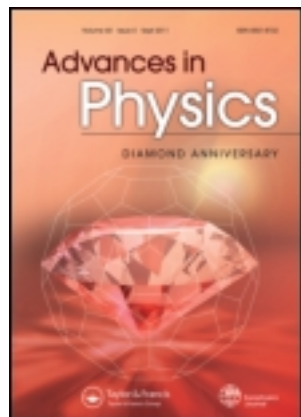


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Some Theoretical Aspects of Rock-Magnetism

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SUMMARY

The memoir is devoted to a brief theoretical study of the most typical magnetic properties of rocks. In particular §§ 3–16 are on ferrimagnetism, §§ 17–35 on single domain particles and §§ 36–57 on large multi-domain particles.

Theoretical studies are made of the following aspects of the subject and compared with the experimental results: remanent magnetization (§ 38), initial susceptibility (§ 39), variation with applied field of thermo-remanent magnetization (abbreviated to T.R.M.) (§§ 40, 41, 57), the ratio Q_k of T.R.M. acquired in a given field to the induced magnetization in the same field (§ 42), the additivity of partial T.R.M.'s in the case both of small grains (§ 28) and large grains (§ 57).

Considerable space is devoted to the magnetic 'viscosity' due to thermal agitation in small grains (§§ 24–27) and in larger ones (§§ 49–56). Expressions are given for magnetic 'viscosity' in the range of Rayleigh's relations (§ 51) particularly with a demagnetizing field present (§ 54). The theoretical and experimental results on the irreversible decrease in isothermal remanent magnetization are briefly quoted both for small (§ 30) and large (§ 55) grains.

Different reversing mechanisms are reviewed which could cause a negative T.R.M., that is one directed in the opposite sense to the field applied during cooling. Some are related to negative Weiss–Heisenberg exchange forces: reversal by diffusion involving ionic exchange between the two sub-lattices in a ferrimagnetic (§ 7), reversal by anomalous thermal variation in spontaneous magnetization (§§ 11, 12), reversal by diffusion with complete change of composition (§ 16). The others are effects of the demagnetizing field: reversal in mixtures of two constituents with different Curie Points (§§ 31–34), reversal by segregation, allotropy and chemical alteration (§ 35). The actual examples so far known are recalled.

§ 1. INTRODUCTION

IN the general scheme of magnetic theory, the problems of the magnetic properties of rocks are distinguished by certain peculiarities which it is convenient to make clear at the outset.

In the first place, the carriers of magnetic properties are the various more or less pure oxides of iron, magnetite, titanomagnetites, hematite, maghemite, etc. . . . , that is, substances which are ferrimagnetic or anti-ferromagnetic rather than classical ferromagnetics. A notable result is that the thermal variation of saturation magnetization of rocks can be of very different types from that of iron or nickel.

A second point to be emphasized is that the magnetic constituents are a small proportion, perhaps a few per cent, distributed amongst the practically non-magnetic bulk of the rock. The problem is that of magnetic grains more or less far from one another so that the demagnetizing field due to shape is very important.

A third point is that, since the geophysicist is especially interested in the magnetic properties of rocks relative to the earth's field, the properties in fields small compared with the coercive force are of particular interest.

Finally, magnetic viscosity and the effects of time on magnetic phenomena in general are of great importance, because the time scale concerned is the geological one.

§ 2. THE THREE PROCESSES OF CHANGE IN MAGNETIZATION

A detailed study and investigation of the magnetic properties of rocks could be the basis of a complete treatise on magnetism, and naturally there is no place for that here. We shall consider only the most important particular points, referring for the rest to the classical works on ferromagnetism⁽¹⁾.

According to Weiss' already classic theory, a ferromagnetic substance is divided into *elementary domains* of varying size within which the magnetization is uniform. The direction of this magnetization varies from one domain to another but its magnitude J_s remains constant and is called the *spontaneous magnetization*. In practice, J_s depends only on the temperature T and the temperature at which it falls to zero is called the Curie Point. On the other hand the shape and size of the elementary domains as well as the orientation of their spontaneous magnetizations depend on many factors: the applied field, the internal demagnetizing field and that due to shape, magneto-crystalline and magneto-elastic couplings, the presence of dislocations or impurities, etc.

The magnetization of ferromagnetic bodies, considered as a function of magnetic field and of temperature, thus depends on three distinct processes: (a) the reversible change in the *magnitude* of the spontaneous magnetization with temperature; (b) the changes of direction or rotations of the spontaneous magnetization within the domains, whose boundaries remain fixed; (c) the displacement of the walls separating elementary domains whose direction of magnetization remains fixed.

We have to study the effects of these different processes on the properties of rocks and baked clays.

THE FERRIMAGNETISM OF ROCKS

§ 3. DEFINITION OF FERRIMAGNETISM

The simplest kind of ferromagnetic substance is typified by iron: all the atoms are identical and have the same permanent magnetic moment. A coupling exists between the moments of neighbouring atoms which favours the parallel orientation of these moments so that, at temperatures low enough for the energy of thermal agitation kT to be small compared with the energy of coupling, all the atomic moments are parallel to each other: this is the strict definition of *ferromagnetism*.

But more complicated kinds can be imagined, such as where there are two types of atoms with couplings of such magnitude and sign that at low temperatures the atomic moments of one type all point in one direction and those of the other type all in exactly the opposite direction. One is then dealing with ferrimagnetism⁽²⁾.

In both cases a small element of volume dv of the substance, large compared with atomic dimensions, has a permanent spontaneous magnetic moment $J_s dv$, where J_s is the spontaneous magnetization defined above.

§ 4. THE SIMPLE INVERSE FERRITES

Many of the ferromagnetic constituents of rocks, in particular the titanomagnetites, are of the spinel type with properties more or less analogous to those of the ferrites MFe_2O_4 , where M is a divalent metal. In these ferrites the metallic ions can occupy two crystallographically different types of sites: the lattice has, per unit molecule, one tetrahedral site A, surrounded by 4 oxygen atoms and two octahedral sites B surrounded by 6 oxygen atoms.

It has been shown experimentally⁽³⁾ that several types of spinel ferrites exist: the *normal ferrites* have the M ion on the A site and the two Fe^{+++} ions on the B sites, as in zinc ferrite. These ferrites are not magnetic. There are also the *inverse ferrites* in which the A site is occupied by an Fe^{+++} ion and one of the B sites is occupied by the M ion and the other by the second Fe^{+++} ion; these ferrites are magnetic.

The interatomic couplings are, from a magnetic point of view, most powerful when they act between an ion on an A site and one on a B site; these AB interactions are *negative* and tend to align the atomic moments of the two interacting atoms antiparallel. The interactions between atoms occupying the same types of site, the AA or BB interactions, are generally much weaker and play only a secondary role. Owing to the strong negative AB interactions the magnetic lattice is, at low temperatures, divided into two sub-lattices A and B, corresponding to the A sites and B sites, whose spontaneous magnetizations J_A and J_B are oriented in opposite directions: this is a typical case of *ferrimagnetism*⁽²⁾.

These conclusions were reached from a profound study of the magnetic properties of these substances and have been very directly confirmed by

neutron diffraction. Shull and his co-workers have shown⁽⁴⁾, for example in magnetite (where $M=Fe^{++}$), that the magnetic moments of atoms on A sites are in fact antiparallel to those of atoms on B sites. Thus in the inverse ferrites the molecular moment, close to absolute zero, is simply given by the atomic moment of the M ion, since the moments of the Fe^{+++} ions on A sites exactly cancel those of the Fe^{+++} ions on B sites. In fact it is found that with $M=Ni^{++}$, Co^{++} , Fe^{++} , Mn^{++} the molecular moments of the corresponding ferrites are close to 2, 3, 4 and $5\mu_B$ which are the values of the spin magnetic moments of these ions. The slight remaining differences are probably due to residual orbital moments.

§ 5. THE DISTRIBUTION OF IONS ON THE DIFFERENT SITES IN SPINELS

Assuming that in the ferrites the elementary atomic moments of sub-lattice A are aligned antiparallel to those of sub-lattice B, then the magnetic properties will be closely related to the distribution of cations between the two types of sites. This distribution depends on factors which are not yet fully understood. According to Verwey and Heilmann⁽³⁾ and Romeijn⁽⁵⁾, Zn^{++} , Cd^{++} , Ga^{+++} , In^{+++} and Ge^{++++} ions have a preference for A sites, Ni^{++} , Cr^{+++} , Ti^{++++} and Sn^{++++} ions for B sites while Mg^{++} , Al^{+++} , Fe^{++} , Co^{++} , Mn^{++} , Fe^{+++} and Cu^{++} ions can occupy either A or B sites according to circumstances.

In certain cases, the tendency of the ions to be placed in a definite ordered distribution is feeble enough for the distribution to change considerably with temperature. This effect is observable in $ZnFe_2O_4$ and $NiFe_2O_4$ and is important in $CdFe_2O_4$ while in $MgFe_2O_4$ and $CuFe_2O_4$ a detailed quantitative study has been made of it⁽⁶⁾.

Letting w be the energy necessary to transfer a bivalent ion M from a B site to an A site, this transfer being of course accompanied by that of a ferric ion in the opposite direction, and letting y and $1-y$ be the proportions of M ions, on the A and B sites at temperature T , then Boltzmann's law shows that⁽²⁾

$$\frac{y(1+y)}{(1-y)^2} = \exp\left(-\frac{w}{kT}\right).$$

Thus y is a function of T . The state of thermodynamic equilibrium at any temperature T can in principle be preserved in false equilibrium at room temperature by quenching. If the atomic moments of Fe^{+++} and M^{++} ions are respectively 5 and m Bohr magnetons, the saturation molecular moment M_s observed at low temperatures will be

$$M_s = [m + 2y(5 - m)]\mu_B.$$

These ideas have been confirmed by Pauthenet's work⁽⁶⁾ on Mg and Cu ferrites in which he followed the variation of saturation moment with the temperature of quenching and found values of w/k equivalent to 1220°K and 1540°K respectively.

If the quenching temperature T is below 500–600°K thermodynamic equilibrium is no longer established at that temperature even after several hours. This shows the possibility of preserving a false equilibrium at room temperature for a time which is long compared with the length of experiments. But this would no longer be true after some tens of millions of years; then the moment M_s of the ferrite considered would correspond to y_0 , the value of the equilibrium parameter appropriate for the prevailing temperature T_0 . If this true equilibrium state happens to be destroyed, for instance by heating, no laboratory method can ever restore it. This is an example of the important effect that the enormous scale of geological time can have on the physical state of rocks as well as on their magnetic properties.

§ 6. SUBSTITUTED FERRITES: THE CASE OF ALUMINIUM

Important results are given by a study of substituted ferrites such as $\text{NiFe}_{2-m}\text{Al}_m\text{O}_4$, which can be described as NiFe_2O_4 in which some Al^{+++} ions have replaced Fe^{+++} ions. If all the Al ions replaced ferric ions on octahedral B sites, a decrease of saturation molecular moment at absolute zero would be observed proportional to the amount m of substituted Al ions. In particular for $m=0.4$, the saturation moment ought to be zero and the negative values given by the formula for $m>0.4$ would simply correspond to the spontaneous magnetization of sub-lattice A becoming greater than that of sub-lattice B.

In fact as E. W. Gorter has shown⁽⁷⁾ this is roughly what happens for well-annealed specimens except that the moment is zero for $m=0.62$ showing that a small fraction of the Al^{+++} ions occupy A sites. On the contrary for quenched specimens the moment does not fall to zero and thus never becomes negative even for the composition NiFeAlO_4 : the necessary conclusion is that in the quenched state a much larger proportion of Al^{+++} ions occupy A sites. Thus annealing causes some Al ions to move from A sites to B sites, giving a decrease of spontaneous magnetization since the number of Fe^{+++} ions, carrying $5\mu_B$, on A sites increases. This effect is most marked for $m=1$ when the molecular moment of the quenched specimen is $+0.42\mu_B$ while that of the annealed one is $-0.64\mu_B$.

§ 7. CHANGE OF SIGN OF SPONTANEOUS MAGNETIZATION BY ANNEALING

Since the spontaneous magnetization of NiFeAlO_4 changes sign on annealing the remanent magnetic moment of a specimen of this substance, magnetized at high temperature and then quenched, must change sign spontaneously on reheating: there is an *inversion of spontaneous magnetization*. This inversion is produced by diffusion of Al ions from A to B. To produce the inversion in the laboratory several hours at 400°C are needed, but the same effect would probably occur at ordinary temperatures in some millions of years. Naturally thi

inversion of the spontaneous magnetization involves reversal of any remanent magnetization. From Gorter's data⁽⁷⁾ the same inversion effect should occur over the whole range $0.62 < m < 1$. Also it seems probable that the compounds in the range $0.50 < m < 0.62$ which in the laboratory always have a positive moment, whether they are quenched or annealed, could, after some millions of years at ordinary temperatures acquire a negative moment: it is only necessary that, at the rather high temperature at which annealing in the laboratory still has a noticeable effect, the equilibrium concentration of the Al^{+++} ions be but slightly positive. Then the lower annealing temperature, made possible by the enormous length of the process, will displace the equilibrium towards negative moments. Such a substance would in all possible laboratory experiments always have a positive thermo-remanence but in the course of geological time would acquire a negative spontaneous magnetization and a remanent magnetization opposite to its original one.

This curious behaviour of the ferrites of the type $\text{NiFe}_{2-m}\text{Al}_m\text{O}_4$ is important although similar effects could probably not be observed in the natural substituted magnetites which form many of the ferromagnetic constituents of rocks. The reason is that in the nickel ferrites the magnetic moments of the two sub-lattices A and B are very close $5\mu_B$ and $7\mu_B$ so that it is much easier for the A sub-lattice to have a greater moment than the B than in magnetite where the moments of the two sub-lattices, at 5 and $9\mu_B$ are much less close.

§ 8. SUBSTITUTED FERRITES: THE CASE OF TITANIUM

Many of the ferromagnetic constituents of rocks are titanomagnetites, derived from magnetite Fe_3O_4 by substitution of Ti^{++++} ions for Fe^{+++} ions, together with a change of ionization of an Fe^{+++} ion to an Fe^{++} ion. This gives solid solutions of spinel type with the general formula $\text{Ti}_m\text{Fe}_{3-m}\text{O}_4$ which were first studied by Michel and Pouillard⁽⁸⁾. If it is assumed that the Ti^{++++} ions always occupy B sites and that the remaining B sites are filled by Fe^{++} ions, the saturation molecular moment ought to be given by $(4-6m)\mu_B$ in the interval $0 < m < 0.5$ and by $(2-2m)\mu_B$ when $0.5 < m < 1$. The experimental facts are not enough to decide if these suggestions, especially on the distribution of Fe^{++} ions, are correct. All that is known is that the saturation moment and the Curie Point fall regularly as m increases.

Recently Kawai, Kuma and Sasajima⁽⁹⁾ have observed that solid solutions of this type, which immediately after quenching have a single clearly defined Curie Point, change gradually so that after several months at room temperature they have two Curie Points, one at about 100°C and the other close to that of magnetite. It is tempting to interpret this change as a segregation into two phases, one rather weakly magnetic and the other near to magnetite.

Finally mention must be made of maghemite which is similar to the cubic sesquioxide $\text{Fe}_2\text{O}_3\gamma$ and has a spinel structure rather like that of magnetite but with some B sites empty : it is also a ferrimagnetic.

