SWITCHING IN MAGNETITE: A THERMALLY DRIVEN MAGNETIC PHASE TRANSITION*

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We have performed a variety of experiments on switching phenomena in a metal oxide, magnetite. Our findings are consistent with Joule microheating which drives the Verwey transition occurring at 119 K. We conclude that considerations of band structure, direct electric-field-induced transitions, tunneling, injection, and space-charge phenomena are not required to explain any of our observations.

Nonlinear electrical transport properties, negative resistance, and electrical switching have been observed in many different systems, including glasses,[1-3] transition-metal oxides, and other compounds.[4-9] While a variety of mechanisms[10-14] have been proposed to explain switching, to date it has not proven possible to marshall sufficient evidence to permit an unambiguous determination of the principal mechanism.

In this Letter we restrict ourselves to the low-frequency properties of a single system showing negative resistance: magnetite. We present a body of experimental and theoretical evidence which makes, we believe, a compelling case that for this material the gross features of the switching mechanism are largely thermal in origin. High-frequency and dynamic characteristics will be discussed in a later paper.

Magnetite (Fe_3O_4) undergoes a Verwey transition at 119.4°K.[15,16] It is ferrimagnetically ordered both above and below the transition: At the transition a crystallographic modification occurs and the hyperfine magnetic-field distribution alters appreciably.[17,18] The most striking feature of the transition is the change in resistivity ρ by about two orders of magnitude.[16,19] The low-temperature phase is semiconducting with an activation energy of 0.03 eV at low temperatures increasing to 0.15 eV at the transition temperature.[19] The thermal conductivity κ [20] and the specific heat C_p [21] are also anomalous at the transition. The transition is affected by impurities, strain, and other defects which tend both to shift and to broaden it. However, pure magnetite is sometimes considered[4] the prototype of the Mott, or metal-insulator, transition.[22] Because of the lattice distortion which accompanies the phase change it remains uncertain whether lattice or electronic instability drives the transition,[22] or indeed, whether these effects are separable.[14] For the purposes of the present paper, such questions are not important, and the experimentally observed properties will be used without regard for their causes.

Possibly the first discovery of switching in magnetite was made by Christopher et al.,[5] who observed negative resistance at helium temperatures in tunneling junctions made with oxidized iron. No quantitative explanation for the phenomenon has yet been proposed, although recently Mattis[13,14] suggested a mechanism by which the Mott transition is driven by tunneling in an applied electric field. Following this idea, Lipsicas et al.[6] observed switching and oscillation in magnetite powders held at 77 K. We now know that not only can magnetite powders be switched but also thin films and single-crystal samples, and that even lack of purity of the material does not quench the effect.

In Fig. 1 we present an experimentally observed current through a cylinder of magnetite versus the applied voltage (solid curve). The thickness is 0.447 cm and the mean radius is about 0.375 cm. The sample is mounted in a special gas-flow cryostat in which cold gas flows continuously over the sample walls. The sample temperature is monitored with a thermocouple. The occurrence of a threshold voltage and negative resistance is apparent in this dc characteristic.

These and other observations on switching in magnetite can be semiquantitatively understood

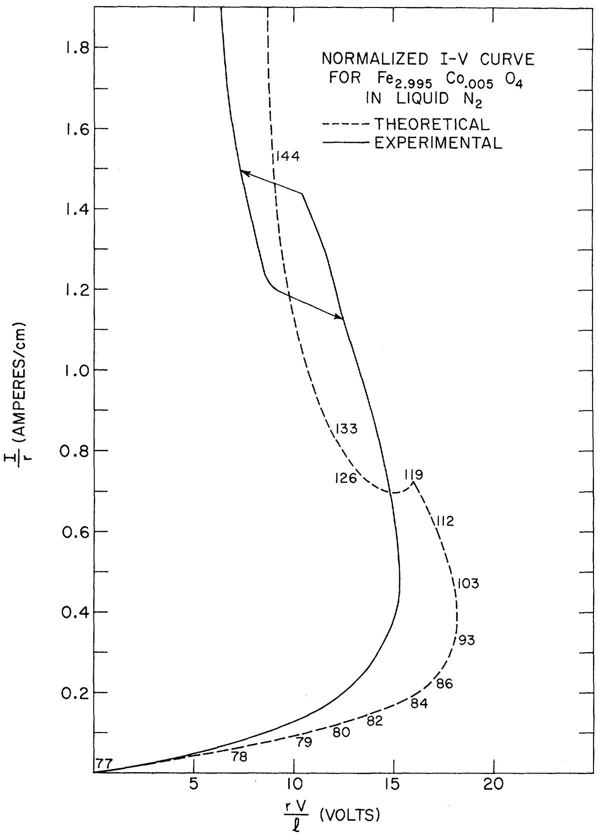

FIG. 1. The experimental I-V characteristic of the magnetite sample described in the text with a boundary temperature $T_b = 85$ K (solid curve), and the I-V characteristic for magnetite calculated from published values of the conductivities assuming a thickness of 0.447 cm and a diameter of 0.750 cm and $T_b = 90$ K (dashed curve). Computed maximum temperatures within the sample are indicated at various points. The data are scaled according to the requirements of Eq. (1).

