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Ferromagnetic behaviour of interacting superparamagnetic particle aggregates in basaltic rocks

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Abstract. Studies on two rare cases of magnetic behaviour in basaltic rocks are reported. In both the cases a peak in susceptibility occurs at −160°C. However, one sample shows only normal hysteresis loops at low temperatures in a wide range of fields, while the other sample shows a constricted hysteresis loop in 1000 Oe at −190°C. Both types of behaviour can occur as a result of differing states of aggregation of interacting superparamagnetic particles in the respective samples.

Keywords. Ferromagnetism; superparamagnetism; basaltic rocks.

1. Introduction

Recent studies (Radhakrishnamurty and Likhite 1970a, Radhakrishnamurty, Likhite and Sastry 1971) on basaltic rocks have provided evidence for the presence in some cases of fine single-domain particles of iron oxide exhibiting superparamagnetic (SP) behaviour. The low-field (10 Oe) constricted hysteresis loop shown by some of the basalts has been attributed by Radhakrishnamurty and Sastry (1970) and Néel (1970) to interaction among fine particles. Evdokimov (1963) showed that interacting fields of the order of 1000 Oe could be easily obtained in dense aggregates of nickel SP particles and that such 'molecular' fields might not exceed 10^4 Oe. This can be shown as follows.

The average field $\bar{H}$ at a distance d due to a ferromagnetic particle of volume V and saturation intensity J_s is given by

$$\bar{H} = \frac{VJ_s \langle 3\cos^2\theta - 1\rangle}{d^3} \quad (1)$$

Substituting $V=\frac{4}{3}\pi r^3$ for a spherical particle and $\langle 3\cos^2\theta-1\rangle=\frac{1}{2}$,

$$\bar{H}=\tfrac{2}{3}\pi J_s r^3/d^3 \quad (2)$$

For Ni particles of radius 15 Å with J_s=510 G, the field at 20 Å is about 1000 Oe. Since J_s for magnetite is 500 G, the order of molecular fields would be the same as those obtainable for Ni particles. Also, the field would be negligible at distances of a few times the particle diameter.

One of the most important features of interacting SP particles is the reappearance of ferromagnetic behaviour for the cluster. A consequence of this is the presence of a transition temperature or so-called first Curie point, below which the cluster behaves like a ferromagnet and above which as a strong paramagnet. Thus, a sample containing interacting SP particles will show two Curie points: one resulting from a break-down of interaction between the macroscopic moments and the other from the break-down of interaction between the spins themselves. That such a first transition point for SP particles occurs has been shown by Evdokimov (1964) and it is given by:

$$T_1 = \tfrac{1}{3} a (VJ_s)^2 n/k \tag{3}$$

where a is a molecular field coefficient which has an estimated value between 1 and 3·3, and which determines the effective field acting when the cluster is subjected to an external field; n is the number of particles in unit volume and k is the Boltzmann constant.

$$T_1 \sim (VJ_s)^2/kd^3 \tag{4}$$

as $n \sim 1/d^3$

For a mean distance of 100 Å between the particles the above relation gives $T_1 \sim 10$ K for particles of volume 10^{-19} cc and 0·1 K for those of 10^{-20} cc.

Since basalts have been shown generally to contain SP particles, a search for samples with the first transition point well below 0°C was made. Fortunately, a few such samples have been found and their magnetic behaviour is described here.

2. Results

The magnetic properties studied were (i) thermal variation of initial susceptibility (χ), and (ii) hysteresis in different fields and temperatures for which procedures have been described earlier by Radhakrishnamurty and Likhite (1970b) and Likhite *et al* (1965).

A large number of samples from our own rock collections and some test samples received from others have been analysed using the magnetic methods. Here we report rare types of magnetic behaviour of two rock samples, which are possibly unknown among synthetic magnetic materials.

The first rock sample (M007) has been picked out from twenty test samples obtained from Professor R L Wilson of Liverpool University, England. M007 belongs to one of the flows of basic igneous rocks of the Tertiary period (70 to 1 million years) from Skye, Scotland. It is a normal basalt with little alteration, and polished surface studies reveal few grains of magnetite and nothing is unusual about its petrological character. Only a small sample (15·2g) of M007 is available and no destructive analysis could be undertaken on it because of its rare magnetic behaviour.

The second sample, SK28, was obtained from the collection of one of us (E.R.D.). This sample came from Ordovician or Silurian (500 to 400 million years) volcanic rocks of Skomer Island, Wales. Petrologically it has a composition intermediate between basalt and trachyte and contains a few per cent of magnetite or titanomagnetite. It is a fine grained rock and has suffered some alteration due to its age.