§ 9. THE THERMAL VARIATION OF THE MAGNETIZATION OF FERRITES

The thermal change of spontaneous magnetization J_s in rocks is particularly interesting as they have generally acquired their natural magnetization in a temperature range close to their Curie Point where J_s is much smaller than at ordinary temperatures. In an assemblage of elementary domains, in which the boundaries and direction of spontaneous magnetization of each domain remain fixed, the mean magnetization of the aggregate will be proportional to, and vary reversible with, J_s . Thus a small magnetization acquired near the Curie Point can increase reversibly during cooling of the specimen. As will be shown later (cf. §§ 32-35) this can have curious results in mixtures of several ferromagnetic constituents with different Curie Points. For most ordinary ferromagnetic substances such as iron, nickel, cobalt and their alloys, the curves of J_s against temperature have very similar shapes, typically a slow variation of J_s at low temperatures (less than 10% up to $T=0.6\theta$) and a rapid one near the Curie Point θ . In the case of rocks, although the J_s - T curve of pure magnetite is very similar to that of metals, very different types are also found, such as a practically linear change of J_s with T from absolute zero right up to the Curie Point. This variability is typical of the ferrimagnetics.

§ 10. THE MOLECULAR FIELD THEORY APPLIED TO FERRIMAGNETISM

As a first approximation to a theory of the thermal variation of spontaneous magnetization the Weiss molecular field theory can be used. This, being purely phenomenological, replaces the interactions between the elementary magnetic moments by an imaginary magnetic field called the molecular field which is proportional to the magnetization \mathbf{J} and is given by

$$\mathbf{H}_m = N\mathbf{J}$$

where N is the molecular field coefficient.

The magnetization law for a paramagnetic in which the atomic moments are quite independent of each other and can be freely oriented is of the form

$$J = B(H/T).$$

If then a ferromagnetic can be considered as a paramagnetic which is magnetized and given its spontaneous magnetization J_s by its own molecular field H_m , J_s will be the solution of the implicit equation

$$J_s = B(NJ_s/T).$$

The classical discussion of this equation need not be given here except to recall that the shape of the $J_s(T)$ curve depends on the form of the

function $B(H/T)$ which itself depends on the value of j , the total angular momentum quantum number of the magnetic atom concerned. The $J_s(T)$ curves of ferromagnetic metals correspond roughly to the value $j = \frac{1}{2}$, indicating that the magnetic carriers are isolated spins.

Néel⁽¹⁰⁾ has slightly modified the molecular field theory by supposing H_m to be proportional to the mean magnetic moment of closely neighbouring atoms. For substances like the ferrimagnetics having two sub-lattices A and B with magnetizations \mathbf{J}_a and \mathbf{J}_b two molecular fields must be considered, \mathbf{H}_a acting on atoms on A sites and \mathbf{H}_b on those on B sites. They are given by

$$\mathbf{H}_a = n_{aa}\mathbf{J}_a + n_{ab}\mathbf{J}_b,$$

$$\mathbf{H}_b = n_{ab}\mathbf{J}_a + n_{bb}\mathbf{J}_b,$$

involving three molecular field coefficients n_{aa} , n_{ab} , n_{bb} representing the AA, AB and BB interactions. If $B_a(H/T)$ and $B_b(H/T)$ are the paramagnetic magnetizations of ions on the A and B sub-lattices respectively, it can be shown that, in the absence of an applied field, the system has a spontaneous magnetization \mathbf{J}_s

$$\mathbf{J}_s = \mathbf{J}_a + \mathbf{J}_b.$$

It is the vector sum of the two partial spontaneous magnetizations of the two sub-lattices A and B, J_a and J_b which are solutions of the complementary equations

$$J_a = B_a(\mathbf{H}_a/T),$$

$$J_b = B_b(\mathbf{H}_b/T).$$

In the important case of the ferrites, n_{ab} is negative and large compared with the other two coefficients n_{aa} and n_{bb} . The partial spontaneous magnetizations are then antiparallel and J_s is simply the arithmetic difference between J_a and J_b . If these have different absolute values the system will have a finite resultant spontaneous magnetization, that is to say an apparent ferromagnetism, created by negative interactions.

The two partial spontaneous magnetizations J_a and J_b disappear together at the Curie Point θ above which simple paramagnetism is observed. However the reciprocal of the susceptibility χ does not vary linearly with temperature, following the Curie-Weiss law of ordinary ferromagnetics, but according to a hyperbolic law of the form

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \theta},$$

where C is the theoretical Curie constant of the ions present and χ_0 , σ and θ depend on n_{aa} , n_{bb} and n_{ab} . This hyperbolic variation is characteristic of ferrimagnetic substances.

The three coefficients of the molecular field can be found from a study of the susceptibility above the Curie Point⁽¹¹⁾ and hence the thermal variation of spontaneous magnetization below the Curie Point can be deduced without recourse to any other data. Good agreement between theory and experiment has been found by Pauthenet⁽⁶⁾ for nickel, cobalt

and iron ferrites and more recently by Clark and Sucksmith⁽¹²⁾ for manganese ferrite.

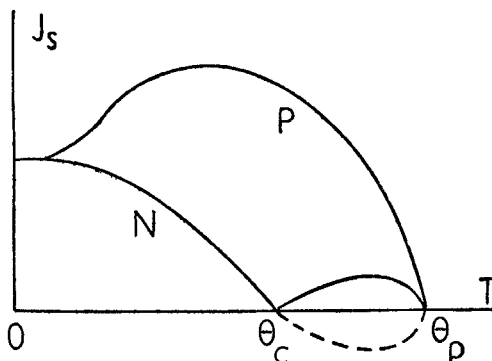
Despite these good agreements it must not be forgotten that theory based on the molecular field approximation sometimes gives very inaccurate results as in the case of linear chains of atoms.

§ 11. INVERSION OF THE SPONTANEOUS MAGNETIZATION

Although the ferrites mentioned above already have a very different thermal change of spontaneous magnetization from the classical ferromagnetics, much more extraordinary curves can be conceived. That this is likely can be seen *a priori*, given the number of different factors on which the variation of $J_s(T)$ depends: values of j for the A and B ions, of the ratios n_{aa}/n_{ab} and n_{bb}/n_{ab} , and of the spontaneous magnetizations at absolute zero J_{as} and J_{bs} of the sub-lattices A and B. Curious forms are found especially when J_{as} and J_{bs} have closely similar magnitudes as in observing their slight difference their own irregularities are magnified.

Thus curves of type P (fig. 1) are possible, showing an increase of spontaneous magnetization from absolute zero to a maximum value. Such curves have actually been observed by E. W. Gorter⁽⁷⁾ in ferrites of general formula $\text{Ni}_{1.5-\alpha}\text{Mn}_\alpha\text{FeTi}_{0.5}\text{O}_4$ when α lies in the range 0.4–0.675.

Fig. 1



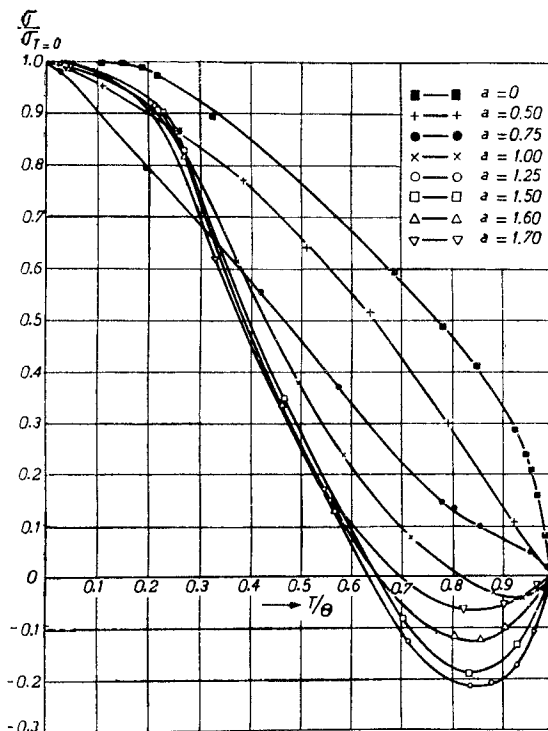
Two unusual types of thermal change of spontaneous magnetization characteristic of ferrimagnetic substances.

N is an even more remarkable type of curve in which the spontaneous magnetization decreases normally and disappears for the first time at temperature θ_c but then begins to increase again, reaches a maximum and finally disappears at a Curie Point θ_p . θ_c is not a Curie Point but only the temperature at which the spontaneous magnetization changes sign. Below θ_c the spontaneous magnetization J_a of sub-lattice A, say, is greater than that of B while above θ_c the reverse is true. θ_c can be called the *compensation temperature* at which the absolute values of the

spontaneous magnetizations of the two sub-lattices are equal. Two conditions would appear to favour the appearance of this curious phenomenon: the two sub-lattices must have rather similar saturation magnetizations and at the same time rather different values of j .

This type of curve whose existence was forecast theoretically in 1948 was found some years later by E. W. Gorter⁽⁷⁾ in the mixed ferrites $\text{Li}_{0.5}\text{Fe}_{2.5-a}\text{Cr}_a\text{O}_4$ for values of a between 1.00 and 1.70 (cf. fig. 2).

Fig. 2



Curves of thermal change of spontaneous magnetization in the ternary ferrites $\text{Li}_{0.5}\text{Fe}_{2.5-a}\text{Cr}_a\text{O}_4$ after E. W. Gorter.

The interpretation of θ_c as a temperature at which the spontaneous magnetization changes sign can be confirmed by an elegant experiment. A remanent magnetization is given to the specimen at a temperature below θ_c . It is then heated in a zero magnetic field past θ_c and the remanent magnetization is found to change sign spontaneously when the temperature of the specimen is θ_c . This is a very neat and direct proof of the existence of two magnetic sub-lattices in ferrites.

More recently other instances of the N type have been found in a new group of ferrites discovered by Forestier. These are the rare earth ferrites of general formula $\text{Fe}_2\text{M}_2\text{O}_6$ when M is a trivalent rare earth

element⁽¹³⁾. Guiot-Guillain, Pauthenet and Forestier⁽¹⁴⁾ have shown if M is Gd, Er or Dy these ferrites have N-type curves. They have also shown that the first point where the spontaneous magnetization disappears is in fact a compensation temperature by means of the spontaneous reversal of remanent magnetization at θ_c . Néel⁽¹⁵⁾ has shown that as there are probably three sub-lattices the explanation is still more complicated. In other respects the magnetic properties of these rare earth ferrites are somewhat similar to those of rhombohedral ferric oxide $\text{Fe}_2\text{O}_3\alpha$ which will be considered later.

§ 12. DISTINCTION BETWEEN COMPENSATION TEMPERATURE AND CURIE POINT

Although the spontaneous magnetization disappears at the compensation temperature just as at the Curie Point, the possibility of thermo-remanent magnetization in a small field H which distinguishes the Curie Point, does not occur at the compensation temperature. In fact at this temperature while the couple HJ_s exerted by the external field on the resultant spontaneous magnetization J_s falls to zero because J_s falls to zero, the perturbing magneto-crystalline and magnetoclastic forces remain finite as they are of the order of the squares J_a^2 , J_b^2 of the partial spontaneous magnetizations: thus there is no possibility of magnetization by a small field.

The result is that if a substance with a compensation point θ_c is acted on by a small field H when cooled from above its Curie Point, it will acquire near the latter a thermo-remanent magnetization (or T.R.M.) which from a few tens of degrees lower, will change practically reversibly remaining proportional to the spontaneous magnetization, independent of any variations in the applied field provided this remains of the order of H . In particular the T.R.M. will change sign with the spontaneous magnetization at θ_c . At room temperature such a substance will then have a T.R.M. opposite to the sense of the field to which it is due.

It should be noticed that this reversed T.R.M. is fundamentally due to a difference between the thermal changes of the two sub-lattices. It is a different mechanism from that described before (§ 7) involving an exchange of ions between the two sub-lattices below the Curie Point.

§ 13. TRIANGULAR SYSTEMS

Finally mention should be made in the study of ferrimagnetism of more complicated phenomena which appear if within say the B sub-lattice, negative BB interactions occur which are comparable with the AB interaction between the sub-lattices, the B sub-lattice can then be divided in its turn into two secondary sub-lattices. Such are the *triangular* systems studied by Yafet and Kittel⁽¹⁶⁾; no certain examples of them are yet known.

§ 14. RHOMBOHEDRAL FERRIC OXIDE

Rhombohedral ferric oxide $\text{Fe}_2\text{O}_3\alpha$, the mineral *hematite*, is an important ferromagnetic constituent of rocks and baked clays. Unfortunately its magnetic properties are not yet fully understood despite much study. The effects⁽¹⁷⁾ are approximately those of a paramagnetism only slightly dependent on temperature, with a specific susceptibility of about 20×10^{-6} , superimposed on a very feeble ferromagnetism with a molecular saturation magnetization of about one-hundredth of a Bohr magneton and a Curie Point at 675°C , definitely higher than that of magnetite (595°C).

The paramagnetism derives from a *fundamental antiferromagnetism* due to the distribution of ferric ions on two equal sub-lattices with equal and opposite spontaneous magnetizations. This distribution was suggested by detailed analysis of the magnetic properties and has subsequently been directly confirmed by neutron diffraction (Shull *et al.*⁽⁴⁾). At temperatures below 250°K , the direction of antiferromagnetism, that is the direction to which the spontaneous magnetizations of the two sub-lattices are parallel or antiparallel, lies in the basal plane of the crystal⁽¹⁸⁾ and can turn freely in that plane. The result is that the paramagnetic susceptibility, which is related to distortion of the antiparallel arrangement of spontaneous magnetizations under the action of the applied field, is practically independent of the crystallographic orientation of this field. On the other hand, above 250°K , the direction of antiferromagnetism changes and becomes parallel to the ternary axis of the crystal with the result that the susceptibility becomes much smaller in this direction than in the basal plane, as is found experimentally.

The temperature at which ordering in the two antiferromagnetic sub-lattices disappears (the Néel temperature) is probably 675°C because there is, at this temperature, a large specific heat anomaly which, having a magnitude comparable to that of magnetite, cannot be attributed to the feeble ferromagnetism.

The problem of the superimposed ferromagnetism is much more difficult. It has sometimes been thought, owing to the low value of the saturation magnetization, that it was due to ferromagnetic impurities such as magnetite or the cubic sesquioxide $\text{Fe}_2\text{O}_3\gamma$, but this hypothesis runs into difficulties over the change of magnetic properties according to thermal treatment. Also it has been shown that the ferromagnetism is oriented with respect to the lattice; for instance, above 250°K , the ferromagnetic part of the magnetization is much greater in directions in the basal plane than along the ternary axis. To explain this it has been suggested that the ferromagnetism is due to small crystals of magnetite, deformed and oriented by intergrowth in the larger crystals of the sesquioxide. This explanation may be partly true in some cases, but it seems more likely that the source is rather in lattice defects, such as errors in the regular alternation of layers of iron atoms magnetized antiparallel, which defects might be related to dislocations of the lattice;

there would then be a sort of ferromagnetic plane surrounded by an antiferromagnetic matrix. Or it could be described as an imperfection in the antiferromagnetism of the rhombohedral sesquioxide which caused a slight asymmetry between the two sub-lattices and thus produced a small resultant spontaneous magnetization: in general there would be a slight ferrimagnetism. The strongest argument for this hypothesis is the coincidence of the ferromagnetic Curie Point with the Néel temperature of the fundamental antiferromagnetism.

Whether they be due to impurities or to lattice defects, it seems that the magnetic properties of $\text{Fe}_2\text{O}_3\alpha$ can be represented as those of very small ferromagnetic domains, having the properties of hysteresis, buried in a paramagnetic matrix. The magnetization of the matrix is always small and proportional to the applied field so that it is of little interest in rock-magnetism.

§ 15. THE ILMENITE-HEMATITE SERIES

Another series of compounds occurs in rocks, with the general formula $\text{Fe}_{2-m}\text{Ti}_m\text{O}_3$ which can be considered⁽¹⁹⁾ as a combination in varying proportions of ilmenite FeTiO_3 and hematite Fe_2O_3 ; these compounds form two series of solid solutions, one of ilmenite type and one of hematite type separated by a solubility gap which probably increases in size as the temperature falls⁽¹⁹⁾.

