large ratio ρ_T/ρ_L which occurs in these high-purity crystals. ρ_T and ρ_L are the transverse and longitudinal magnetoresistivity, respectively. The details of the contributions to the magnetoresistance in the multidomain region due to domain reorientation have been analyzed by Shumate, Coleman, and Fivaz.[8]

The present results coupled with our experiments on the multidomain crystals would lead us to conclude that the intrinsic temperature dependence of the electrical resistivity in single-domain longitudinally magnetized iron crystals is proportional to T^2 from 20°K down to 0.28°K. Additional features such as breaks in slope or the appearance of linear temperature terms are likely to be associated in some way with the presence of domain structure. We cannot completely rule out the presence of magnetic contributions to the temperature dependence, but the present behavior of the single-domain state does not seem to be significantly different from nonmagnetic transition metals.

The results obtained here are strikingly similar to the numbers obtained by White and Tainsh[2] for nickel and are listed below along with their values for comparison. Below 4°K, for iron,

$$\rho_i \approx 31 \times 10^{-12} T^2, \quad W_i \approx 27 \times 10^{-4} T,$$

$$L_i = 1.16 \times 10^{-8} \text{ W } \Omega/\text{deg}^2;$$

for nickel,

$$\rho_i \approx 34 \times 10^{-12} T^2, \quad W_i \approx 34 \times 10^{-4} T,$$

$$L_i = 1.0 \times 10^{-8} \text{ W } \Omega/\text{deg}^2.$$

From 5 to 20°K, for iron,

$$\rho_i \approx 29 \times 10^{-12} T^2, \quad W_i \approx 27 \times 10^{-4} T,$$

$$L_i = 1.09 \times 10^{-8} \text{ W } \Omega/\text{deg}^2;$$

for nickel,

$$\rho_i \approx 26 \times 10^{-12} T^2, \quad W_i \approx 25 \times 10^{-4} T,$$

$$L_i = 1.0 \times 10^{-8} \text{ W } \Omega/\text{deg}^2.$$

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Negative Magnetoresistance and Magnetically Controlled Switching in Fe$_3$O$_4$ Single Crystals*

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The negative magnetoresistance in Fe$_3$O$_4$ crystals at 77°K was found to saturate at about 9 kG and to increase with increasing electric field. The magnetoresistance data are explained in terms of spin disorder scattering. In the presence of a magnetic field the switching in this material can be advanced if voltage pulses are applied, and delayed if current pulses are applied. These findings are shown to be in quantitative agreement with the magnetoresistance data and the expectations from Joule self-heating.

Of the transition-metal oxides,[1] Fe$_3$O$_4$ is the only material that exhibits a transition from insulator to metal as well as having a net magnetic moment per unit cell. It is thus expected that the coupling between the electronic and magnetic properties in this material can bring about some

new effects and provide an "extra handle" for the study of the insulator-to-metal transition.[2] In this Letter we will focus our attention on an effect that is a result of the combination of the relatively large negative magnetoresistance, associated with the ferrimagnetic nature of the ma-

terial, and the thermally induced transition from insulator to metal. The coexistence of its unique properties thus makes Fe_3O_4 a candidate for a magnetically controlled switch.

Negative magnetoresistance (NM) in Fe_3O_4 was observed about twenty years ago[3] but to our knowledge no data were published as to the NM dependence on the applied magnetic and electric fields. Recently Burch et al.[4] have noticed an effect of a magnetic field on thermal switching under steady-state conditions in natural magnetite, but no explanation was given for this effect. Here we would like to present new data for the negative magnetoresistance in Fe_3O_4 single crystals and to show that they account quantitatively for the magnetic field dependence of the thermal switching under transient conditions. In a forthcoming paper[2] we will present more detailed data and analysis on this magnetically controlled switching in single crystals as well as in thin films of Fe_3O_4.

The crystals used were grown from Fe_3O_4 powder by a chemical transport reaction using HCl gas as the transport agent.[5] The single crystals that were obtained had a pyramidal shape with typical edge lengths of 1 to 2 mm. The crystals were polished to rectangular shape and contacts were attached to the two end surfaces perpendicular to the desired current-flow direction. Ohmic contacts were obtained by soldering indium to the sample end surfaces after wetting them with In-Hg amalgam. The temperature dependence of the conductivity was similar to that found by Siemons[6] for crystals that were also grown by the above method. All the measurements to be described below were taken with the sample immersed in liquid nitrogen. However, the thermal contact with the surroundings was quite poor (see below), as the sample was mounted on a quartz slide and coated with Duco-Cement glue.

