Conduction Phenomena in Thin Layers of Iron Oxide*

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Results on studies of tunneling and conduction phenomena in thin metal–iron-oxide–metal sandwiches at helium temperature are described in this paper. Characteristic *I-V* curves have been studied for both dc and ac applied voltage signals. The main features of interest are a voltage breakdown observed above certain critical currents, and a large negative-resistance region observed on the decreasing current leg of the *I-V* curve. The breakdown phenomenon exhibits a delay time that is a function of the overvoltage applied to the junction, and comparison with nucleation theory has suggested that some type of phase transition is occurring. We suggest a model based on the order-disorder transition that is known to occur in magnetic iron oxide, Fe_3O_4. We also discuss possible field ionization processes that could be playing a role in the transition. The sandwiches have been successfully utilized as amplifiers, and can also be set into self-oscillation under certain conditions. Examples of these features are included in the paper. The transition from high to low resistance observed in these sandwiches is similar to those observed in glassy semiconductors at higher temperatures, and certain comparisons may be useful in trying to understand the glassy-semiconductor behavior.

INTRODUCTION

IN a previous paper[1] we reported on some unusual features observed in the dc voltage-current characteristics of junctions in which thick iron oxide barrier layers were used. These junctions were measured in the helium temperature range and exhibited a breakdown characteristic for increasing current and a large negative resistance for decreasing current. We have extended these investigations to include both ac and dc characteristics and have studied the breakdown behavior in much greater detail.

These junctions show many features that we believe to be connected with the electronic properties of iron oxide, and in particular with a possible field-induced phase transition. The junctions in fact show a behavior similar to that observed in some types of amorphous semiconductors,[2–6] in which it is also thought that a phase transition may be playing a role.

We have analyzed our results in terms of a number of possible processes and in particular have suggested a model based on the order-disorder transition known to occur in Fe_3O_4. We will first review the experimental results and then compare them to behavior predicted by theory.

EXPERIMENTAL RESULTS

For junctions with FeO_x barriers in the range 1000–3000 Å the zero bias dc resistance at 4.2°K is on the order of 10^4–10^8 Ω. Application of a dc voltage results in a very rapid drop of resistance, and for the characteristic group of junctions discussed in this paper, no Ohmic behavior has been observed although this may be due to present experimental limitations. Typical data taken at 4.2°K are shown in Fig. 1, where the log of the dc resistance is plotted as a function of junction voltage. The region close to zero bias cannot be measured accurately, because the junction resistance becomes too great to be within impedance limits of the present equipment. The high-voltage ends of the curves are limited by the onset of breakdown. This breakdown is demonstrated in Fig. 2, which shows the junction current as a function of junction voltage. The junction voltage was measured while the current was increased to a maximum value and then decreased. The arrows indicate the direction of current change in the portions of the curve where the increasing and decreasing legs do not coincide. The increasing leg shows a sharp break-

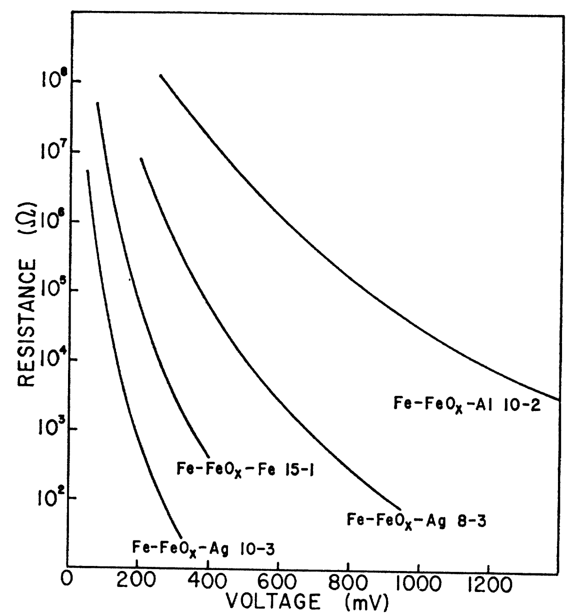

FIG. 1. dc resistance on a log scale as a function of voltage at 4.2°K for four junctions with FeO_x barriers.

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down of voltage across the junction (dotted line) and further increase of current occurs at substantially lower junction voltages indicating a critical point on the *I-V* curve at which the effective resistance of the junction drops sharply. The junction voltage increases rather smoothly for decreasing current, giving rise to a substantial negative-resistance region. For currents below a critical value both the increasing and decreasing *I-V* curves correspond. However, above the critical current values there is a substantial hysteresis, and this can be seen in Fig. 2. The initial breakdown occurring during the increasing current leg is often very abrupt and in the less stable examples does not always occur at the same point after recycling. On the other hand, the decreasing current leg is quite smooth and stable, with the negative resistance region being reproducible from cycle to cycle. This behavior has suggested that some type of nucleation occurs during the increasing cycle and that phase superheating is responsible for the hysteresis. This point will be considered further in the discussion section.