Ilmenite is antiferromagnetic. Crystallographically its structure is derived from that of $\text{Fe}_2\text{O}_3\alpha$ by replacing every other layer of iron atoms by a layer of Ti atoms. These, in the ionic state Ti^{++++} , are not magnetic so that the alternations of the layers of cations can very probably be represented as: (+Fe) (Ti) (-Fe) (Ti) (+Fe) . . . where each layer is represented by brackets and the + and - signs represent the antiparallel orientations of the spontaneous magnetizations of the iron layers. In $\text{Fe}_2\text{O}_3\alpha$ the alternation is (+Fe) (-Fe) (+Fe)

Near the composition $\text{Fe}_{4/3}\text{Ti}_{2/3}\text{O}_3$ which is close to the limit of solid solution the compounds become definitely ferromagnetic with a molecular saturation moment of about $2\mu_B$. Such a large magnetic moment cannot be attributed to impurities or lattice defects but rather to a ferrimagnetic arrangement such as (+A) (-B) (+A) (-B) . . . in which the positive spontaneous magnetization of the A layers is a little greater than the negative one of the B layers. For instance, Nagata⁽²⁰⁾ suggests the compositions $(+\text{Fe}_{1/6}^{++}\text{Fe}_{2/3}^{+++}\text{Ti}_{1/6}^{++++})$ for the A layers and $(-\text{Fe}_{1/2}^{++}\text{Ti}_{1/2}^{++++})$ for the B layers giving a resultant molecular moment of $2\mu_B$.

§ 16. A POSSIBLE REVERSAL OF SPONTANEOUS MAGNETIZATION BY CHANGE OF COMPOSITION

As stated above, the solubility gap which exists around $m=0.5$ probably becomes wider when the temperature becomes lower. Suppose that this process extends to the composition $\text{Fe}_{4/3}\text{Ti}_{2/3}\text{O}_3$: a new phase close to

Fe_2O_3 and very rich in iron will be formed at the expense of the original phase, which will then lose iron and gradually tend towards ilmenite in which the alternation of layers is $(\text{Fe}^{++})(\text{Ti}^{++++})(\text{Fe}^{++}) \dots$. This leads to an increase in the spontaneous magnetization of the A layers and a decrease in that of the B layers. At the beginning the magnetic alternation of layers is $(+A)(-B)(+A)(-B) \dots$ and remains thus under the influence of the negative interactions between consecutive layers. But from the antiferromagnetic structure of ilmenite given above, there must also be negative interactions between the A layers. These negative interactions of AA type may become greater and greater as the spontaneous magnetization of A increases while on the other hand the AB interactions decrease with the decrease in spontaneous magnetization of B. A point would then be reached when the magnetic structure $(+A)(-B)(+A)(-B)(+A) \dots$ with a positive *resultant* spontaneous magnetization, would become unstable and would invert to the more stable structure $(+A)(-B)(-A)(-B)(+A)$ by reversal of the spontaneous magnetization of alternate A layers. This structure has *negative* resultant spontaneous magnetization. This reasoning presupposes that the spontaneous magnetization of the B layers maintains its original orientation despite both the reversal of some of the A layers and the thermal agitation. For this to be true it seems that there must be large enough positive interactions between B atoms in the same layer.

Whether this is true or not it is *a priori* not absurd that segregation of a solid solution into two phases during cooling could cause a reversal of T.R.M. by an atomic process involving negative molecular fields. It is evidently necessary to study the magnetic properties of compounds of the $\text{Fe}_{2-m}\text{Ti}_m\text{O}_3$ type carefully and to determine, preferably by neutron diffraction, the details of the antiferromagnetic structure and its modifications according to thermal treatment and change of concentration.

It will be seen later that exsolution can also give rise to a reversed T.R.M. by means of a demagnetizing field due to shape (cf. § 35).

SINGLE DOMAIN PARTICLES

§ 17. WALL THICKNESS AND GRAIN SIZE

In the range of magnetic fields in which hysteresis occurs, change of magnetization in ferromagnetic bodies is due to *rotation* of the spontaneous magnetization of the elementary domains and to *movement of the walls* separating them. In general the second process is more important in fields small compared with the coercive force.

The separating walls must not be regarded as infinitely thin surfaces but rather as zones of transition of finite thickness in which the magnetization gradually changes from the direction on one side to that on the other. The theory of these walls was put forward by F. Bloch⁽²¹⁾ and has since been developed by others⁽²²⁾: the *thickness* of the zone is given in order of magnitude by

$$p = a(NJ_s^2/K)^{1/2}$$

where a is the distance between neighbouring magnetic atoms, N the Weiss molecular field coefficient and K the magnetocrystalline anisotropy energy. This gives wall thicknesses of the order of a few hundred to a few thousand Angströms.

These results show immediately that very small grains of dimensions of the order of and less than p , can only contain a single domain since there is no space for a wall. In these very fine *single domain* grains, the magnetization is uniform and equal to the spontaneous magnetization J_s . The upper limit of grain size has been determined elsewhere (Néel⁽²³⁾).

With such single domain grains changes of magnetization can only occur by the rotation process so that the phenomena are particularly simple.

As the ferromagnetic constituents of rocks are dispersed in very small grains it is natural to see how far their magnetic properties can be explained on the model of single-domain grains.

§ 18. ELEMENTARY MAGNETIZATION CYCLES⁽²⁴⁾

In a single domain grain the internal magnetization energy depends only on the orientation of the magnetic moment with respect to certain axes in the grain. Considering, for simplification, magnetically uniaxial grains the energy E is given by

$$E = Kv \sin^2 \theta$$

where v is the volume of the grain and θ the angle between the magnetic moment and the axis.

The anisotropy constant K can arise in various ways. It can be due to a magnetocrystalline coupling so that K is equal to the anisotropy constant of a large crystal of the same material. It can arise from an anisotropy of shape: if the grain is an ellipsoid of revolution with demagnetizing field coefficients n along the axis and m in the equatorial plane, then

$$K = \frac{1}{2} (m - n) J_s^2.$$

Finally an anisotropy due to mechanical stress gives a value of K

$$K = \frac{3}{2} \lambda \sigma$$

where σ is a tension parallel to the axis and λ is the longitudinal saturation magnetostriction of the material of the grain. The three mechanisms can of course act simultaneously.

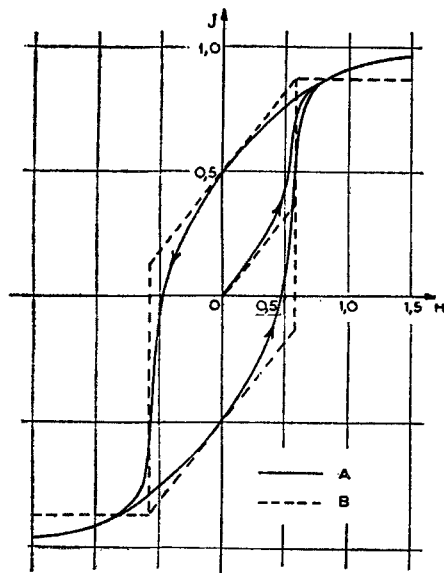
In an actual system these would be a very large number of grains, oriented at random. But the properties of a grain depend greatly on its orientation with respect to the applied field.

When the axis of the ellipsoid is parallel to H , the hysteresis cycle is rectangular, with an overall height of $2J_s$ and overall width of $2H_c$. The coercive force H_c being given by $2K/J_s$. At $H = +H_c$ and $H = -H_c$ there are discontinuities in the magnetization, elsewhere the susceptibility is zero.

Conversely there is no hysteresis at all when the axis of the grain is perpendicular to the magnetic field. The component of the magnetic

moment along the field is constant and equal to vJ_s , when $H < -H_c$, varies linearly from $-vJ_s$ to $+vJ_s$ as H changes from $-H_c$ to $+H_c$ and is constant at $+vJ_s$, when $H > +H_c$.

Fig. 3



Limiting hysteresis cycle and initial magnetization curve (full lines) for an assemblage of independent randomly oriented grains.

In a randomly oriented assemblage of independent grains, the average limiting cycle is⁽²⁵⁾ similar to fig. 3, with a remanent magnetization J_r equal to $\frac{1}{2}J_s$ and a coercive force of $0.96 K/J_s$, about half the maximum coercive force of the individual grains⁽²⁶⁾. The initial susceptibility is $J_s^2/3K$. The limiting hysteresis cycle is analogous to that of 'hard' magnetic materials (Alnico, Ticonal etc.) which are now used for good permanent magnets.

§ 19. OBJECTIONS TO THE INTERPRETATION OF THE MAGNETIC PROPERTIES OF ROCKS BY MEANS OF THE THEORY OF SINGLE DOMAIN GRAINS

It is now possible to interpret the magnetic properties of a rock as those of an assemblage of randomly oriented single domain grains.

First there is a rather theoretical fundamental objection. The grains of ferromagnetic minerals in rocks vary from one to several hundred microns in size. Now for magnetite the critical diameter should be about $0.02-0.03 \mu$ and certainly less than 0.1μ . This value should be reasonably accurate as an order of magnitude since the formula used to get it⁽²³⁾ gives results for iron which are confirmed by direct measurement of the grain size with x-rays or an electron microscope.

The second objection is more experimental and concerns the ratio of the remanent magnetization of a rock specimen to its saturation magnetization: it can be shown experimentally (§ 38) that this ratio is proportional to the coercive force, whereas the theory of single-domain grains predicts a constant value of $\frac{1}{2}$. Also, Nagata⁽²⁷⁾ has shown that the coercive force of rocks increases as the grain-size decreases while theoretically it should not depend on size after the single domain size is reached.

However, all these facts will later be found explicable in terms of multi-domain grains.

The above arguments are based on the experimental data for rocks with fairly low coercive forces of less than 1000 oe in which the magnetic constituents are magnetites or titanomagnetites. They do not apply to rocks with minerals of the ilmenite-hematite type which have far higher coercive forces sometimes of several thousand oersteds.

In these, as already mentioned, it is possible that the model of single-domain grains does correspond to the actual structure of the rock. To prove this definitely their magnetic properties must be more closely studied. Valuable information can be got in this way particularly from application of Rayleigh's relations.

§ 20. LORD RAYLEIGH'S RELATIONS AND SINGLE-DOMAIN PARTICLES

The Rayleigh relations concerned here are those applying to magnetization in fields very weak compared to the coercive force. A statement of these relations will be given later with an interpretation of them obtained by considering the macroscopic hysteresis cycle as the sum of a large number of unsymmetrical elementary cycles. Each unsymmetrical cycle will correspond with a point (a, b) in a plane where a and b are the lower and higher coercive forces (cf. § 44).

An assemblage of single domain grains does not obey the two Rayleigh relations. Each grain in fact has a *symmetrical* cycle, so that $a = -b$ and all the points representing elementary cycles lie on the second bisector of the plane (a, b) . Thus although it is possible to satisfy the first of Rayleigh's relations by an appropriate density of representative points on 0δ , it is impossible to satisfy the second relation because on the returning branch of the hysteresis cycle when the field H decreases from its maximum H_m to zero, the magnetization J maintains its maximum value J_m and only begins to decrease when H becomes negative. See § 44 and figs. 13-16.

§ 21. THE ROLE OF MAGNETIC INTERACTION BETWEEN GRAINS

In principle this provides a method of deciding whether the independent grains are multi-domains or single domains by finding whether they do or do not obey Rayleigh's second relation.

But when single-domain grains are sufficiently close to each other interactions become important and the problem is somewhat altered. We have shown elsewhere⁽²⁸⁾ that it is then convenient to distinguish different effects.

First, the magnetic shape anisotropy is decreased by proximity and the mean coercive force is thus decreased from H_c to $H_c(1-v)$ where v is the volume of ferromagnetic grains in unit volume.

Then there is a sort of Lorentz field to be considered equal to $\frac{4}{3}\pi J_m$ where J_m is the mean magnetization per unit volume; it is a *magnetizing* field which makes the whole hysteresis cycle more upright.

Last but most important from the present point of view are the variations of the Lorentz field from its mean value from place to place. The interacting magnetic field h applied to a grain by its neighbours is different for each grain but remains constant in direction and intensity provided the external field is small. The effect is as if the representative point of the primitive cycle $(-a, a)$ became instead $(-a-h, a-h)$ thus representing an unsymmetrical cycle. The two Rayleigh relations are then automatically obeyed without the need for any special distribution of anisotropy of the elementary grains.

It is interesting⁽²⁸⁾ that when the grains are very close ($v=0.5$) the ratio BH_c/A at 0.70 is similar to the value 0.42 for the same ratio given by the domain wall theory⁽²⁹⁾ when the walls are very close to each other. Similarly the values of coercive force given by the wall theory and by the theory of single-domain grains are about the same when the volume occupied by magnetic substance and the unoccupied volume are of the same order. Generally speaking the properties of very imperfect substances are treated equally well by the wall theory or by the theory of single domains very close to each other.

Usually the volume of ferromagnetic constituents in a rock is very small, of the order of a few per cent so that interactions are weak but not negligible compared with the earth's field. In fact it has been shown⁽²⁸⁾ that the root-mean-square of the fluctuating field is of the order of vJ_s . If $J_s=500$ and $v=0.02$ this gives 10 oe. 2% of single-domain grains dispersed in a non-magnetic matrix should thus obey the two Rayleigh relations between -10 and $+10$ oe. If the coercive force were large, say several hundred or several thousand oersteds, the discrepancies from Rayleigh's relations outside this interval, -10 to $+10$ oe should be easy to detect and should give a conclusion as to whether or not single-domain grains were concerned.

The range of validity of Rayleigh's relations is much greater in more complicated structures such as in aggregates of grains where the total relative volume of the aggregates is small but within each aggregate the grains are very close to each other. The theory of interacting single-domain grains is then very useful as will be seen later (cf. § 32).

§ 22. THERMO-REMANENT AND ISOTHERMAL REMANENT MAGNETIZATION

Although the dimensions of ferromagnetic grains in igneous rocks are generally too large for the theory of single-domain grains to be applied and although it leads to some conclusions which do not agree with certain experimental facts it is still of great interest because of its simplicity and the fact that in some cases (such as $\text{Fe}_2\text{O}_3\alpha$) it is probably correct.

In particular it allows of a very simple interpretation of the *magnetization by heating* of rocks in general. This is the property by which a rock, heated above its Curie Point and cooled to room temperature in a magnetic field H small compared with the coercive force, acquires a *permanent magnetization* at ordinary temperatures called the *thermo-remanent magnetization* (T.R.M.) which has the following properties⁽³¹⁾. It is much greater and more stable than the *isothermal remanent magnetization* (I.R.M.) obtained by the classical process of applying the same field H and then removing it, at constant temperature. Sometimes the T.R.M. acquired in a given field can be hundreds of times greater than the I.R.M. produced by the same field. The negative field required to destroy the magnetization is much greater for a T.R.M. than for an I.R.M. when only a field about the same as or even less than the original magnetizing field is needed. Finally the I.R.M. due to a small field can be destroyed by heating to a quite moderate temperature while the corresponding T.R.M. is unaffected.

§ 23. OUTLINE INTERPRETATION OF T.R.M.⁽³²⁾

To obtain an approximate explanation of these properties consider an assemblage of single domain grains whose individual coercive forces are distributed between zero and an upper limit which is a little higher than the overall coercive force H_c ; H_c being large compared to the magnetizing field H .

The I.R.M. produced by the field H is exclusively due to the grains having a coercive force less than H and therefore magnetized irreversibly by this field. This I.R.M. is small since only a small proportion of the order of H/H_c of the grains are affected and evidently it can be destroyed by an opposing field of about the magnitude of H .