The magnetoresistance $\Delta\rho(H)/\rho_0$ versus the applied magnetic field H, where ρ_0 is the sample resistivity ρ at $H = 0$, was measured by using either a regular dc bridge or short (1 μsec wide) voltage pulses. Accurate readings of the current under pulse-application conditions were made possible by using a Tektronix type W plug-in unit. The magnetoresistance versus the applied magnetic field measurements, in the (110) direction, were carried out on the two crystals on which the switching data[2] were taken. The results were found to be much the same for the two samples and for both the transverse and the longitudinal orientations of the magnetic field. In
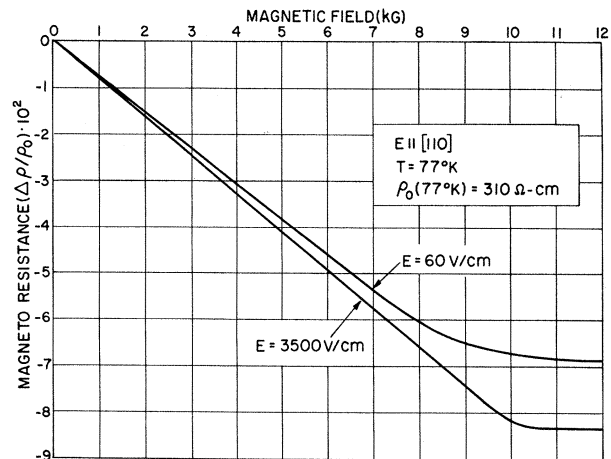

FIG. 1. Transverse and longitudinal magnetoresistance versus applied magnetic field for samples No. 3 and No. 6. The upper curve was obtained from dc and pulse measurements; the lower curve from pulse measurements only.

Fig. 1 we show the curves that exhibit the best fit with the experimental points. It is to be emphasized, however, that none of the many experimental points deviates by more than the experimental error $[(\Delta\rho/\rho_0) \times 100 \lesssim 0.2]$ from the curves shown. The upper curve is a result of dc and pulse measurements when the applied field E is 60 V/cm. The lower curve is the result obtained for $E = 3500$ V/cm, where only pulse measurements were taken in order to avoid significant heating effects. The magnitude of the NM when E was applied in the (111) or the (100) directions was found to be, by at least a factor of 4, smaller than in the (110) direction. The higher magnitude of the NM in the (110) direction was already observed in the early work of Domenicali.[3] As we would like to show the maximum effect of the above magnetoresistance on switching, the results reported below will all be concerned with current flow in the (110) direction. It should be emphasized here that the magnitude of the negative magnetoresistance reported[7] in Ti_2O_3 or in switching materials[8] is an order of magnitude smaller than that shown in Fig. 1.

There are two significant new results exhibited by the present data: saturation of the NM at about 9 kG and its dependence on the electric field amplitude. The saturation of the magnetoresistance and the saturation of the magnetization[3,6,9] at 77°K in the (110) direction take place at about the same magnetic field. The anisotropy of the NM and its dependence on the magnitude of E are very unlikely to be explained by an effect of the magnetic field on the band edges.[10]

These are rather better explained in terms of spin disorder scattering[7,11]: The larger the magnetic field, the larger is the magnetic order and consequently the spin-spin scattering of the carrier by the Fe ions becomes more coherent. Thus an increase of magnetic field brings about an increase in the negative magnetoresistance. In the (110) direction the Fe^{+3} and the Fe^{+2} ions occupy adjacent sites and have their corresponding $S = \frac{5}{2}$ and $S = 2$ spins aligned parallel. Thus in this direction the concentration of magnetic scatterers is much larger than in any other crystallographic direction. The low mobility[6] (probably due to other transport mechanisms such as self trapping), and the possible large cross section for spin scattering of the Fe^{+3} ions,[7] suggest that indeed in the (110) direction the spin scattering will be relatively large causing the large NM. The increase of the NM with electric field was not, as far as we know, reported thus far in any material. This effect is in accord with the above explanation as it is very likely that the increase in the carrier velocity is causing a decrease in the cross section for spin scattering (as in usual impurity scattering). However, it should be noted that all the above results can also be explained by the double-exchange model[12] suggested[13] for Fe_3O_4. This model is very attractive as it can explain the hole conduction found[6] in this material and the randomization of the $S = \frac{5}{2}$ and $S = 2$ spins in the (110) direction below the Néel temperature. As expected from the double-exchange model, hopping between ferromagnetically coupled Fe^{+3} and Fe^{+2} ions is much larger than that between antiferromagnetically coupled ions,[13] and thus larger NM is expected in the (110) direction. The magnetic ordering as well as the faster propagation of the carriers are expected to enhance the double-exchange conduction in comparison with other transport mechanisms. However, no transport data for Fe_3O_4 are available to give strong support to the double-exchange model for conduction and only studies of the temperature and magnetic field dependence of the mobility, in the various crystallographic directions, can indicate whether indeed the contribution of double exchange is really significant.