in terms of a self-heating model, in which Joule heating provides local self-heating. For sufficiently high power input a threshold is passed, and the sample develops a negative resistance characteristic. The thermal diffusion equation is

$$-\vec{J}\cdot\vec{E} = -\rho C_p \partial T/\partial t + \nabla\cdot(\kappa\nabla T), \qquad (1)$$

where $\vec{J}$ is the current density and $\vec{E}$ is the electric field. This equation has been solved utilizing published values of the thermal conductivity[20] and the isothermal electrical conductivity of the sample measured in our laboratory. Equation (1) must be supplemented with equations governing the external electronic circuit, when dynamic response is calculated.

Because (1) is nonlinear, it is necessary to resort to numerical solutions. For simplicity we have restricted most of our attention to cylindrical geometry, with the current along the z axis and the cylinder walls maintained at a specified boundary temperature T_b. Advantages of this geometry are that Eq. (1) is readily solved, and that it is possible to construct an experimental system approximating these boundary conditions. A major approximation in our calculation is the use of Ohm's law, since our measurements show magnetite to be highly non-Ohmic, especially in the low-temperature phase.

The dashed curve in Fig. 1 presents a numerical steady-state solution of Eq. (1) with $T_b = 77$ K. No adjustable parameters are used. The agreement in the low- and high-current regimes is apparent. Further, in the low-current regime, the thermal calculation correctly predicts the experimental result $I \propto V^{3/2}$ without any consideration of space-charge effects. The doubling back of the theoretical curve results from the complicated temperature dependence of the input parameters. Owing to external circuit requirements this intermediate structure is difficult to verify experimentally the steady state. However, using published values of σ for pure Fe_3O_4, the calculations would predict more hysteresis. This has been observed. In this particular sample negative resistance sets in when the computed core temperature reaches 105 K. However, switching occurs when the core temperature reaches the Verwey transition temperature. The maximum temperature inside the sample is indicated at various points on the calculated curve.

Additional confirmation of the validity of calculation may be obtained by varying the wall-temperature boundary condition. Figure 2(a) presents computed and observed switching voltages for two natural magnetite samples of radii 0.030 and 0.036 in. and thicknesses 0.015 and 0.009 in. as a function of the wall temperature. Again, agreement is excellent, and there are no adjustable parameters. The disagreement for $T_b \sim 75$ K results from excess conductivity of our sample at low temperatures as compared with the published resistivity used in this computation. Figure 2(b) shows the calculated current density versus radial position for several points on the I-V characteristic and for $T_b = 77$ K. The filamentary conduction mechanism is clearly indicated. However, there is no pronounced core in the temperature profiles at these points. Even for relatively large transport currents only a small fraction of the total cross section is actually heated above the Verwey temperature. This prediction has been verified directly in Möss-

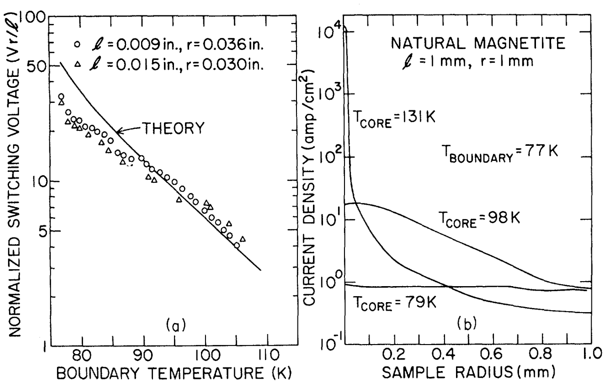

FIG. 2. (a) The experimentally measured threshold voltages for two different samples and the calculated threshold voltage (solid curve). There are no adjustable parameters in this calculation; the thickness and radius were taken to be those measured on the natural magnetite sample described in the text. For temperatures below about 75 K the activation-controlled resistivity used in the calculation exceeds the observed sample resistivity, accounting for the increasing discrepancy in switching voltage. (b) The computed current distribution for three bias conditions. The formation of a filamentary core at high current is apparent.