To understand the thermo-remanent case it must be remembered that the individual coercive forces of the grains are of the order of K/J_s and tend to zero at the Curie Point. This is an experimental fact explained theoretically by the variation of K as J_s^2 whether K is due to shape anisotropy or a magneto-crystalline anisotropy arising from interactions similar to the magnetic dipolar coupling: thus H_c varies as J_s and tends to zero at the Curie Point (cf. § 41 again). Therefore even a very small magnetic field will suffice, near the Curie Point, to magnetize irreversibly all the grains of the assemblage. As the temperature falls the intensity of the magnetization of the grains will increase proportionally to the spontaneous magnetization while the direction in each grain remains fixed. At room temperature a T.R.M. is thus produced which is equal to the maximum possible I.R.M. J_r . To produce J_r isothermally a magnetic field of the order of the maximum coercive force H_c would be necessary. Evidently such a T.R.M. will be much higher and much more stable than the I.R.M. acquired in the same field.

This reasoning succeeds in explaining some of the curious properties of the T.R.M. but unfortunately leads to the conclusion that it is independent of the field H applied during cooling and always equal to the maximum

remanence J_r of the limiting hysteresis cycle. This does not agree with the experimental facts that in small fields the T.R.M. varies as H and in slightly higher fields as $H^{1/2}$ (cf. § 42). Some factor, possibly the thermal agitation, must have been neglected.

§ 24. THERMAL AGITATION IN A SINGLE-DOMAIN GRAIN⁽³²⁾

The magnetic moment $v J_s$ of a single-domain grain such as those considered earlier (§§ 17 and 18) can, in the absence of any applied magnetic field, take up two orientations both of equal minimum energy: $\theta=0$ and $\theta=\pi$. Obviously if the height of the potential barrier between these two positions is very large compared with kT , thermal fluctuations cannot move the magnetic moment from one position to the other so that it remains always in the direction to which it was originally brought by a magnetic field. However since the height of this potential barrier is $v H_c J_s / 2$ a value of v can always be found, so small that its height is of the order of kT , in which case thermal fluctuations can cause the moment to change spontaneously from one position to the other.

In these conditions if a remanent moment M_0 is given to each grain of an assemblage of identical grains, it will tend to zero exponentially, thus

$$M_r = M_0 \exp(-t/\tau_0)$$

where τ_0 is the relaxation time of the grain.

§ 25. DETERMINATION OF THE RELAXATION TIME

This relaxation time depends on perturbing couples acting on the magnetic moment of the grain. When there are no such couples the only force acting on the moment is the classical couple due to the energy term $Kv \sin^2 \theta$ which, since the atomic moments are analogous to gyroscopes, produces a continuous precession of the moment around the axis of symmetry of the grain, θ remaining constant. This is no longer true when there are perturbing couples in the equatorial plane capable of changing the polar angle θ and allowing the magnetic moment to cross the equatorial plane.

It seems that the most active of these perturbing couples arise from elastic deformations of the grain by thermal agitation. Because of these deformations the grain loses its spheroidal symmetry and takes up the shape of, for instance, a triaxial ellipsoid. This causes the appearance of a magneto-elastic couple and a transverse demagnetizing field both of which tend to turn the magnetic moment in a meridian plane. Boltzmann's principle gives the distribution in energy levels close to the equatorial plane. Using this and knowing the speed of precession due to the perturbing couples it is easy to calculate the number of moments $v J_s$ which cross the equatorial plane per second and hence find the relaxation time. Thus if we put

$$C = \frac{eH}{2m} |3G\lambda + DJ_s^2| \left[\frac{2v}{\pi GkT} \right]^{1/2}$$

then

$$\frac{1}{\tau_0} = C \exp \left\{ -\frac{vH_c J_s}{2kT} \right\}, \quad \dots \dots \dots (1)$$

where e , m are the charge and mass of the electron, G the shear modulus and D a numerical constant depending on the shape of the grain equal to about 3.

Similar calculations can be applied to the case where there is an external magnetic field h , parallel to the axis of the grain. There are two relaxation times $\tau(0, \pi)$ and $\tau(\pi, 0)$ for movement from the position $\theta=0$ to $\theta=\pi$ and conversely. These are

$$\frac{1}{\tau(0, \pi)} = C \left(1 + \frac{h}{H_c} \right) \left(1 - \frac{h^2}{H_c^2} \right)^{1/2} \exp \left\{ -\frac{vJ_s (H_c + h)^2}{2H_c kT} \right\},$$

$$\frac{1}{\tau(\pi, 0)} = C \left(1 - \frac{h}{H_c} \right) \left(1 - \frac{h^2}{H_c^2} \right)^{1/2} \exp \left\{ -\frac{vJ_s (H_c - h)^2}{2H_c kT} \right\}.$$

§ 26. CRITICAL DIAMETER : BLOCKING TEMPERATURE

It is interesting to apply formula (1) to grains of iron in which $H_c=1000$, $J_s=1700$, $e/m=1.76 \times 10^7$, $\lambda=20 \times 10^{-6}$, $G=0.77 \times 10^{12}$ and $k=1.38 \times 10^{-16}$. This gives relaxation times τ_0 varying from 10^{-1} sec to 10^9 sec as v/T varies from 3.2×10^{-21} to 7.0×10^{-21} . Thus at room temperature spheres of iron 160 Å in diameter can keep the initial magnetization indefinitely while spheres only a little smaller, of 120 Å diameter are demagnetized almost instantaneously, in less than 0.1 sec.

These figures show that at a given temperature there is a fairly well defined critical diameter D_T separating the grains into two groups.

Grains in the first group with diameters greater than D_T keep the initial orientation of the magnetic moments indefinitely in false equilibrium despite the action of any magnetic field h which is small vis-à-vis the normal coercive force H_c .

In the second group of grains with diameters less than D_T , thermodynamic equilibrium is reached almost instantaneously. In a small field h , parallel to the axis of the grain the only two possible positions for the moment are parallel or antiparallel to the field; then the mean magnetic moment of the grain is given by

$$M(T) = vJ_s(T)th \frac{v h J_s(\tau)}{kT}. \quad \dots \dots \dots (2)$$

The expression $J_s(T)$ is used to emphasize that J_s is a function of temperature. This moment $M(T)$ follows exactly any variations occurring in the applied field h .

The blocking temperature T_B is the temperature at which the diameter of the grain is the critical one or in other words the temperature at which the relaxation time becomes of the order of the duration of the experiments made on a rock. Thus in an assemblage of grains of very different volumes the blocking temperature can vary from the Curie Point for large grains to nearly absolute zero for very small grains.

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§ 27. PROCESS OF ACQUIRING T.R.M.⁽³²⁾

The process by which such an assemblage of grains acquires a T.R.M. can now be analysed. Consider the system cooled from above its Curie Point to room temperature in a weak magnetic field $h(T)$ which is a function of the temperature. At any temperature the grains of diameter D_T acquire a mean moment given by eqn. (2) with $h=h(T)$ and then keep this same moment as the temperature falls below T because the relaxation times become too long for the moment to change from one equilibrium position to the other. Strictly, taking account of the thermal variation of J_s the mean magnetic moment at room temperature $M(0)$ is

$$M(0) = vJ_s(0)th \frac{vJ_s(T)h(T)}{kT} \dots \dots \dots (3)$$

Thus at room temperature each grain has a mean magnetic moment which depends on the field $h(T)$ which was acting at the temperature T when the critical diameter became equal to the actual diameter of the grain. Hence the name blocking temperature.

The mean moment acquired in this way is not affected by chance variations in the field $h(0)$. On heating the system, thus magnetized, progressively in zero field the grains with blocking temperature T only lose their moment at T , that is at exactly the same temperature as they acquired this moment. As Thellier has put it, these grains have a magnetic memory and preserve the history of the magnetic field in which they cooled.

Equation (3) shows that the T.R.M. is proportional to the applied field h , when this is small enough.

Except for the small proportion acquired close to room temperature, the T.R.M. is particularly stable. In fact a field of the order of the coercive force of the grains, which may be very high, is needed to change it; similarly the relaxation time for spontaneous demagnetization is enormously long.

In contrast to this peculiar stability of T.R.M., an I.R.M. can be removed by an opposing field only about as great as that which produced it; in the same way the relaxation times are very much smaller than for a T.R.M. since the height of the potential barrier between the two stable positions of the magnetic moment is only of the order of $\frac{1}{2}vJ_s h$ instead of $\frac{1}{2}vJ_s H_c$.

§ 28. PARTIAL THERMO-REMANENT MAGNETIZATIONS (P.T.R.M.'s)

The properties ascribed by this theory to the T.R.M. of an assemblage of single-domain grains correspond remarkably well to the thermo-remanent properties of bricks and baked clays first described by Thellier⁽³¹⁾ and to those of the rocks studied by Nagata⁽³³⁾. These properties have been well summarized by Thellier as follows⁽³⁴⁾: "To any temperature interval T_1, T_2 ($T_0 < T_1 < T_2 < \theta$) there corresponds for

a given specimen and a given magnetic field h , a particular magnetic moment which is acquired by the specimen when cooled from T_2 to T_1 in this field h . This moment is directed parallel to h and is unaffected by any heating to temperatures less than T_1 but disappears completely by heating to T_2 . Further it is quite independent of other thermoremanent moments acquired in temperature intervals outside T_1 and T_2 even though they be due to fields h that are different in magnitude and direction. All these moments are added geometrically but, paradoxical though it may seem, each is quite independent and preserves a sort of exact memory of the temperatures and field which produced it."

Can it be concluded from this agreement of theory and experiment that the ferromagnetic constituents of these specimens are single-domain grains? This is quite likely if the constituent is rhombohedral ferric oxide in which the ferromagnetic elements must be very small. But magnetites and titanomagnetites generally occur in grains of diameter much greater than a micron and the theory of single-domain grains cannot be applied to them. In addition, as will be shown later, the theory of large grains accounts for their properties much better than that of small grains. Thus it ought to be possible to explain the properties described by Thellier on other models than that of single domain grains (cf. § 57).

Thellier's⁽³¹⁾ and Nagata's⁽³³⁾ experiments show that the blocking temperatures of magnetic rocks range from room temperature up to the Curie Point. But when there is only one ferromagnetic constituent, most of the T.R.M. is acquired in a fairly small temperature range about 50° below the Curie Point, so that for simplification each ferromagnetic constituent can be associated with a single blocking temperature.

§ 29. TIME-VARIATION OF ISOTHERMAL REMANENT MAGNETIZATION (I.R.M.)

Suppose that an assemblage of single-domain grains has been magnetized by a field H_m and that the remanent magnetization at time t_0 is σ_{r0} , the time origin being the instant at which the field H_m was removed. Roughly speaking, at time t_0 those grains with time constants τ less than t_0 will have lost their magnetization while those with $\tau > t_0$ will have kept theirs unchanged. Later at time t the remanent magnetization will have fallen to a lower value σ_r since grains with time constants between t_0 and t will have been demagnetized in their turn. Now the relation between the constants of a grain (v, H_c, \dots , etc.) and its relaxation time τ is

$$\frac{vH_c J_s}{2k} = T_0(Q + \log \tau), \quad \dots \dots \dots (4)$$

where $Q = \log C$. Hence the decrease in remanent magnetization $\sigma_{r0} - \sigma_r$ must be proportional to the change in $T(Q + \log t)$ from t to t_0 provided this change is small, thus :

$$\sigma_r = \sigma_{r0} - AT_0(\log t - \log t_0). \quad \dots \dots \dots (5)$$

The constant A depends on the distribution of the grains as a function of v and H_c .

Thus the decrease in remanent magnetization is proportional to the logarithm of the time. Some interesting results of Thellier's can be explained in this way; in particular, for some specimens he found a logarithmic law for values of t from 20 sec to 5×10^6 sec. This decrease in remanent magnetization with time is only one of many aspects of the phenomenon of 'magnetic viscosity' shown by an assemblage of fine single-domain grains; fuller details will be found in an earlier paper⁽³²⁾.

§ 30. THE EFFECT OF RISE OF TEMPERATURE ON REMANENT MAGNETIZATION

As above, let σ_{r0} be the remanent magnetization remaining at time t_0 at room temperature T_0 , and suppose that the temperature is raised very quickly to T_1 and maintained constant at that level for a period of the same order as t_0 . During this process $T(Q + \log t)$ increases by about $Q(T_1 - T_0)$, producing demagnetization of a certain number of grains which remain demagnetized when the temperature is lowered again. A decrease of thermal origin has occurred in the spontaneous magnetization, given by

$$\sigma_r = \sigma_{r0} - A Q (T_1 - T_0), \quad \dots \dots \dots (6)$$

where A has the same value as above. The decrease in remanent magnetization is proportional to rise in temperature.

This phenomenon has been observed by Thellier⁽³¹⁾. From (5) and (6) one can obtain

$$\frac{\partial \sigma_r}{\partial \log t} \bigg/ \frac{\partial \sigma_r}{\partial T} = \frac{T_0}{Q}. \quad \dots \dots \dots (7)$$

The ratio of the two derivatives is equal to T_0/Q . Assuming reasonable values for the different parameters in the expression for Q one gets that Q varies from 19.9 to 23.4 as H_c varies from 10 to 10^4 oe. Taking the values $Q=22$ and $T=300^\circ\text{K}$, T_0/Q is about 13.5. Thellier found for one specimen (No. C 25) the value 8.95.

Actually this argument is a little too simple because in the calculation of $\partial \sigma_r / \partial T$ the variations of H_c and J_s in eqn. (4) have been ignored. Both these decrease with rising temperature though exactly how is still poorly known. Therefore the decrease in σ_r with T is a little more than that calculated from eqn. (4) and the ratio of the two derivatives, equal to T_0/Q according to eqn. (7), is in fact a little less as in the experimental results.

§ 31. T.R.M. OF A MIXTURE OF TWO CONSTITUENTS⁽³⁵⁾

When there is a mixture of two ferromagnetic constituents A and B with clearly different Curie Points, the T.R.M. of the mixture sometimes has curious properties. As explained above (cf. § 26) the T.R.M. of constituent A is fixed at a blocking temperature T_a which is assumed here to be above the Curie Point of constituent B . Below T_a the T.R.M.

of A increases reversibly with the spontaneous magnetization of A as the temperature falls, independently of the applied field. But the T.R.M. of B is entirely dependent on the field acting on B at its own blocking temperature T_B . This field is the geometrical sum of the external applied field H and the demagnetizing field created by the previously magnetized grains of A . It can happen that this resultant field is opposite in direction to H and strong enough for the T.R.M. of B at room temperature to be greater than that of A . In these conditions, since the T.R.M. of B is negative, the total T.R.M. of the mixture is in the opposite sense to the field which caused it.

This phenomenon only occurs with a high concentration of ferromagnetic constituents. It certainly cannot happen if the grains of A and B are independently dispersed in a non-magnetic medium in the low proportions of a few per cent characteristic of igneous and sedimentary rocks. But it is the local proportions of A and B that matter, not the overall proportion in the rock. Negative T.R.M. can appear if the grains of A and B are gathered in concentrated aggregates. As the total concentration is small these aggregates must be far apart but that does not affect the issue.

The existence of such aggregates is not an artificial hypothesis: it amounts to saying that the two constituents have a common origin; they could for instance have formed by exsolution into two phases, during slow cooling, of a homogeneous solid solution that was stable at higher temperatures, as must often occur in the system $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-FeO}$ (cf. § 35). Furthermore such exsolution often gives rise to crystallites of very unsymmetrical shapes such as plates or rods which are, as will be explained later, favourable to the appearance of negative T.R.M.'s.