The voltage-pulse technique is widely used for the study of the voltage-induced low- to high-conductivity transition, the so-called "switching." The relationship between the pulse amplitude V and the time interval τ elapsed from pulse application until the switching (the sharp drop in the resistance of the sample) can yield valuable in-

formation as to the nature of the induced transition.[14] Freud and Hed[15] have shown that in Fe_3O_4 layers this relationship indicates that the effect of the applied voltage is to heat the sample from the ambient temperature T_0 to the insulator-to-metal transition temperature T_m (which is 119°K in the present case[1-4]). In a more detailed paper[2] we will go further than Freud and Hed in a more quantitive and more detailed study of the $\tau(V)$ relationship, while here we will emphasize the dependence of this relationship on application of magnetic field.

In Fig. 2(a) we show a typical current response and the corresponding voltage under constant-voltage (CV) conditions. Following pulse application the voltage drop across the sample is fairly constant while the current I increases. After the delay time τ for switching (defined in the figure) the voltage drops to its "holding" value V_h, while the current rises to its holding value I_h (not shown). As can be seen, the effect of the magnetic field is to increase the current by about 8% before switching, and to decrease τ by about the same percentage. It should be mentioned here that the ratio of the "switching time" τ_s to the delay time τ is quite constant in our experiments and increases significantly only when $\tau \lesssim 1$ μsec. The time interval τ_s is associated with more detailed properties of the transition and
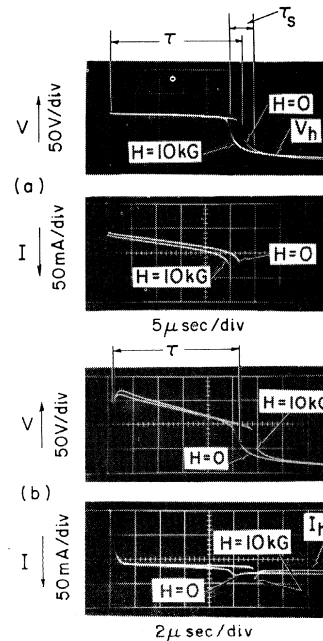

FIG. 2. Oscillograms of voltage (upper traces) and current (lower traces) as obtained (a) under CV conditions and (b) under CC conditions, on sample No. 6.

will be discussed elsewhere.[2] In Fig. 2(b) we show similar results under constant-current (CC) conditions. Here the voltage drop across the sample decreases with time and the effect of the magnetic field is to decrease the voltage drop and to prolong the delay time τ by about the above percentage.

The increase of current with time for $t < \tau$ under CV conditions and the decrease of voltage for this time interval under CC conditions can be explained as due to the Joule self-heating of the sample and the corresponding decrease in its resistance R. Indeed Joule self-heating can also explain the effect of the magnetic field, as described above. Under CV conditions the power delivered to the sample is V^2/R while under CC conditions it is I^2R. Correspondingly the NM will cause an increase of the power in the first case and a decrease of the power in the second case. Assuming negligible heat loss to the surroundings,[2] a fixed amount of energy $Q\tau$ is needed for heating the sample from T_0 to T_m and thus $1/\tau$ will be proportional to these powers. Consequently, the change of these powers due to the magnetoresistance (the magnetoresistance was found to be quite constant for the above temperature range[3]) explains the observed changes in τ. The slight difference in the effect of the magnetic field on τ in Figs. 2(a) and 2(b) is also apparent; short τ and the corresponding high V provide smaller heat loss relative to $Q\tau$ on one hand and larger magnitude of the NM on the other hand. The holding voltage[16] and the holding current are responsible for balancing the heat loss after the sample has reached T_m and are determined by the intersection of the load line with the switched I-V characteristic.

The explanation given above for the change in τ due to the application of magnetic field becomes more apparent from the measurement of τ vs V in the whole τ range under study ($1 \leqslant \tau \leqslant 50$ μsec). The predictions of Joule heating for such a measurement are obtained by integrating the heat flow equation:

$$gc_p(\partial T/\partial t) = JE + \nabla \cdot (\kappa \nabla T), \qquad (1)$$

where g is the material density, c_p is its specific heat, κ is its thermal conductivity, and J is the current density. If high-power pulses (short τ's) are used, the heat-conduction term can be neglected while for low-power pulses (long τ's), thermal equilibrium ($\partial T/\partial t = 0$) is approached. Integrating Eq.(1) over the proper intervals in

the limit $\tau \to 0$ for CV conditions yields

$$V^2\tau = l^2 \int_{T_0}^{T_m} \{gc_p[\rho_0 - \Delta\rho(H)]\}dT \equiv A, \qquad (2)$$

where l is the sample thickness. We have indeed observed the parabolic dependence $V^2\tau = A$ and the expected dependence of A on H and on l^2. The values of A were obtained by fitting the experimental results with the above parabolic law. We found that the advancing of switching due to magnetic field application in the whole range of τ is in the same proportion as the increase in the magnetoresistance (see above). These results indicate that the magnetically controlled switching is quantitatively predictable, and self-heating theory seems to account well for the observed behavior. Details of this measurement and the justification for the use of the $\tau \to 0$ approximation will be discussed in the forthcoming paper.[2]

