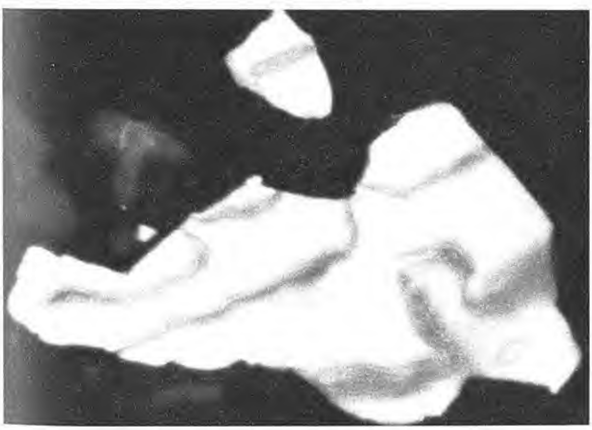

6

Fig. 4. Lamellae-shaped domains of a large ore grain. Diameter of the figure is 120 μm

Fig. 5. Four domain grain with a diameter of 20 μm

Fig. 6. Large ore grain (length: 50 μm) with a more complicated domain configuration accompanied by a two domain and a single-domain grain

can be estimated according to Kittel (1949) and Soffel (1971) to be:

$$\gamma_w = 2\pi\, d I_s^2/9$$
$$= 1\ \mathrm{erg/cm^2} \qquad (1)$$

using $d = 1.6 \cdot 10^{-6}$ m and $J_s = 96$ kA/m $= 96$ Gauss. γ_w is therefore of about the same value as for other ferromagnetic and ferrimagnetic materials (Kneller,

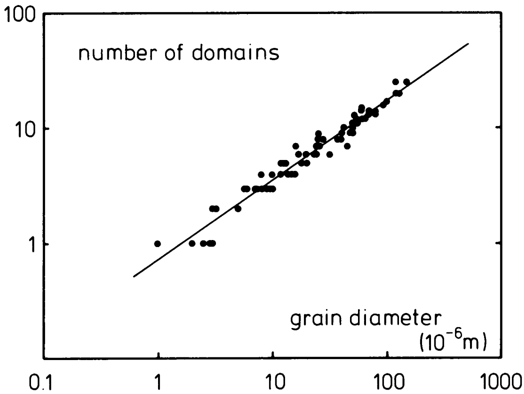


Fig. 7. Number of lamellae-shaped domains versus grain diameter

1962; Stacey and Banerjee, 1974). Due to the low saturation magnetization of pyrrhotite most of the still easily visible ore grains between 1 and 2 μm are already in the single domain state.

4. Intensity of Stable Remanence and Experimental Evidence for Pseudo-Single-Domain Effects

The observed abundance of true single-domain particles in the investigated rock samples is very low. They cannot explain the intensity of the stable component of NRM which was shown to be 0.082 A/m (=82 μG) in the average (see Sect. 2). According to Néel (1949) and Soffel (1969) the TRM of a rock specimen containing p % of uniformly dispersed and randomly oriented single domain particles is given by:

$$J_{\mathrm{TRM},\, H_0,\, T_0} = \tfrac{1}{3}\, p\, J_s(T_0)\, \mathrm{tgh}\, \frac{v\, J_s(T_B)\, H_a(T_B)}{k\, T_B}$$

where $H_a(T_B) \approx 0.5$ Oe is the intensity of the external field when the blocking temperature T_B (≈ 590 K) is passed. $J_s(T_B)$ is the saturation magnetization for this condition and is believed to be about 1/3 of the saturation magnetization $J_s(T_0)$ at room temperature (Stacey, 1963); v is the mean volume of a single-domain grain ($\approx 10^{-12}$ cm^3) and k is Boltzmann's constant. With $J_s(T_0) = 105$ cgs units and $p = 0.5\,\% \times 0.001\,\% = 5 \cdot 10^{-8}$ we have:

$$J_{\mathrm{TRM},\, H_0,\, T_0} = \tfrac{1}{3} \times 5 \cdot 10^{-8} \times 105\, \mathrm{tgh}\, \frac{10^{-12} \times 35 \times 0.5}{1.38 \times 10^{-16} \times 590}$$
$$= 1.75 \times 10^{-6}\ \mathrm{G}.$$

This is only about 2% of the observed stable component of NRM (82 μG). It is unlikely that only such a small fraction of the actually present single domain particles has been detected by the polished section studies. The more reasonable explanation of the discrepancy is that substantial parts of the stable component of NRM must be located in zones of the larger multidomain particles with pseudo-single-domain behaviour.