§ 32. REVERSED T.R.M. : SINGLE-DOMAIN GRAINS

The problem for single-domain grains has been discussed elsewhere by the author⁽³⁵⁾. The result is as follows for the simple case in which the concentrations of the two ferromagnetic constituents in the aggregate are both equal to $3c$. Suppose that the volume susceptibilities of the two constituents at their respective blocking temperatures are both equal to s , and that the magnetic grains are of elongated shape with a demagnetizing field coefficient of $\frac{4}{3}\pi - n$. Let R be the relative increase of spontaneous magnetization in each constituent from the blocking temperature to room temperature (the increase in the spontaneous magnetization of A from the blocking temperature T_B of B to room temperature is assumed negligible).

In these conditions it can be shown that the aggregates acquire a negative T.R.M. provided that

$$cnRs > \frac{2 - 8c + \frac{16}{3}c^2}{1 - 2c - 2/R(1 - 3c)} \dots \dots \dots (8)$$

Adopting the values $R=4$, $s=7$, $n=1.7$ which the magnetic properties of rocks show to be reasonable, the inequality is satisfied if the concentration $3c$ of each of the constituents is greater than 0.27.

As $3c$ can vary from 0 to 0.5 it appears that negative T.R.M. is certainly possible in grains with properties similar to those of actual grains in ordinary lavas.

The inequality (8) also shows that negative thermo-remanence is favoured by a large anisotropy of the grains (n), by a large irreversible susceptibility (s) and by a high concentration of the two constituents (c). The Curie Points of A and B must also be far enough apart for the relative increase in spontaneous magnetization of A from T_a to T_b to be close to its final value R .

§ 33. REVERSED T.R.M. : LARGE GRAINS

The theory just summarized applies to single-domain grains but it is easy to show that aggregates of large grains could also develop negative T.R.M.'s. The argument depends only on the assumption that large grains have a blocking temperature; this assumption will be proved later (cf. § 57). Consider a dense spherical aggregate composed of alternate layers of A and B , the thicknesses of the layers being equal and small compared to the radius of the aggregate; each layer is equivalent to a large grain. At its blocking temperature T_a constituent A takes on a magnetization J_a such that the mean internal field of the aggregate is zero, hence

$$J_a = \frac{3H}{4\pi},$$

where H is the applied field. At the blocking temperature T_b of the second constituent the magnetization of A has increased to RJ_a , where R is the ratio of spontaneous magnetizations at T_b and T_a . The field within the aggregate which is the resultant of the applied field and the demagnetizing field of A is therefore $H(1-R)$. This is negative and must be compensated by the positive demagnetizing field due to a negative magnetization J_b of B given by

$$J_b = \frac{3H(1-R)}{4\pi}.$$

In this argument the reversible part of the susceptibility is neglected and the irreversible susceptibility of both constituents is assumed to be large compared to $3/4\pi$.

At room temperature the magnetizations of the two constituents become $R'RJ_a$ and $R''J_b$, R' and R'' being the relative increases of spontaneous magnetization for A and B respectively from T_b to room temperature. The mean T.R.M. J_{tr} of the whole aggregate at room temperature is therefore

$$J_{tr} = \frac{3H}{4\pi} (R'R + R'' - RR').$$

If the blocking temperatures T_a and T_b are sufficiently far apart R' will be close to 1, while if the magnetic properties of A and B are similar (except for the blocking temperatures) one can assume $R=R''$. The T.R.M. then has the sign of $(2-R)$ and is negative when the relative increase in spontaneous magnetization between the blocking temperature and room temperature is greater than 2.

This result is very similar to that for single domains. The inequality (8) shows that in fact that for $3c=0.5$, R must be greater than 1.5 for there to be negative T.R.M. even if s is infinite.

§ 34. EXPERIMENTAL RESULTS ON THE REVERSED T.R.M. OF MIXTURES OF TWO CONSTITUENTS

Such phenomena as described above appear to have been experimentally observed by Nagata and his co-workers⁽³⁸⁾ in the dacitic lavas of Mt. Haruna and Mt. Asio, Japan. These rocks acquire a reversed thermoremanence in the laboratory and contain two distinct ferromagnetic constituents A and B separable by a magnetic extraction at a temperature between the two Curie Points. The constituent A with a Curie Point at about 500°C is a titanomagnetite spinel and has a magnetization curve very similar to that of magnetite. The B constituent having a Curie Point of about 200°C is a rhombohedral ferrimagnetic solid solution of ilmenite-hematite type and has a spontaneous magnetization which changes practically linearly with temperature all the way from absolute zero to the Curie Point. The magnetic properties of A and B are obviously very dissimilar so that the simplified theories given above are scarcely applicable. The concentration of B is extraordinarily small, only a few per cent of that of A . The fact that despite this the mixture acquires a reversed T.R.M. must be due to some peculiar capacity of B for acquiring a large T.R.M. This could be due to the high coercive force of rhombohedral lattices and also to the high values of R which are probably associated with the linear variation of spontaneous magnetization.

§ 35. REVERSED T.R.M. DUE TO EXSOLUTION

It is shown in § 32 that under certain conditions the shape demagnetizing field can produce a negative T.R.M. in a mixture of two constituents. It is there supposed that the two constituents exist before the thermal treatment in a magnetic field. But this condition is not absolutely necessary; as the following example shows a negative T.R.M. can also develop during a slow exsolution at room temperature.

Consider a spherical single-domain grain of a constituent A with spontaneous magnetization J_s and suppose that an exsolution occurs at room temperature precipitating a second magnetic phase B , accompanied of course by a change in composition of A . The first crystallites of the new phase B grow in the demagnetizing field of A , given by $\frac{4}{3}\pi J_s$. If the magnetocrystalline field of B is less than this, which it usually is, and if the exchange coupling between A and B is negligible

the spontaneous magnetization of the crystallites of *B* will necessarily be oriented antiparallel to that of *A*. Further, once the process has started it will continue automatically during formation of phase *B* from phase *A*. This is true even if *A* disappears completely as in an allotropic transformation, when the final phase *B* would have a spontaneous magnetization opposite to that of the original *A* phase.

In an assemblage of grains of *A* having originally a mean T.R.M. in a particular direction, this process necessarily implies that as the *B* phase is precipitated the T.R.M. will decrease in intensity and, when the concentration of *B* is high enough, will change sign.

A detailed but more complicated analysis shows that similar, but perhaps less definite, phenomena can also occur in large multi-domain grains.

It should be noticed that this process of development of reversed T.R.M. is of great generality since it can accompany any allotropic transformation and any exsolution into two phases and does not depend on the relative positions of the Curie Points of the two phases. The ternary system $\text{TiO}_2\text{-Fe}_2\text{O}_3\text{-FeO}$ which is of enormous geomagnetic importance, is particularly rich in the kind of transformation concerned. Not only are there solubility gaps at room temperature in the systems $\text{Fe}_{2-m}\text{Ti}_m\text{O}_3$ (Pouillard) and $\text{Fe}_{3-m}\text{Ti}_m\text{O}_4$ (Kawai, Kume and Sasajima) but also, according to Pouillard⁽⁸⁾, intermediate compounds $\text{Fe}_{3-m-n}\text{Ti}_m\text{O}_{4-n}$ can exsolve into two phases each belonging to one of the first two series.

Besides these another process has been suggested by Graham⁽³⁷⁾ consisting of an alteration of constituent *A* to another constituent *B*, particularly oxidation of magnetite to maghemite; magnetically the process is very much as that described above.

Finally it is important to realise that the demagnetizing fields which cause these reversals are *local* demagnetizing fields, often of great intensity, related to the topography of the elementary domains. The exchange coupling between the crystallites of *A* and *B* has been neglected; this is reasonable when there is no crystallographic continuity between *A* and *B* but is doubtful if *B* is oriented in *A* by intergrowth. This exchange coupling, arising from the Weiss-Heisenberg forces can sometimes favour the development of reverse T.R.M. but more probably inhibits it. To say exactly what it does do, much more information is needed than is usually to hand, on the development and detailed structure of the precipitated phase. Thus negative T.R.M. by exsolution must be considered possible but not certain.

LARGE GRAINS

§ 36. VARIATION OF COERCIVE FORCE WITH GRAIN SIZE

Generally speaking substances have a much smaller coercive force in the massive state than they have when finely divided in single-domain grains. The reason for this is that in the massive state the changes of

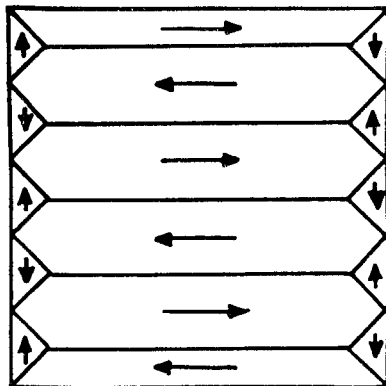
magnetization in the hysteresis cycle are due to wall displacements, which in an unstrained and perfect substance require no expenditure of energy.

It can also be shown by experiment that as a massive substance is powdered into finer and finer grains, by physical or chemical means, the coercive force increases regularly and gradually tends towards the limiting value for single-domain grains⁽³⁸⁾. The coercive force is roughly speaking inversely proportional to the diameter p of the grains.

Although this result is extremely simple it has not yet been given any satisfactory explanation. The basic reason for this failure is that we have no precise idea at all of the mechanism of reversal of magnetization in medium-sized grains. Although Kittel proposed a mechanism some years ago⁽³⁹⁾ involving 'nucleation' of a phase magnetized antiparallel to the principal phase, quantitative application of his ideas gives results in complete disagreement with experiment.

Perhaps it is possible to suggest an approach which will give at the very most a lower limit to the coercive force of a large grain. During a complete hysteresis cycle the grain must twice pass through a state of zero total magnetic moment, corresponding to a particular subdivision of the grain into elementary domains. This state, with internal energy W (say), must be reached irreversibly so that the energy expended in single cycle, which is of the order of $2H_c J_s$, must be at least $2W$.

Fig. 4



Subdivision of a cube into elementary domains giving zero total magnetic moment.

Consider a cube of side p of a magnetically uniaxial substance which has a magnetocrystalline energy, E_c , given by

$$E_c = K \sin^2 \theta,$$

where θ is the angle between the spontaneous magnetization J_s and the axis. In the demagnetized state the simplest domain system consists of elementary lamellar domains of thickness e completed, when K is

small compared to J_s^2 , by triangular closure domains (fig. 4). The corresponding energy is

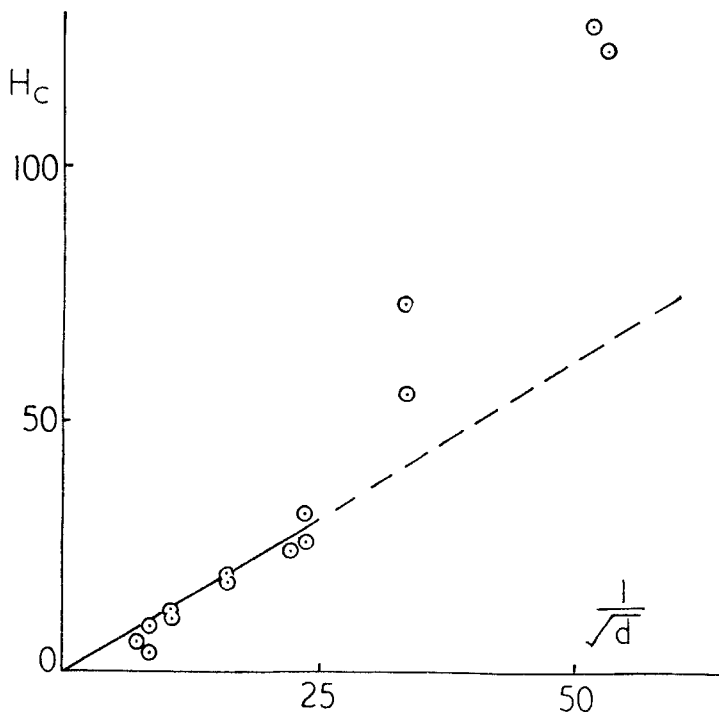
$$W = \frac{\gamma p^3}{e} + \frac{1}{2} K e p^2,$$

where γ is the wall surface energy. The thickness e takes the value at which this energy W is a minimum. Then equating $H_c J_s$ to this minimum value of W gives

$$H_c = \left(\frac{2K}{p J_s^2} \right)^{1/2} \dots \dots \dots (9)$$

This formula has been applied to magnetite, assuming $K=10^5$ erg/cm³, $\gamma=1$ erg/cm² and $J_s=450$, and the results compared with Gottschalk's⁽³³⁾ experimental results for powdered magnetite. Figure 5 shows that for p greater than 10^{-3} cm, eqn. (9) is in good agreement but that for smaller grains it gives too low a value for the coercive force.

Fig. 5



Coercive force of powdered magnetite as a function of $1/\sqrt{d}$, when d is the mean diameter of the grains. (Gottschalk's experimental results compared with the theoretical straight line given by formula (9).)

This discrepancy must be due to the difficulty of forming nuclei magnetized in the opposite direction to the principal phase. Since a demagnetizing field and a multiplicity of directions of easy magnetization

favour the formation of such nuclei, the discrepancy from eqn. (9) should be very large in substances with only one direction of easy magnetization and with a demagnetizing field which is small compared to the magneto-crystalline fields. In fact for Mn-Bi which is such a substance, eqn. (9) gives coercive forces ten times smaller than those determined by Guillaud⁽⁴⁰⁾.

To summarize, it can be said that a satisfactory theory of the coercive force of large grains has still to be proposed.

§ 37. THE DEMAGNETIZING FIELD OF LARGE GRAINS

The variation of coercive force H_c with the diameter ρ of the grain has just been described. Fundamentally this increase of coercive force derives from the fact that the size of the elementary domains becomes smaller as the grain becomes smaller. A similar increase occurs in a massive substance if a decrease in the size of the domains is produced by other means such as the formation of internal stresses varying irregularly on a small scale of distance. It is this decrease in domain size which causes an increase in the coercive force and therefore a general expansion of the hysteresis cycle along the H axis although the remanent magnetization is not changed and remains about half the saturation magnetization J_s .

In large grains another factor appears, the magnitude of the demagnetizing field. The demagnetizing field coefficient n is of the order of that for a sphere $4\pi/3$ and gives for an intensity of magnetization of 500 e.m.u. a considerable demagnetizing field of the order of 2000 oe. The effect of this can be simulated by 'inclining' the hysteresis cycle. This is done by using the same cycle and the same axis of magnetic fields in the (J, H) plane but a new sloping axis of intensity of magnetization with a gradient of $-1/n$.

The hysteresis cycle then appears flatter than the original cycle; in particular the remanent magnetization decreases and can be much less than half the coercive force. This characteristic property allows the presence of a demagnetizing field to be detected purely experimentally.

§ 38. REMANENT MAGNETIZATION OF AN ASSEMBLAGE OF LARGE GRAINS

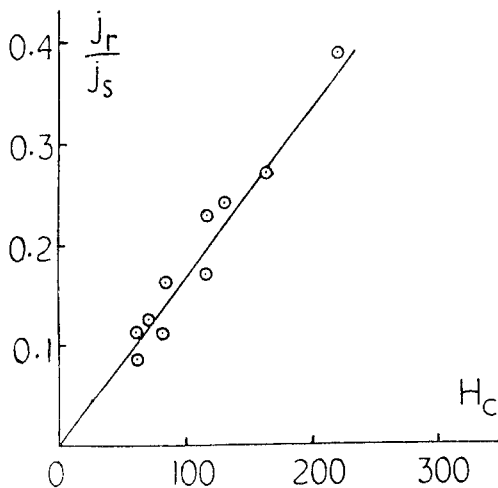
The remanent magnetization J_r of a large grain with a demagnetizing field coefficient n , after saturation in a field much higher than the coercive force, is given by the intersection of the descending branch of the limiting hysteresis cycle with a line of slope $1/n$ passing through the origin. If n is large the ordinate of the point of intersection is approximately equal to H_c/n . Then the ratio of the remanent to the saturation magnetization j_r/j_s is given by

$$\frac{j_r}{j_s} = \frac{H_c}{nJ_s}.$$

And, other things being equal, this ratio is proportional to the coercive force H_c .