Before describing the properties of the above two samples, a remark on the interpretation of magnetism of rocks may be made. The magnetic properties are due to a few per cent of iron oxide grains in rocks; these are not directly correlatable to the size and composition of the grains estimated from optical and chemical studies respectively as pointed out earlier (Radhakrishnamurty, Likhite and Sastry 1971). Hence, the emphasis has been restricted to magnetic analysis in the present study of the rock samples.

In figure 1 a, the solid curve depicts the temperature variation of χ measured in a field of 0·5 Oe for the basalt sample M007. It is interesting to note that the sample has a much higher χ at -190°C than at 25°C, and has a peak value at -160°C. This is in contrast to a curve due to a normal ferromagnet shown by the dashed line, which

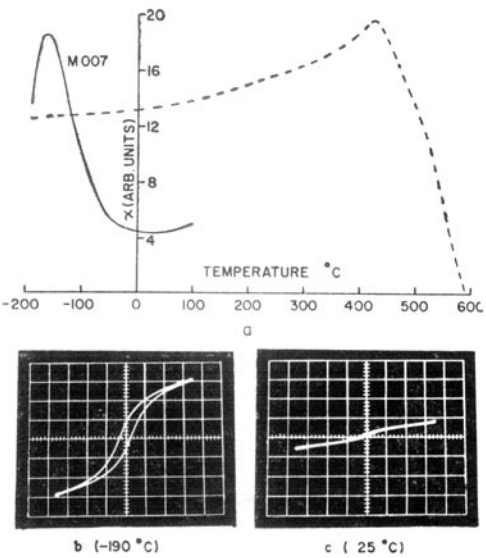

Figure 1. Susceptibility *vs* temperature curve and hysteresis loops for a 15·2 g sample of M007. Dashed line in (a) is χ-T curve for a normal basalt. Scale for (b) and (c): one small division on X-axis=90 Oe; on Y-axis=0·7 emu.

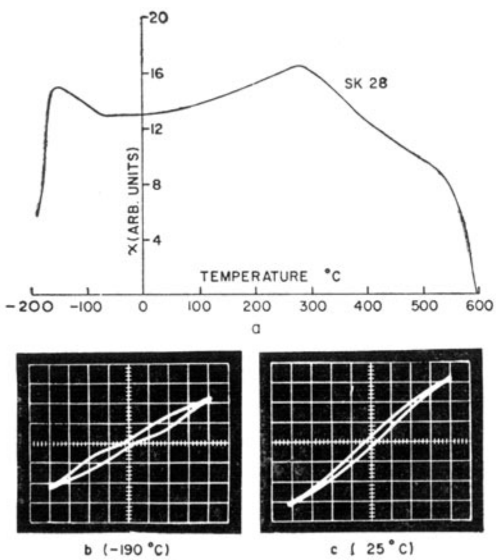

Figure 2. χ-T curve and hysteresis loops for a 4·6 g sample of SK28. Scale for (b) and (c): one small division on X-axis=50 Oe; on Y-axis=1·0 emu.

rises monotonically with increasing temperature to a maximum and then falls off rapidly towards the Curie point. M007 has not been heated beyond 100°C to avoid any irreversible changes taking place in it. The hysteresis loops of the sample in 1500 Oe both at −190°C and at 25°C are shown in figures 1 b and 1 c respectively. The samples shows four times more saturation intensity at −190°C than at 25°C. It may be mentioned that this sample shows only normal loops over a wide range of fields (upto 2000 Oe) at low temperatures. The field of 1500 Oe is chosen to show the loop clearly.

Figure 2 shows the magnetic behaviour of the sample, SK28. The χ-T curve (figure 2 a) has two peaks, one at about −160°C and the other at 280°C. The hysteresis loop obtained in 1000 Oe at 25°C (figure 2 c) is normal, whereas that at −190°C (figure 2 b) is a constricted loop. The constriction in the loop appears only in a narrow range of temperature (−190° to −160°C) and tends to disappear in higher fields of the order of 2000 Oe even at −190°C. The constricted loop for this sample obtained at −190°C in 1000 Oe is reminiscent of that reported earlier for some basalts in 10 Oe at 25°C (Radhakrishnamurty and Sahasrabudhe 1967). It will be shown that these cases occur due to a similar process, and represent two special cases of the same physical phenomenon.