As in the transient conditions [Fig. 2(a)], the current in the steady-state conditions (observation of the I-V characteristic on a 60-Hz Tektronix model 575 curve tracer) is increased because of the NM when a magnetic field is applied.[2] However, under steady-state conditions the switching voltage[4] (that is determined by the intersection of the negative resistance portion of the I-V characteristic and the load line) depends on the resistance in series with the sample. Thus, although the relative change in the I-V characteristic due to magnetic field application is small, a large decrease (down to 50 %) in the switching voltage was obtained by a large increase in the series resistance. Consequently the 9% change in switching voltage due to $H = 8$ kG as reported by Burch et al.[4] is not well defined. This change is probably associated with NM that is of smaller magnitude in comparison with our findings, as their results were obtained on crystallographically unoriented natural magnetite.

In conclusion, we have presented the negative magnetoresistance in the (110) direction at 77°K in Fe_3O_4 single crystals. It was shown that in the transient conditions where heat loss is quite small, the effect of magnetic field is to change the delay time for switching, so that the relative change in the delay time is equal to the magnitude of the magnetoresistance. The results seem to fit well into the self-consistent picture of switching due to Joule self-heating in transition-metal oxides.

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Optical Gap of Strontium Titanate (Deviation from Urbach Tail Behavior)

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The absorption of $SrTiO_3$ below the fundamental edge shows, near liquid-nitrogen temperature, an oscillatory behavior, for which an explanation is proposed in terms of indirect transitions $\Gamma_{15} \rightarrow X_3$, centered around 3.27 eV and involving a 51-meV LO phonon. There is no evidence of excitonic effects. The first direct transition is probably $X_{5'} \rightarrow X_3$ and is located at ~3.46 eV. Broadening effects mask the indirect structure at higher temperatures where the absorption curves gradually evolve into normal Urbach tailing.

Studies of the optical threshold of perovskite-type ferroelectrics[1-6] always show the occurrence of Urbach tails,[7] except in impure crystals.[8,9] For this reason, although LCAO (linear combination of atomic orbitals) band-structure calculations[10] indicate, for $SrTiO_3$, a valence-band maximum at Γ and a conduction-band minimum at X, the latter feature being well established also by transport experiments,[11-16] the presence of indirect transitions has never been detected.

This Letter reports the first observation of fine structure in the absorption coefficient of $SrTiO_3$ near liquid-nitrogen (LN) temperature. The structure is absent at room and dry-ice temperatures (RT and DI), where Urbach behavior is exhibited over at least three decades, with saturation at high absorption levels.[17] This gives, to our knowledge, the first experimental evidence of indirect transitions in a ferroelectric perovskite. Somewhat similar behavior has been observed in other materials (e.g., AgBr,[18] CdTe,[19]

and SnO_2[20]). The data allow a description of the optical band gap of $SrTiO_3$ which adds information to what is known from transport results. Measurements were taken on eleven samples of thickness 13 to 1300 μm, cut from two single-crystal boules provided by the National Lead Company at different times. One boule was specifically requested to be of high purity. Two monochromators were used, a double-pass glass-prism Perkin Elmer (Zürich) and a prism-plus-grating Cary 14 (Rome). In both cases energy calibration was accurate to within 3 meV and resolution better than 1 meV. These data were always reproducible within experimental errors; in particular, no significant discrepancies were found in samples from different boules. Experimental curves are shown in Fig. 1. The linear range of RT and DI data can be described by Urbach's equation

$$\alpha = \alpha_0 \exp[(h\nu - E_0)/kT^*], \quad (1)$$

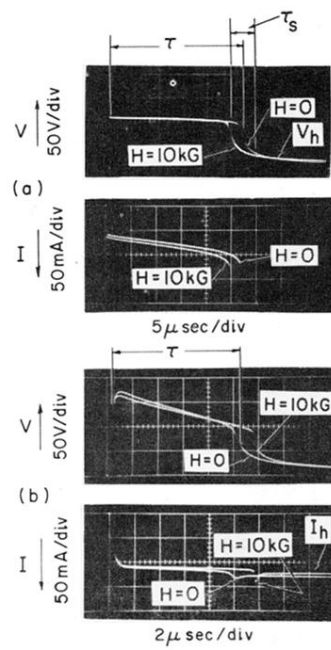where E_0 is related to the energy gap and T^* is

FIG. 2. Oscillograms of voltage (upper traces) and current (lower traces) as obtained (a) under CV conditions and (b) under CC conditions, on sample No. 6.