Figure 6 constructed from data gathered by Nagata⁽²⁷⁾ for different rock specimens shows that this is approximately true. The experiment value of the constant of proportionality $1/nJ_s$ is about $\frac{1}{600}$. Assuming the average value of the saturation magnetization of the rocks given by Nagata⁽²⁷⁾ as 230 e.m.u. a mean value of 1/2.6 is got for $1/n$ which is very reasonable.

Fig. 6



The ratio of remanent magnetization j_r to saturation magnetization j_s plotted against coercive force for some eruptive rocks. (Nagata's experimental results compared with the straight line of formula (10).)

The approximation used above becomes inaccurate when j_r/j_s exceeds 0.3 since for high coercive forces it tends to a limiting value of 0.5. Amongst Nagata's data there can in fact be found two specimens with coercive forces of 465 oe and 345 oe and values of the j_r/j_s ratios J_r/J_s equal to 0.40 and 0.35 respectively. As expected they give points well below the straight line of fig. 6.

Thus the study of the remanent magnetization of rocks of low coercive force shows that the ferromagnetic constituents are in large grains and not in fine single-domain grains.

§ 39. INITIAL SUSCEPTIBILITY OF AN ASSEMBLAGE OF LARGE GRAINS

The apparent initial susceptibility of a ferromagnetic substance is strongly affected by the presence of a demagnetizing field (with coefficient n , say). Its apparent and real values, A' and A are related by

$$A' = \frac{A}{1+nA}.$$

When nA is large compared to 1 the apparent susceptibility A' is nearly equal to $1/n$.

In most magnetic substances A varies inversely as the coercive force and is about 0.2 when $H_c=500$ oe. For a sphere $1/n=0.24$. Hence the apparent susceptibility of rocks with coercive forces of less than 500 oe, such as the eruptives studied by Nagata, must depend more on the demagnetizing field effects than on the intrinsic susceptibility of the material.

However ferromagnetic grains with very irregular shapes are better represented by triaxial ellipsoids than by spheres. The three demagnetizing coefficients along the three principal axes n_1 , n_2 and n_3 are all different and

$$n_1+n_2+n_3=4\pi.$$

The apparent susceptibility of an aggregate of grains, *oriented at random* is then given by

$$A' = \frac{A}{3} \left(\frac{1}{1+An_1} + \frac{1}{1+An_2} + \frac{1}{1+An_3} \right).$$

It is easily shown that this is always greater than that of a sphere of the same material.

Obviously it will appear as if the demagnetizing coefficient n of the average grain is less than $\frac{4}{3}\pi$. Nagata, from an experimental study of the susceptibility of some igneous rocks, estimates that the average value of n is about 3.5 with $A'=0.23$ and $A=0.12$. With artificial mixtures of sand and large grains of powdered magnetite, n is found to be 3.15 when the susceptibility A of the same magnetite in the massive state is 0.43. The smaller value of A in natural specimens is probably connected with the higher value of their coercive force, which would imply a smaller value of A .

Thus the experimental results on the initial susceptibility of rocks are in excellent agreement with the large grain hypothesis. Though much less naturally explained by the theory of single-domain grains, they are not actually inconsistent with it.

§ 40. DISPLACEMENT OF A SINGLE WALL

To interpret the magnetic properties of large grains more fully it is necessary to consider the mechanism of the magnetization process. Wall displacements are, as stated above, the mechanism concerned. Consider the substance as composed of elementary domains which can be crossed from end to end by a wall.

The fundamental process is the movement of a single wall P (supposed plane) of surface-area S , its position being represented by the abscissa, z , of its intersection with an axis OZ perpendicular to the wall. This wall P separates two elementary domains with spontaneous magnetizations $+J_s$ and $-J_s$ and can move from $z=0$ to $z=L$, that is through a distance L which is called the *free path of the wall*. For $z=0$ the magnetic moment of the domain is $-LSJ_s$ and for $z=L$, $+LSJ_s$.

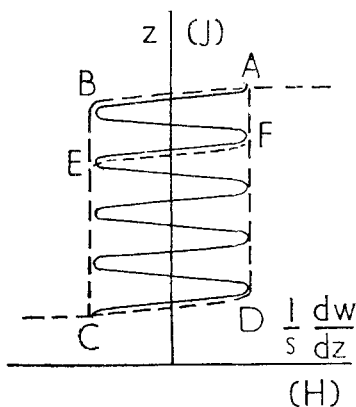
In a perfectly pure substance, the energy of the system W has a constant value W_0 in zero magnetic field, which is independent of the position z of the wall. In a field H , parallel to J , a pressure of $2HJ_s$ acts on the wall. An infinitely small positive field is enough to move the wall to its limit at $z=L$ and in infinitely small negative field brings it back to $z=0$. There is no hysteresis.

But in a real substance, which is always somewhat imperfect, W is a complicated function of z which varies haphazardly around the mean value W_0 . With no applied field the wall is in equilibrium at points when W is a maximum. Application of a field H moves the wall until the equilibrium condition

$$2J_s H = \frac{1}{S} \frac{dW}{dz}$$

is satisfied. If the equilibrium is to be stable the second derivative d^2W/dz^2 must be positive. Thus to saturate the domain in the positive direction a field of at least the maximum value of $\frac{1}{2SJ_s} \frac{dW}{dz}$ must be applied. Therefore the coercive force depends on the maximum gradient of W .

Fig. 7



Hysteresis cycle given by a free path obstructed by equally spaced barriers all of the same height; the full line represents the opposition, the broken one the hysteresis cycle.

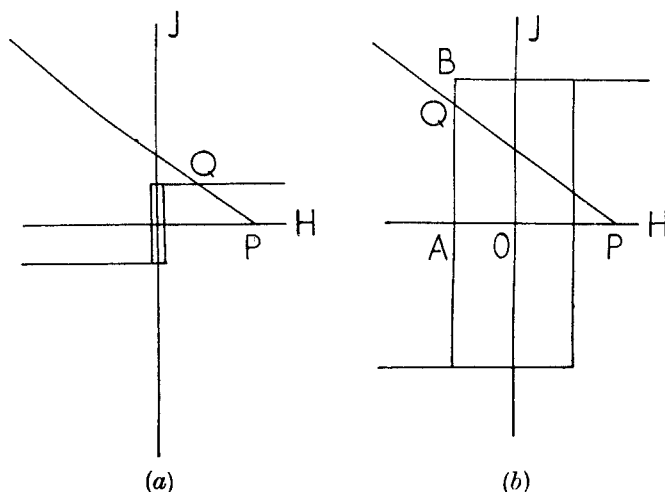
Lliboutry⁽⁴¹⁾ gives a very suggestive graphical representation of these phenomena. He plots the quantity $(1/S)dW/dz$ which he calls the *opposition* as abscissa against the position z of the wall as ordinat \acute{e} . As stated above, z is proportional to the magnetization. This gives a curve C whose intersections, where its slope is positive, with the lines given by $x=2J_s H$ give points M corresponding to possible equilibrium states of the system. Except for certain volume changes, movements of M correspond to variations in magnetization with H .

The simplest model which has hysteresis, is obtained by representing the opposition as a sine curve $A \sin pz$ where p is large compared with $1/L$. This is the dotted line of fig. 7. The limiting hysteresis cycle ABCD (dashed line) approached a rectangle as p becomes greater. If at the point E on the vertical part of the return cycle the movement is stopped and the magnetic field increased again, the point representing the magnetization will follow the path EF which is nearly horizontal when p is large. For completeness it must be supposed that the coefficient A decreases as the temperature rises and tends to zero at the Curie Point.

§ 41. THERMO-REMANENT MAGNETIZATION OF THE MODEL WITH A SINGLE WALL

This model can be used to determine the thermo-remanent magnetization J_r , produced by cooling in a constant field H . It depends essentially on the mode of variation of the spontaneous magnetization J_s and the coercive force H_c with temperature, especially close to the Curie Point. Unfortunately experimental data on this are extremely scarce, while Forrer and Baffie⁽⁴²⁾ have shown that these phenomena are often very complicated.

Fig. 8



The process of acquiring T.R.M. (see text).

Generally speaking theory and experiment agree that the true remanent magnetization J_r and the spontaneous magnetization J_s vary as $(\theta - T)^{1/2}$ in the neighbourhood of θ . But the form of the thermal variation of coercive force H_c is very different from one substance to another. This is not surprising since the coercive force is a complicated function of many independent factors. Forrer⁽⁴³⁾ found a variation of H_c with $(\theta - T)^{1/2}$ in large crystals of magnetite which had the low coercive force of 4 oe at room temperature, while for the very fine magnetite grains of a ferromagnetic rock with a very high coercive force Akimoto⁽⁴⁴⁾ found that H_c varied nearly as $(\theta - T)$.

Being concerned here with rocks of high coercive force such as these latter it seems better to use this last result. Then one has

$$\frac{H_c}{H_{c0}} = \left[\frac{J_s}{J_{s0}} \right]^2, \quad \dots \dots \dots (11)$$

H_{c0} and J_{s0} being the values of H_c and J_s at room temperature. The simplest form of hysteresis cycle is considered, as before; a rectangular limiting cycle of height $2J_s$ and width $2H_c$ with all the partial cycles of the same width $2H_c$.

The demagnetizing field of the grain with a mean coefficient n plays an important part. Very close to the Curie Point the hysteresis cycle has the form of fig. 8 (a) and in an applied field $H=OP$ the magnetization is represented by the point of intersection Q , of a line of slope $-1/n$ through P , with the upper branch of the hysteresis cycle. As the temperature falls the cycle widens and takes the form of 8 (b) while the line PQ remains fixed, so that the point Q moves back along the upper branch of the cycle. It continues to move back as long as the ratio $r=AQ/AB$ continues to decrease. Now

$$r = \frac{H+H_c}{nJ_s}$$

and the derivative dr/dT vanishes when

$$\frac{dH_c}{dT} = \frac{H+H_c}{J_s} \frac{dJ_s}{dT}$$

or from eqn. (11) when $H=H_c$ and r has the value $n_0=2H/nJ_s$. From this temperature r increases as the temperature falls but Q the point representing the magnetization cannot move back up the descending part of the cycle BA . It describes (in reduced coordinates) a horizontal branch of the cycle of reduced height r_0 .

At room temperature the specimen thus has a T.R.M. given by

$$J_{tr} = r_0 J_{s0}$$

It is not altered when H is removed and hence from eqn. (11)

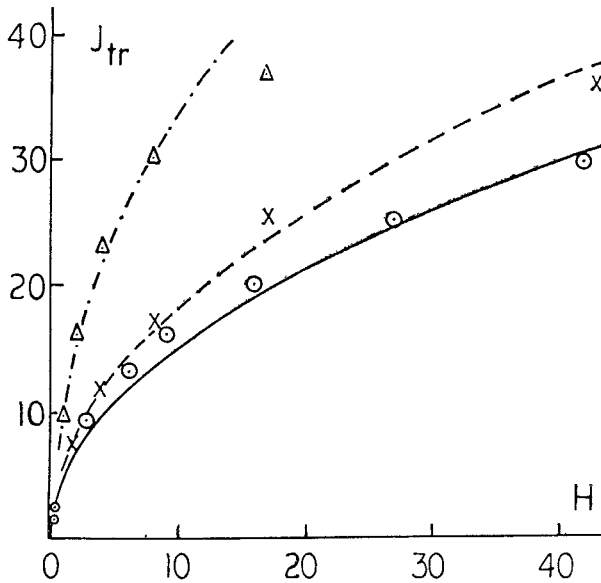
$$J_{tr} = \frac{2H^{1/2} H_{c0}^{1/2}}{n} \dots \dots \dots (12)$$

The T.R.M. is thus proportional to the square root of the applied field and the square root of the coercive force.

§ 42. COMPARISON WITH EXPERIMENTAL RESULTS ; VALUE OF Q_k

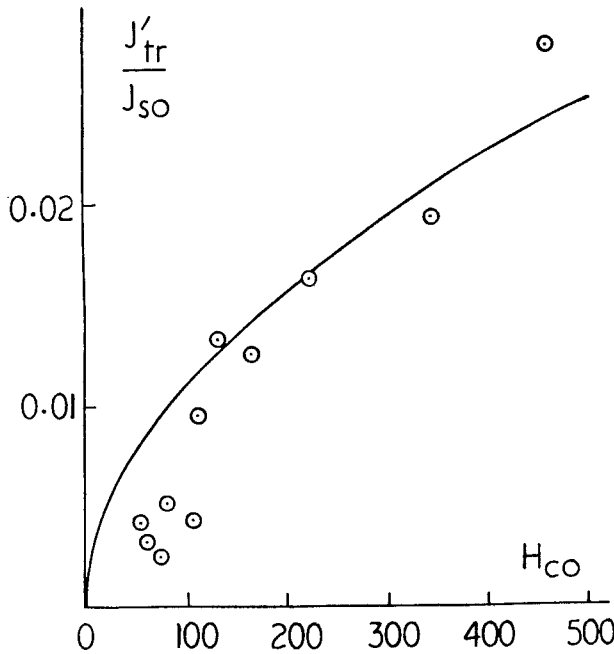
This theoretical formula is compared in fig. 9 with Nagata's⁽²⁷⁾ experimental results on a rock specimen (No. 60), with Mlle. Roquet's⁽⁴⁵⁾ results for a dispersion of fine grains ($\frac{1}{10} \mu$) of artificial magnetite in kaolin (M_2') and for artificial ferric oxide (F_5). In all cases the parabolic law represents the facts quite well, except in very low fields. This point will be considered later (§ 57).

Fig. 9



Variation of T.R.M. J_{tr} with the applied field H compared with the theoretical parabola (\odot =Spec. No. 60, Nagata; \times =Spec. M_2^1 , Mlle. Roquet; Δ =Spec. F_s).

Fig. 10



The ratio of T.R.M. in a field of 1 oe. J_{tr}^1 to the saturation magnetization J_{s0} plotted against the coercive force H_{co} . (Comparison of Nagata's results with the theoretical parabola of formula (12).)

Equation (12) shows that if J_{tr}^1 is the T.R.M. acquired in a field of 1 oe (Nagata's saturated T.R.M.) the ratio J_{tr}^1/J_{s0} should be equal to $2H_{c0}^{1/2}/nJ_{s0}$. Figure 10 shows the value of this ratio determined by Nagata for different specimens plotted against the value of H_{c0} and compared with the theoretical curve obtained with an assumed value of 1800 for nJ_{s0} (given by the theoretical values of $J_{s0}=450$ and $n=4.19$).

Q_k is the ratio of T.R.M. in the earth's field Z to the magnetization induced by the same field. Since the induced magnetization is about Z/n

$$Q_k = 2 \left(\frac{H_c}{Z} \right)^{1/2} \dots \dots \dots (13)$$

For $Z=0.5$, Q_k should vary from 4 to 400 as H_c varies from 2 to 20 000 oersteds. Experiments do in fact show that Q_k is greater for rocks with a higher coercive force.

§ 43. STATEMENT OF LORD RAYLEIGH'S RELATIONS

The expressions for the magnetization of ferromagnetic bodies in *weak fields*, called Rayleigh's relations are particularly interesting in the case of rocks because the earth's magnetic field is always very weak compared to the coercive force of a rock.

Only a brief statement of them is necessary. The magnetization of a body, which has been previously demagnetized by an a.c. field gradually decreasing to zero, is a quadratic function of the applied field H :

$$J = AH + BH^2.$$

This is *Rayleigh's first relation*.