3. Discussion

Basalts usually contain a few percent of iron oxide grains dispersed in a non-magnetic matrix of silicates. The grains could be of fairly pure magnetite, Fe_3O_4, or may belong to the oxidation chain $Fe_3O_4 \rightarrow Fe_{3-x}O_4 \rightarrow \gamma\text{-}Fe_2O_3$ (maghemite). The phases between magnetite and maghemite are referred to as cation deficient phases and some of their magnetic properties have been reported recently (Radhakrishnamurty, Likhite, Sahasrabudhe and Raja 1971). Many of the cation deficient phases do not show the low temperature (−150°C) transition which is characteristic of magnetite. Often basalts contain a mixture of different phases. The existence of such mixtures can be ascertained from studies of their magnetic properties; other techniques often tend to yield confusing results, mainly because of the difficulties in separating pure grains from the rocks, as has been pointed out by Radhakrishnamurty and coworkers (1971).

The overall behaviour of M007, whose χ-T curve and magnetic hysteresis are shown in figure 1, could be accounted for in the following two alternative ways.

(i) The sample contains two different magnetic minerals with distinct Curie points; one well below 0°C and the other above 0°C, and

(ii) It contains interacting SP particles of one mineral showing a well defined first transition or Curie point.

There seems to be no method for getting direct evidence for either of the above alternatives. However, the occurrence of a phase with Curie point well below 0°C is most unlikely. A mineral that has a Curie point at about −150°C and could occur in basalts is ulvospinel (Fe_2TiO_4), but it is reported by Banerjee and O'Reilly (1966) to be only very weakly ferrimagnetic. Hence, it certainly could not account for the large intensity (figure 1b) shown by M007. On the other hand, fine particles with blocking temperatures down to 20°C have been reported by Radhakrishnamurty and Likhite (1970a) to occur in basalts and thereby the presence of even finer particles was indicated. In view of these observations it seems that the magnetic behaviour of M007 is more likely to be due to SP particles rather than due to a mineral phase with very low Curie point. Thus, the hysteresis loop obtained at −190°C (figure 1b) is most probably the result of the ferromagnetism of interacting SP particles.

The hysteresis behaviour of SK28, especially at −190°C (figure 2 b), provides ample evidence for the presence of strongly interacting SP particles. Most of the characteristics of this hysteresis loop are similar to the one shown by some basalts in 10 Oe at 25°C. The low-field constricted loop was explained by Radhakrishnamurty and Sastry (1970) on the basis of interacting SP particle aggregates. At the same time it was predicted that such constricted loops could possibly be obtained in fields of the order of 1000 Oe, depending on the density of the particle aggregates. One important condition for observing the constricted loops due to SP particles is that the usual contribution to ferromagnetic hysteresis from any bigger grains in the sample should be negligible at the applied fields and temperatures. At 25°C an applied field of 10 Oe is small enough to prevent significant contributions from grains (exceeding SP size) that may be present in a basalt. At low temperatures this maximum applied field could be higher, even as high as 1000 Oe, particularly for particles of magnetic (average coercive force 1000 Oe at −190°C). Thus a dense aggregate of SP particles having a molecular field of the order of 1000 Oe can show up their presence at −190°C in an applied field of about 1000 Oe, as could be the case in SK28. Disappearance of the constriction in the loop in about 2000 Oe is also strong evidence for the presence of interacting SP particles on the model proposed earlier (Radhakrishnamurty and Sastry 1970).

We note that both M007 and SK28 show (figures 1 a and 2 a) χ-peaks at about −160°C. Possibly part of the increase or even peaking of χ at this temperature is due to the phase transition of magnetite, assuming the particles in the samples happen to be magnetite. However, the rapid fall in the χ-value for M007 with increasing temperature towards 0°C suggests that the distribution of particle sizes and inter-particle distances may fall in narrow ranges which could then give rise to a fairly sharp first transition point. In contrast to this, SK28 shows a slow decrease in the value of χ (figure 2 a) above the first transition point and also a second peak near about 280°C. This behaviour may imply that SK28 may contain a wide range of particle sizes and interacting fields.

Experimental difficulties involved in studies of complex materials like basalt prevent the extraction of more precise information. Nevertheless, it is important to place on record the peculiar magnetic behaviour of these rare lava samples, and to note the indirect but strong evidence that points to the presence of interacting superparamagnetic particles in them.

4. Conclusions

1. The magnetic hysteresis and initial susceptibility of two lava samples were measured at different temperatures. The samples showed highly unusual magnetic behaviour, including a peak in χ at -160°C and, in one case, a constricted hysteresis loop in 1000 Oe at -190°C. We believe that the observed behaviour could arise from the presence of interacting superparamagnetic particles in the samples.
2. Observations so far made on basalts and related rocks strongly indicate that grain size effects have to be assessed first before attempting to relate the magnetic behaviour to different mineral phases.

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