The domain configuration of the large multidomain particles was therefore investigated under this special point of view.

5. Evidence for Pseudo-Single-Domain Effects in the Multidomain Grains and Conclusions

The primary pyrrhotite crystals are idiomorphic and rather coarse grained (see Fig. 3). Typical for the material is the occasional occurrence of nonmagnetic inclusions with a diameter of up to several μm in the large ore grains.

According to Stacey (1962) and Stacey and Banerjee (1974) these zones are believed to be the location of pseudo-single-domain effects. Figure 8 shows a large multidomain grain with a cluster of nonmagnetic inclusions in its center. The other areas of the ore grain are more or less free from inclusions. The domain walls appear in the picture as dark lines. They reveal lamellae shaped domains in the zones of the ore grain outside the cluster of inclusions. Single inclusions obviously have no serious effect on the domain configuration. Due to the high concentration of inclusions in the center of Figure 8 the lamellae shaped large domains are obviously replaced by a large number of much smaller domains with irregular boundaries. The application of external fields up to several hundred Oe produced large changes of the domain configuration only in the areas of the ore grain outside the cluster of inclusions. Within the cluster the configuration changed only slightly or not at all. The domain structure of an ore grain with more or less equally distributed inclusions is shown in Figure 9. In this case the domains have still more or less the shape of lamellae. However the domain walls are more irregular and seem to be attached to larger inclusions or smaller clusters of inclusions. In the case of Figure 9 the inclusions have only the effect of increasing the wall friction of the multidomain grains. According to Soffel (1970) only moderate coercive forces ($\approx$100–200 Oe) can be expected from the interaction between domain walls and inclusions. Obviously a critical concentration of inclusions exceeding a critical diameter is necessary for the replacement of the lamellae shaped domains by much smaller domains with irregular boundaries as shown in Figure 8. More detailed investigations of this subject are planned.

Regarding the AF-demagnetization curve (Fig. 1), the initial drop of the intensity of remanence with coercive forces smaller than 100 Oe seems to indicate the destruction of remanence of the large multidomain grains with little or no inclusions. The remanence components with coercive forces between 100 and 300 Oe seem to be located in the large multidomain grains with dispersed inclusions and the very small multidomain grains just above the critical diameter of 1.6 μm for the single-domain – multidomain transition. The areas in the multidomain grains with clusters of inclusions are believed to be zones with pseudo-single-domain behaviour being responsible for the observed magnetically hard component together with the contribution from the true single-domain particles.

From the fact that no stress patterns can be observed on the investigated pyrrhotite after mechanical polishing, the upper limit for the magnetostrictive

Fig. 8. Large multidomain grain with lamellae-shaped domains. The cluster of nonmagnetic inclusions within the ore grain produces extremely small domains with presumably pseudo-single-domain behaviour. The diameter of the figure is 120 μm

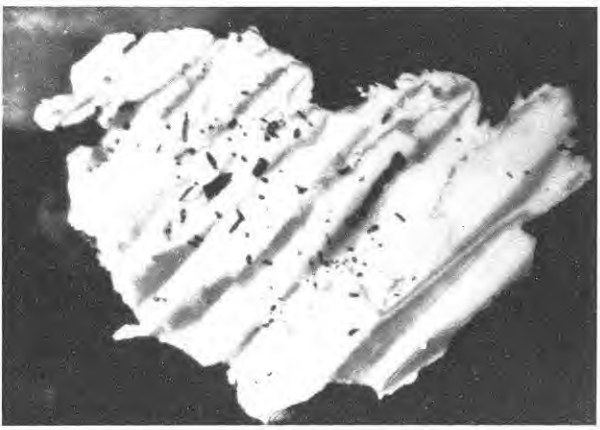


Fig. 9. Domain structure of a large ore grain (diameter: 100 μm) with a more ore less equal distribution of nonmagnetic inclusions

constant of pyrrhotite can be estimated. According to Soffel (1966), the stress along a scratch is in the order of $2.5 \cdot 10^9$ dyne/cm^2. Using the model of Chikazumi and Suzuki (1955), the magnetostrictive constant of pyrrhotite must be smaller than 7×10^{-6} which is one order of magnitude smaller than for magnetite, according to Kneller (1962).