If, when the magnetic field has reached a value H_m , producing a magnetization J_m , it is reduced by an amount ΔH , the magnetization changes by ΔJ which has the same sign as ΔH and is given numerically by

$$|\Delta J| = A |\Delta H| + \frac{1}{2} B |\Delta H|^2.$$

This formula is only valid provided H remains inside the interval $-H_m$ to $+H_m$. Brown⁽⁴⁷⁾ calls this *Rayleigh's second relation*. The term of first order in H always has the form AH hence the coefficient A is called the reversible susceptibility.

From these formulae one can deduce that a magnetic field H_m leaves, when removed, a remanent magnetization J_r given by

$$J_r = \frac{1}{2} BH_m^2.$$

§ 44. THEORY OF RAYLEIGH'S RELATIONS

L. Néel⁽²⁹⁾ has shown that Rayleigh's relations can be explained on the single wall model. For this purpose a slightly more refined expression than that of § 40 must be used to represent the opposition $(1/S)dW/dz$. The curve of $(1/S)dW/dz$ is simulated by a series of straight lines A_1A_2 ,

A_2A_3, \dots . The projection of each section on the z -axis is the same and equal to $2l$ and the ordinates of the ends have a Gaussian random distribution about the mean value zero (fig. 11).

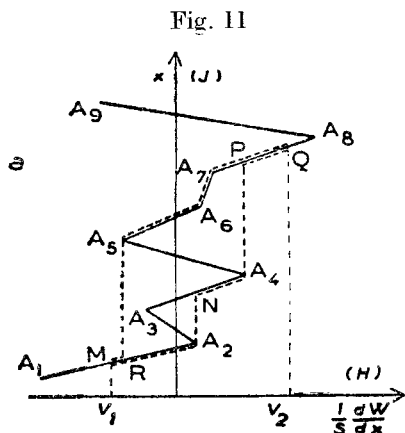
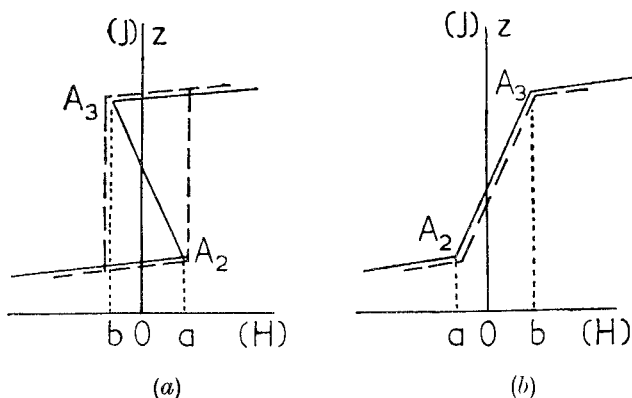


Diagram showing the course of a hysteresis cycle according to Liboutry. The full line is the opposition and the broken one the hysteresis cycle.

In a field H_1 the wall is in equilibrium at the point M on the section A_1A_2 which has a positive slope (therefore stable equilibrium). The abscissa of M is $V_1 = 2H_1J_s = (1/S)dW/dz$. When the field is increased from H_1 to H_2 the point representing the position of the wall follows the path MA_2NA_4PQ with two discontinuities A_2-N and A_4-P ; the return path is $QPA_7A_6A_5RM$ and hysteresis therefore occurs.

Fig. 12

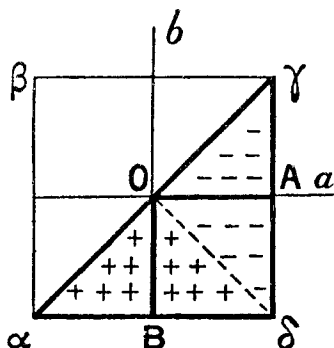


(a) Irreversible and (b) reversible imaginary cycles corresponding to small wall displacements against an opposition represented by straight lines as in fig. 11.

In the range of weak fields these cycles reduce to the two imaginary elementary cycles of fig. 12, the first (*a*) representing the irreversible part of the phenomena and the second (*b*) the reversible part. If *a* and *b* are the critical fields corresponding to the abscissae of the points A_2 and A_3 each of the imaginary cycles can be represented by a point (*a*, *b*) in the plane *Q* of fig. 13. When there is a large number of walls, there will therefore be a large number of representative points whose density will be uniform close to *O*, the origin of coordinates in the plane *Q*.

The upper half of the plane (*a*, *b*) in which $a < b$ corresponds to *AH* the reversible term in the magnetization expression, the other half-plane where $a > b$ to the irreversible term in H^2 . It was shown long ago by Weiss and Freudenreich⁽⁴⁸⁾ and later by Preisach⁽⁴⁹⁾ that an assembly of such unsymmetrical cycles corresponding to this second half-plane allows of an immediate explanation of Rayleigh's laws. According to these authors the cycles concerned were real ones such as those of isolated grains whereas in Néel's theory⁽²⁹⁾, here described briefly in a form due to Lliboutry⁽⁴¹⁾, they are imaginary cycles corresponding to partial displacement of walls.

Fig. 13

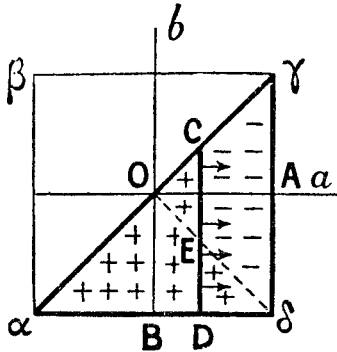


The magnetic state of the imaginary irreversible cycles after demagnetization in a decreasing alternating field. After demagnetization by heating above the Curie Point, cycles in the quadrant *BOA* are magnetized at random, some positively and some negatively.

In zero applied field, the domains of the sector αOB (fig. 13) are always positively magnetized while those of sector $AO\gamma$ are always negatively magnetized. But the domains of the quadrant *BOA* can have either sign according to the initial conditions. It is however easily shown that after demagnetization in a decreasing alternating field, the situation is as in fig. 13 when the domains are positively or negatively magnetized according as their representative points are below or above the second bisector $O\delta$. Application of an increasing field *H* causes reversal of the domains in the triangle *OEC*, the process being represented in fig. 14 where *CD* is a line with abscissa $a=H$. Similarly the return curve

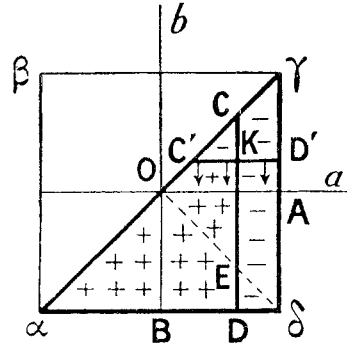
corresponds to the situation in fig. 15 where the abscissa of the line $C'D'$ is equal to the decreasing field. It is obvious without further argument that Rayleigh's two laws can be interpreted in this way.

Fig. 14



Magnetic state of the imaginary cycles during initial magnetization, after demagnetizing in decreasing a.c. field.

Fig. 15



Magnetic state of the imaginary cycles when the descending branch of the real hysteresis cycle is being followed.

§ 45. DEMAGNETIZATION BY HEATING TO ABOVE THE CURIE POINT

This demagnetizing process leads to a very different initial state from that produced in a decreasing alternating field. The two critical fields a and b of the imaginary cycles increase continuously from zero at the Curie Point to room temperature. There is no reason why the magnetization of these cycles should be of one sign rather than another so that in the limit the magnetizations of those in the quadrant BOA (fig. 13) are, after cooling, distributed at random. The result of this is that the initial magnetization curve of a thermally demagnetized body differs from the usual curve. The BH^2 term is smaller (since there are fewer domains to be reversed in the lower half of triangle OEC in fig. 14) and the AH term is larger since it must include terms due to reversal of a proportion of the domains of the trapezium BOED.

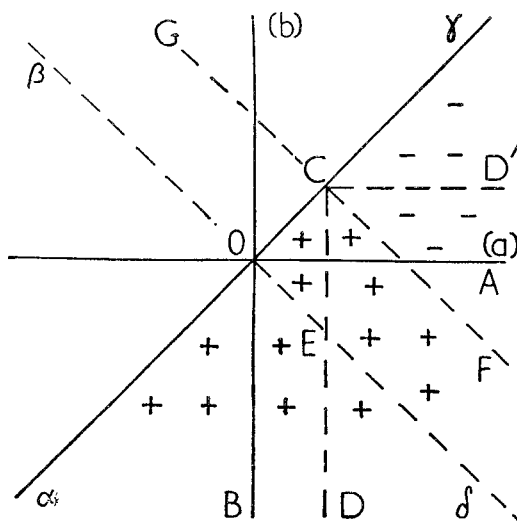
In this simple way Mlle. Roquet's interesting results, on the I.R.M. of artificial rocks, can be interpreted. She found⁽⁴⁵⁾ that the I.R.M. obtained after the first application of a field H is less than that produced after several cycles from $+H$ to $-H$. The difference between the two is roughly proportional to H for small fields while the I.R.M. obtained after several cycles ($\pm H$) is proportional to H^2 so that the phenomenon is more obvious when H is small. In the model outlined above the I.R.M. obtained after cyclical treatment corresponds as usual to the domains of the lower half of triangle OEC which remain positively magnetized. On the other hand the I.R.M. acquired after a single application of the field

involves also the irreversible positive remagnetization of those domains in the area OBDE which have been left negatively magnetized by thermal demagnetization. During the next half-cycle this extra I.R.M. is compensated by one in the opposite direction due to another trapezium similar to OBDE but lying symmetrically on the other side of $O\gamma$; after completion of the cycle everything follows as before (see fig. 14).

§ 46. ANHYSTERETIC MAGNETIZATION

The higher values of anhysteretic magnetization as compared with the ordinary magnetization are also easily explained on this model. The anhysteretic magnetization is obtained by applying a field H and at the same time an alternating field which decreases to zero. It is easily shown that this will correspond to the positive magnetization of the domains of the area $\delta EOCF$ whereas the ordinary magnetization produced by simple application of the same field H would be due only to those domains in the region COE (fig. 16).

Fig. 16



Magnetic state of the imaginary cycles after the action of a constant magnetic field together with a decreasing alternating one (the anhysteretic curve).

§ 47. THE REVERSIBLE TERM AND THE RATIO BH_c/A

Points in the plane (a, b) lying above the first bisector $\alpha\gamma$ correspond to reversible cycles such as in fig. 12 (b). In zero field the magnetic state is represented by all the domains below the second bisectrix 0β being positively magnetized and those above negatively. When a field H is applied the boundary between these two types of domains moves from 0β to CG , when C

is the point with abscissa $a=H$. Thus the change in magnetization of the domains in this upper half of the plane represents the reversible AH term in Rayleigh's relations.

Theory shows⁽²⁹⁾ that the ratio BH_c/A should vary from 0.4 for substances in which $2l$ is of the order of L to about 1 when $2l$ is very small compared to L . It is found experimentally that it is about 0.5 in 'hard' materials (such as used for permanent magnets) and up to several units in 'soft' materials, in qualitative agreement with the theory. In rocks a value of about 0.5 should be expected since their ferromagnetic constituents tend to be 'hard'.

§ 48. THE EFFECT OF THE SHAPE DEMAGNETIZING FIELD ON RAYLEIGH'S RELATIONS

The form of Rayleigh's relations is not altered by the presence of a demagnetizing field. The initial magnetization relation is still expressed by an equation of the type

$$J = A'H + B'H^2$$

but the values of the coefficients are modified. If n is the demagnetizing coefficient it is easily shown that

$$A' = \frac{A}{1+nA}, \quad B' = \frac{B}{(1+nA)^3}.$$

It is also known that the presence of a demagnetizing field does not affect the apparent coercive force H_c' which remains equal to the real value H_c . Hence the relation between the apparent values A', B', H_c' and the real values A, B, H_c is

$$\frac{B'H_c'}{A'} = \frac{BH_c}{A} \frac{1}{(1+nA)^2}.$$

In magnetite A should be of the order 0.5–1 and for the grains found in rocks n is about 3 (cf. § 39). This means that the ratio $B'H_c'/A'$ is probably 6–16 times smaller than the value of 0.5 found for BH_c/A in magnetically hard materials. This is a considerable decrease and provides a very good method for determining whether a material is composed of *large ferromagnetic grains* dispersed in a non-magnetic matrix. It does not seem to have been used yet.

MAGNETIC VISCOSITY IN LARGE GRAINS

§ 49. THE DIFFERENT TYPES OF MAGNETIC VISCOSITY⁽⁵⁰⁾

Time can play an important part in the phenomena of magnetization through a variety of effects.

The fundamental magnetic process, that is the alignment of an elementary atomic moment along a magnetic field, is itself not instantaneous. The magnetic moment undergoes a precession while its direction is moving

into that of the applied field. However the duration of this process of alignment is very small, of the order of 10^{-10} sec ; it is only of importance in high frequency magnetic fields and so is of no interest in rock magnetism.

But *viscosity of diffusion* and *viscosity of thermal agitation* are important. The first is connected with diffusion of elementary material particles, atoms or electrons, within the crystal lattice. Obviously if the distribution of these particles depends on the orientation of the spontaneous magnetization relative to the crystallographic axes any change of magnetization must involve a non-instantaneous rearrangement of the particles. The example of carbon in the lattice of α -iron is the best known. The carbon atoms can occupy 3 different types of interstitial sites since each C atom has two diametrically opposite Fe neighbours, the line of whose centres can make different angles with the spontaneous magnetization and hence have different energies. At room temperature a time of about 1 min is required for a carbon atom to jump from one site to the next. The effect is easily observable since to reach a new equilibrium after a change in the direction of magnetization about the same amount of time is required.

Magnetite, with which we are particularly concerned, shows⁽⁵²⁾ a similar viscosity of diffusion due to movement of electrons from ferrous to ferric ions thus changing their valency. At 100°K these movements require times of about 1 min but at ordinary temperatures they are practically instantaneous and probably do not affect the normal processes of magnetization in rocks. Possibly other diffusion phenomena occur in the magnetic constituents of rocks at high temperatures but as there is no information whatever about them, the subject will not be discussed further, in spite of its great interest.

Generally speaking, viscosity of thermal agitation is due to irregular fluctuations in the forces acting on the spontaneous magnetization which enable it to cross barriers which it otherwise could not. In this way thermal agitation makes irreversible changes of magnetization possible and is an effect common to all ferromagnetic substances.

The effects of this viscosity on rotation processes have already been dealt with in a special application to single-domain particles. Its effects on wall movements must now be considered.

§ 50. THE VISCOSITY FIELD⁽⁵⁰⁾

These effects can be described very simply by supposing that a fluctuating viscosity field $\pm H_f(t)$ is always added to the applied field H and that

$$H_f(t) = S(Q + \log t) \quad (14)$$

where Q is a numerical constant of the order of 40 or 50, t is the time interval since the application of the field H and S , which has the dimensions of a magnetic field, is a constant characteristic of the specimen considered and dependent on the temperature.

In the absence of the viscosity field, we know that after a magnetic field H has given to a ferromagnetic substance a magnetization J_0 , a small increase in the applied field of h produces a change in magnetization of j given by $j=(A+C)h$ while a small decrease gives a change

$$j' = -Ah.$$

A and C are the reversible and irreversible differential susceptibilities at the point (J_0, H) of the hysteresis cycle. With a fluctuating field the magnetization J after a time t is thus

$$J = J_0 + C S(Q + \log t). \quad \dots \dots \dots (15)$$

Barbier's experiments⁽⁵³⁾ show that S has about the same value all round the hysteresis cycle.