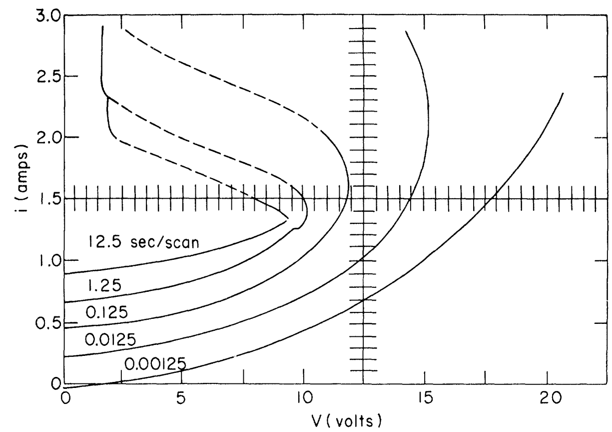

FIG. 3. The single-pass I-V characteristic of a natural magnetite sample, ($l = 0.009$ in., $r = 0.036$ in.) taken at the designated scan rates. Onset of negative resistance is an increasing function of scan rate. The curve is a tracing of an oscilloscope photograph, and the curves are vertically displaced between scans; the dashed portions of the curves are regions of rapid switching.

bauer measurements discussed below.

A scaling analysis of Eq. (1) applied to the cylindrical model indicates that the threshold voltage should vary linearly with the sample length for a fixed boundary temperature and radius. We have observed this dependence in natural magnetite samples with lengths of 0.062 to 0.293 in. with radii ~ 0.095 in. immersed in liquid N_2.

An analysis of Eq. (1) for flat plates cooled on the ends has also been made. This model yields little or no negative resistance but is consistent with some of our observations on thin films. We have also investigated the effect of magnetic field[23,24] on the Verwey transition and on the switching characteristic. Our experiments show a 9% decrease in the switching voltage at 77 K in a field of 8 kOe with only 0.5 K change in T_c for the same magnetic field, both independent of the orientation of the field to the current direction.

Mössbauer experiments offer a useful tool for determining the proportion of a magnetite sample in the high- and the low-temperature phases.[17,18] A 0.005-in.-thick sample was prepared by pressing magnetite powder in a Lucite holder. A thermocouple was embedded within the sample, which was then mounted in a cryostat and cooled to 77 K. Current passing through the sample produced switching, but only a slight temperature rise. Mössbauer hyperfine-field measurements showed that in the switched state at least 85% of the material was in the low-temperature phase, while no more than 20% was in the high-temperature phase. (The hyperfine field shows a discrete change at the Verwey transition, so that the observed spectrum can be decomposed into contributions from the high- and low-temperature phases.) These results are in agreement with the heating theory. They show that no theory is tenable which requires that the entire sample is heated, nor in which the energy gap is changed throughout the entire sample so as to correspond to the high-temperature phase.

Dynamic experiments provide independent evidence for the local-heating model. This type of experiment tests the role of the specific-heat term in Eq. (1). The I-V characteristic of the above-mentioned bulk magnetite sample immersed in liquid N_2 was measured by rapid single voltage scans at various rates (Fig. 3). At the highest scan rates used, the I-V characteristic is extended to voltages more than twice the threshold voltage observed in the constant-current (dc) experiments. This indicates that at 77 K switching from the low-conductivity state to the high-conductivity state is not controlled by the electric field in the manner assumed in Refs. 13 and 14. Rather, the specific heat of the material controls the rate of temperature rise and thus delays switching.[25]

Devices having negative resistance are observed to oscillate spontaneously when properly biased or can be caused to oscillate by means of an external capacitor. Our study on magnetite film samples of the oscillation period versus capacitance shows that relaxation oscillation can occur even in the absence of all electrical capacitance (including stray internal capacitance). Analysis shows that the specific heat of the sample plays the role of a (negative or positive) capacitor and that spontaneous oscillation with no external electrical capacitance is expected for certain thermal boundary conditions. This mechanism provides a simple explanation for the hitherto unexplained observations by Walsh et al.[2] of a field-dependent negative capacitance in glass devices, and will be given in detail in a future paper.

The variety of experimental data presented above together with the predictions of the thermal diffusion equation lead to a consistent picture of switching effects in magnetite. An essential feature of the switching is a geometry permitting the formation of a high-conductivity core or filament within the material. Many other systems behave in a qualitatively similar manner. It remains to be shown whether the thermal mechanism is ubiquitous. In any event, it is now apparent that future investigations designed to demonstrate other mechanisms must show that thermal effects are insufficient to explain the observations.

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[25]It is of course possible to adduce other mechanisms which will delay and shift the switching point.