Acknowledgement. The investigations were made in the Institut für Allgemeine und Angewandte Geophysik, Universität München. The author is indebted to Dipl.-Geophys. H. Zinsser for doing part of the rock magnetic measurements. Thanks are also due to Prof. Dr. G. Angenheister, Dr. E. Schmidbauer, Dr. N. Petersen, Dr. A. Schult and Dr. J. Pohl for many helpful discussions. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

Bin, M., Pauthenet, R.: Magnetic anisotropy in pyrrhotite. J. Appl. Phys. **34**, 1161–1162, 1963

Bitter, F.: On inhomogeneities in the magnetization of ferromagnetic materials. Phys. Rev. **38**, 1903–1905, 1931

Chikazumi, S., Suzuki, K.: On the maze domain of silicon-iron crystal. J. Phys. Soc. Japan **10**, 523–534, 1955

Elmore, W.C.: Ferromagnetic colloid for studying magnetic structures. Phys. Rev. **54**, 309–310, 1938

Hanss, R.E.: Thermochemical etching reveals domain structure in magnetite. Science **146**, 398–399, 1964

Kittel, C.: Physical theory of ferromagnetic domains. Rev. Mod. Phys. **21**, 541–583, 1949

Kneller, E.: Ferromagnetismus. Berlin, Göttingen, Heidelberg: Springer 1962

Néel, L.: Theorie du trainage magnètique des ferromagnètiques en grains fins avec leur applications aux terres cuites. Ann. Géophys. **5**, 99–136, 1949

Soffel, H.: Untersuchungen an einigen ferrimagnetischen Oxyd- und Sulfidmineralien mit der Methode der Bitterschen Streifen. Z. Geophys. **29**, 21–34, 1963

Soffel, H.: Stress Dependence of the Domain Structure of Natural Magnetite. Z. Geophys. **32**, 63–77, 1966

Soffel, H.: Die Bereichsstrukturen der Titanomagnetite in zwei Basalten und die Beziehung zu makroskopisch gemessenen magnetischen Eigenschaften dieser Gesteine. Habilitation thesis, Nat. Fak. Univers. München 1968

Soffel, H.: The origin of thermoremanent magnetization of two basalts containing homogeneous single phase titanomagnetite. Earth Planet. Sci. Lett. **7**, 201–208, 1969

Soffel, H.: The Influence of the Dislocation Density and Inclusions on the Coercive Force of Multidomain Titanomagnetites of the Composition 0.65 $Fe_2TiO_4 - 0.35\ Fe_3O_4$ in Basalts as Deduced from Domain Structure Observations. Z. Geophys. **36**, 113–124, 1970

Soffel, H.: The single-domain – multidomain transition in natural intermediate titanomagnetites. Z. Geophys. **37**, 451–470, 1971

Soffel, H., Petersen, N.: Ionic etching of titanomagnetite grains in basalts. Earth Planet. Sci. Letters **11**, 312–316, 1971

Stacey, F.D.: A generalized theory of thermoremanence, covering the transition from single-domain to multidomain magnetic grains. Phil. Mag. **7**, 1887–1899, 1962

Stacey, F.D.: The physical theory of rock magnetism. Adv. Phys. **12**, 45–133, 1963

Stacey, F.D., Banerjee, S.K.: The physical principles of rock magnetism. Amsterdam, London, New York: Elsevier Scientific Publishing Company, p. 110–114, 1974

Syono, Y.: Magnetocrystalline anisotropy and magnetostriction of $Fe_3O_4 - Fe_2TiO_4$-series with special application to rock magnetism. Jap. J. Geophys. **4**, 71–143, 1965

Received June 25, 1976