§ 51. THE VISCOSITY OF FLUCTUATION IN THE RANGE
RAYLEIGH'S RELATION

Formula (15) can be applied to some particular cases. In the Rayleigh region where the initial magnetization is given by

$$J = AH + BH^2$$

the irreversible differential susceptibility at the point (J, H) is $C = 2BH$ as that including the viscosity term,

$$J = AH + BH^2 + 2BHS(Q + \log t). \quad \dots \dots \dots (16)$$

After application of a field H and then a return to zero field the remanent magnetization is $\frac{1}{2}BH^2$ and the irreversible susceptibility is $C = -BH$ so that the remanent magnetization after a lapse of time is

$$J_r = \frac{1}{2}BH^2 - BHS(Q + \log t). \quad \dots \dots \dots (17)$$

This expression shows that the viscosity of isothermal remanent magnetization increases in relative importance with the size of the field which caused the magnetization.

At different points of the limiting cycle, obtained after saturation in a very high field the magnitudes of the viscosity are greater in absolute value but less in relative value than in the preceding case. They can be calculated from formula (15) with $C = -k J_s/H_c$, where k is a numerical coefficient of about $\frac{1}{10}$ for $H=0$ (remanent magnetization) and several units for $H=H_c$, at which point the absolute value of the viscosity is a maximum.

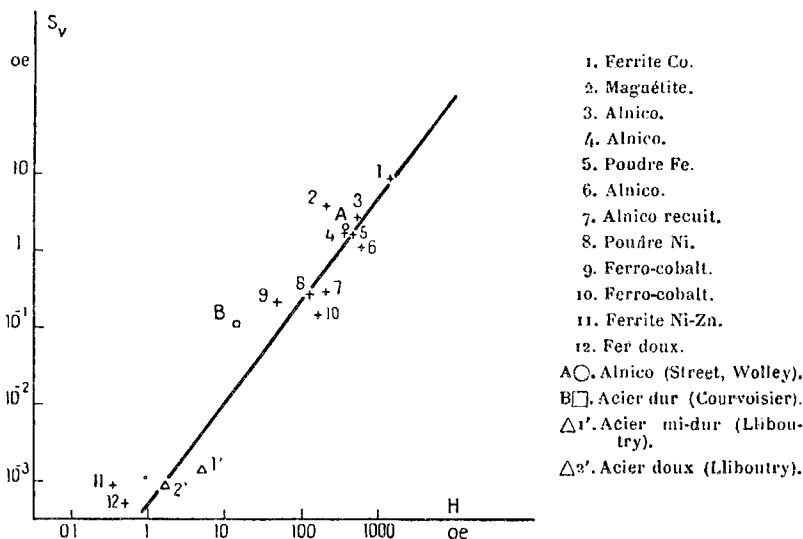
§ 52. THE VALUES OF S ⁽⁵³⁾

Barbier has made a thorough experimental study of these theoretical conclusions and shown them to be well founded.

He has also measured values of S for very diverse specimens and has found that S increases with the coercive force. Figure 17 summarizes his results and shows that S varies from about one thousandth of the coercive

force for soft materials to about four thousandths for hard materials. These results are particularly interesting for they show that in substances with a coercive force of about 100 oersteds the viscosity field $S \log t$ is of the order of the earth's magnetic field.

Fig. 17



Values of the viscosity constant S for various specimens plotted against their coercive force (after J. C. Barbier).

§ 53. THEORETICAL CALCULATION⁽⁵⁰⁾ OF S

These thermal agitations may be considered to act through the mechanism of the internal dispersion fields produced by thermal oscillations of the spontaneous magnetization about its mean value. Suppose that the fluctuation field which helps a wall to cross an obstacle, that is to pass through a volume v (vJ_s corresponds to a Barkhausen discontinuity), is equal to the mean component H_m in a given direction of the dispersion field, over a similar volume v within an elementary domain. This mean value is a random function of time t whose mean square is given by equating the mean energy to kT . More exactly $H\rho$ the root mean square of H_m is

$$H\rho = \sqrt{\left(\frac{4\pi kT}{3v}\right)}.$$

Consider the possible values of H_m as having a Gaussian distribution and let θ be the reorganization time, that is the minimum time interval which must separate two observations in order that the corresponding values of H_m should be practically independent. In these conditions if ϵ is the probability that H_m is greater than a certain value H_f , a time $t = \theta/\epsilon$ must

elapse for H_m to reach the value H_f with a probability of about 1. Then it is found that t is related to H_f by an expression of the type of (14), with the following values of Q and S :

$$Q \sim -2 \log \theta ; S = H_\rho Q^{-1/2}.$$

The reorganization time θ is estimated to be of the order of 10^{-10} sec which gives values of Q of 40 to 50.

As Street and Woolley⁽⁵⁴⁾ have proposed, the thermal agitations can also be considered as affecting the heights of the barriers which oppose wall movements. If the fluctuations in the energy required to cross a barrier are of the order of kT the effects are the same as if the wall were acted on by a fluctuating field whose root mean square H_ρ was

$$H_\rho = \frac{kT}{2J_s v}.$$

The argument then proceeds as before.

These considerations show that, if v is constant, S varies as $T^{1/2}$ if the thermal agitations are those of an internal dispersion field but as T if they are fluctuations in the heights of barriers. Barbier has studied the variations of S in a very wide temperature range and has found that in fact S varies approximately as $T^{3/4}$. Thus it seems probable that both the above mechanisms occur simultaneously but possible changes in v with temperature must also be considered.

§ 54. THE EFFECT OF THE DEMAGNETIZING FIELD ON VISCOSITY OF THERMAL AGITATION

To obtain expressions for magnetic viscosity in large grains the demagnetizing field must now be taken into account. The method used before (cf. § 37) can be employed for these calculations. In the Rayleigh region, where the term in H^2 is small compared to that in H , the initial magnetization relation, for instance, becomes

$$J = RAH + R^3BH^2 + 2R^3BHS(Q + \log t) \quad . . . \quad (18)$$

where the coefficient R is given by

$$R = \frac{1}{1 + nA},$$

n being the demagnetizing coefficient.

Similarly the remanent magnetization left after application and removal of a field H_m is

$$J_r = \frac{1}{2}R^3BH_m^2 - R^3BH_mS(Q + \log t) \quad . . . \quad (19)$$

Thus in large grains as well as small grains the viscosity is proportional to $\log t$ agreeing with Thellier's experimental results⁽³¹⁾. It is impossible to distinguish between the two cases from this point of view. The experimental facts on magnetic viscosity in rocks are also much too meagre to decide whether it varies with H_m as in (19). It would be equally interesting to know the values of S and whether they are related to H_c as in fig. 17.

Outside the Rayleigh region the effect of the demagnetizing field on the magnetic viscosity is more complicated. In particular when the irreversible susceptibility C becomes appreciable compared to the reversible susceptibility A the change of magnetization with time, J_t is given by

$$J_t = \frac{CS(Q + \log t)}{(1 + nA)(1 + nA + nC)}$$

which reduces, when C is large compared to A , to Barbier's⁽⁵³⁾ simple formula

$$J_t = \frac{CS(Q + \log t)}{(1 + nC)}.$$

§ 55. THE EFFECT OF A RISE OF TEMPERATURE ON THE REMANENT MAGNETIZATION⁽⁵⁰⁾

The arguments of § 53 show that the viscosity field

$$H_f = S(Q + \log t)$$

not only increases with time but also with temperature since S varies as $(T/v)^{1/2}$ or as T/vJ_s according to the mechanism involved.

Thus as well as an irreversible linear decrease in remanent magnetization with $\log t$ there should also be an irreversible decrease due to the rise in the viscosity field with temperature.

To observe this phenomenon it is necessary to exclude the reversible thermal variation in the principal term, $\frac{1}{2}R^3BH^2$, of J_r . To achieve this one takes advantage of the fact, predicted by Rayleigh's relations and confirmed by experiment, that a first order *decrease* in the viscosity field only produces a second order effect on the magnetization. Hence the fraction of the thermal variation of J_r due to the thermal increase of H_f can be obtained by determining the decrease in J_r produced by heating the specimen from T_0 to T_1 and then cooling to T_0 again.

However, it is not the increase in the viscosity field itself but the increase in the ratio of the viscosity field to the coercive force H_f/H_c that is important. In fact the walls have to cross barriers whose height decreases as the temperature rises and the coercive force is the measure of these heights. We are therefore concerned with the increase in the quantity

$$H_j' = H_{c0}S(Q + \log t)/H_c.$$

The phenomenon is found experimentally with about the predicted order of magnitude. Barbier⁽⁵³⁾ has studied it in ferromagnetic metal alloys and some artificial oxides with high coercive force. It has been observed by Thellier⁽³¹⁾ and Mlle. Roquet⁽⁴⁶⁾ in baked clays and in dispersions of magnetite.

The ratio of the time variation to the thermal variation of remanent magnetization can be expressed quite simply. We have

$$\frac{\partial J_r}{\partial \log t} \bigg/ \frac{\partial J_r}{\partial T} = \frac{\partial H_j'}{\partial \log t} \bigg/ \frac{\partial H_j'}{\partial T}.$$

Simplifying the right-hand side by neglecting $\log t$ compared to Q and assuming the empirical variation of S with $T^{3/4}$ found by Barbier which lies between the two theoretical predictions, we get finally

$$\frac{\partial J_r}{\partial \log t} / \frac{\partial J_r}{\partial T} = \frac{T}{Q} \left(\frac{3}{4} - \frac{\partial H_c}{\partial T} \right)^{-1}$$

in which all terms except Q can be determined experimentally. This gives a direct method of finding Q .

Assuming that Q is about 40 to 50 and neglecting the thermal change of coercive force, the formula predicts values of the ratio

$$\frac{\partial J_r}{\partial \log t} / \frac{\partial J_r}{\partial T}$$

of the order of 8 to 10 at room temperature. Barbier has in fact found values of between 10 and 13 for magnetically hard materials which are exactly of the expected order of magnitude. Thellier⁽³¹⁾ has found a ratio very close to 9 for a specimen of clay from Noron baked in nitrogen at 665°C. On the other hand Mlle. Roquet⁽⁴⁶⁾ in specimens containing mainly magnetite obtained ratios of 3.5 to 2.9. Possibly these low values are at least partly due to thermal variation of the coercive force. In fact from Forrer and Baffie's⁽⁴²⁾ experiments the value of $(T/H_c) \partial H_c / \partial T$ should be about -0.5 which gives at $T=300^\circ\text{K}$ and $Q=50$ a theoretical value equal to 4.8 of the ratio

$$\frac{\partial J_r}{\partial \log t} / \frac{\partial J_r}{\partial T}.$$

The phenomenon dealt with in the next section may also be responsible.

§ 56. IRREVERSIBLE DECREASE OF REMANENT MAGNETIZATION DUE TO ANY CHANGE OF TEMPERATURE POSITIVE OR NEGATIVE

It is found experimentally that in certain relatively soft materials irreversible decreases of remanent magnetization may occur quite independently of those considered above, due to either *positive or negative* temperature changes. A mechanism entirely different in principle from the preceding ones must be concerned. It is probably a thermal change in the functions relating the energy of the system of walls to their positions in the crystal lattice. The result is an additional decrease of remanent magnetization with temperature and a decrease of the ratio $(\partial J_r / \partial \log t) / (\partial J_r / \partial T)$. In this way Barbier has found a ratio of 2.5 for a ferro-cobalt with a coercive force of 155 oe. The existence of this parasitic phenomenon is also revealed by the irreversible decrease of remanent magnetization J_r produced by cooling below room temperature and then allowing the temperature to rise again. This does not occur in the normal substances with which the original theory dealt.

Finally it should be noticed that thermal agitation produces analogous effects in both single domain and large grains; for instance in both, the same order of magnitude is found for the ratio of the decreases in I.R.M. due to time and due to rise in temperature.

§ 57. THERMO-REMANENT MAGNETIZATION IN VERY WEAK FIELDS

The brief theory of T.R.M. given earlier shows that it is proportional to $H^{1/2}$ (§ 41). In fact it is found experimentally that in very weak fields of about 1 oe it is more proportional to H than to $H^{1/2}$. The theory should not actually be valid for such small fields for no account has been taken of the thermal agitation field. In particular the blocking of walls probably cannot take place until the coercive force has reached a value at least equal to H_f , the thermal agitation field at temperatures near the Curie Point. In this region assuming the validity of (11), the spontaneous magnetization J is given by

$$\frac{H_f}{H_{c0}} = \left(\frac{J_s}{J_{s0}} \right)^2.$$

The magnetization acquired in a field H is then equal to H/n and assuming that the blocking occurs at this moment the T.R.M. at room temperature J_{tr}'' is given by multiplying again by J_{s0}/J_s :

$$J_{tr}'' = \frac{H}{n} \left(\frac{H_{c0}}{H_f} \right)^{1/2} \dots \dots \dots (20)$$

This gives a proportionality to H in very small fields. From (12) and (20) J_{tr} should be equal to J_{tr}'' for $H=4H_f$ showing that the transition from one law to the other occurs for a field of 4 times the value of the fluctuation field at the Curie Point.

There are no experimental data to verify formula (20).

§ 58. THE ADDITIVITY OF PARTIAL T.R.M.S
IN THE LARGE GRAIN MODEL

To what extent can the model of an assemblage of large grains account for Thellier's laws of the additivity of partial T.R.M.? It has already been shown (cf. §§ 27, 28) that all Thellier's laws are simply and naturally explained on the single domain model by the action of thermal agitation. Similar considerations will probably provide a start for attacking the problem in the large grain model.

Consider the free path L of a wall. A first approximation (§§ 40, 41) assumes the free path to be obstructed by a number of equally spaced barriers all of the same height; the second approximation, used in considering Rayleigh's relations (cf. §§ 44-46) supposes that the barriers are of different heights. Suppose now that the substance is acted on by a field H , small compared with the fluctuation field but large enough for the ratio vJ_sH/kT to be much greater than 1 (v is the volume through the wall passes in moving from one barrier to the next). In these conditions the possible crossing of the barrier depends on the magnitude of the fluctuation field compared to the height of the barrier.

Consider a temperature T_1 less than the Curie Point θ and compare the total T.R.M. due to a field H with the partial T.R.M.'s acquired from θ to T_1 and from T_1 to room temperature in the same field. For this purpose the barriers are classed into two types: the first, A, including all

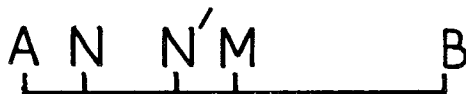
barriers which can be crossed with the help of the thermal fluctuation field at temperatures below T ; the second type, B, includes all the others, numbering q .

After demagnetization the wall lies, on the average, at the centre M of its free path AB ($AB=L$). If the field H acts continuously from θ to room temperature the wall crosses all the barriers and moves to the end A of its free path AB where it is found at room temperature definitely blocked. The path AM corresponds to the complete T.R.M.

If the field H acts only between θ and T_1 , the wall again crosses all the barriers and reaches A, but after the field is removed at T_1 it can cross back over barriers of type A and is only stopped by those of type B. Thus on the average the wall is finally at a point N at a distance $AN=L/2q$ from A. The partial T.R.M. acquired between θ and T_1 is then proportional to the distance MN.

If H is applied only from T_1 to room temperature the wall remains at M on the average until T_1 is reached. After the field is applied at this point, it crosses all A-type barriers and stops when it meets the first of B type at N' at a mean distance from M of $L/2q$. The partial T.R.M. from T to room temperature is then proportional to the distance MN' .

Fig. 18



Since $NM+N'M=AM$ the total T.R.M. is equal to the sum of the two partial ones, and an important law of Thelliers is explained. The others can be derived similarly.

At first sight this argument seems to show that the different T.R.M.'s are independent of the field H . This is not true since in reality the free path AB must itself be considered as depending on H .

The whole argument is based on the assumption that the two types of barrier, high and low, are independent and that this distribution is not affected by temperature. It is no doubt a rough and ready mode of reasoning and could be improved, but it has the advantage of showing that it is possible to interpret Thellier's laws in the scheme of a theory of wall displacements.

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