A number of examples of the breakdown behavior are shown in the *I–V* curves of Fig. 3. Similar types of behavior have been observed for different combinations of metal electrodes and a representative selection is included in Fig. 3. Figure 3(a) shows data for a Fe-FeO_x-Ag sandwich and corresponds to the standard behavior which we have studied in most detail. Figure 3(b) indicates a fairly rare case in which no observable hysteresis is present. Figure 3(c) shows an example where the breakdown behavior on the increasing current leg occurs in a number of well-defined steps although the negative-resistance region on the decreasing current leg is fairly smooth and reproducible. Figure 3(d) shows data for a junction with gold electrodes on

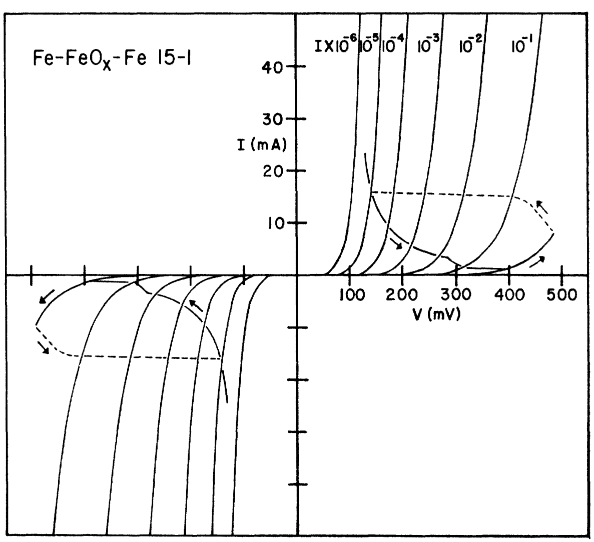


FIG. 2. Typical dc voltage-current characteristic curve for junction with FeO_x barrier at 4.2°K.

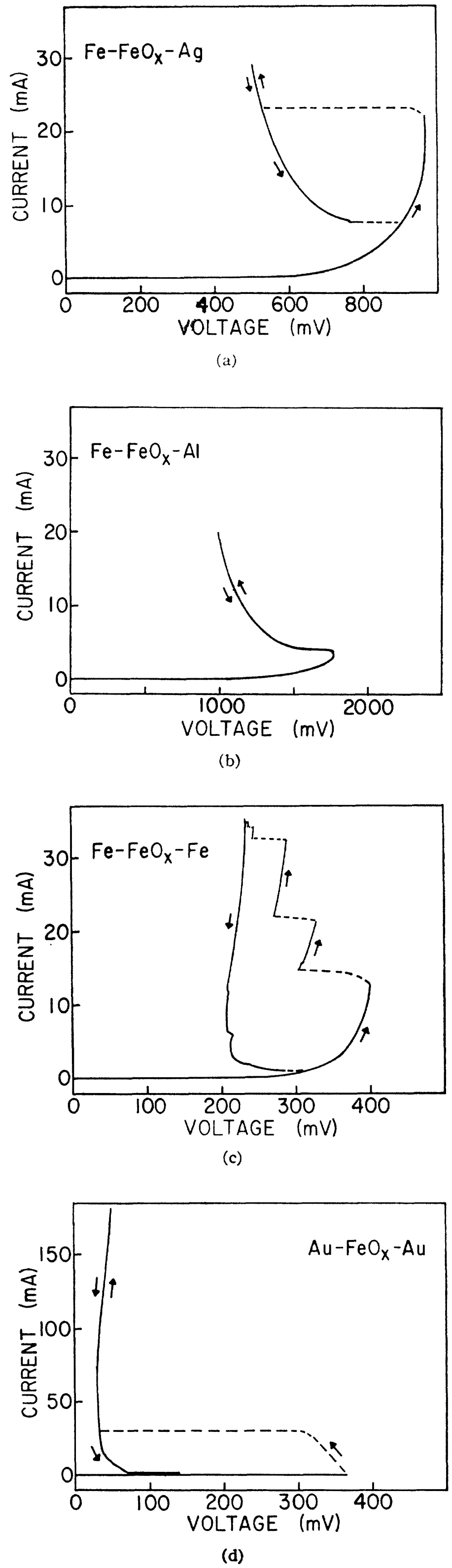
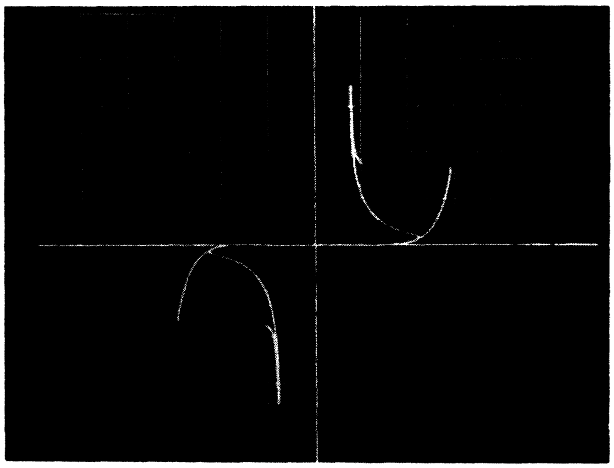
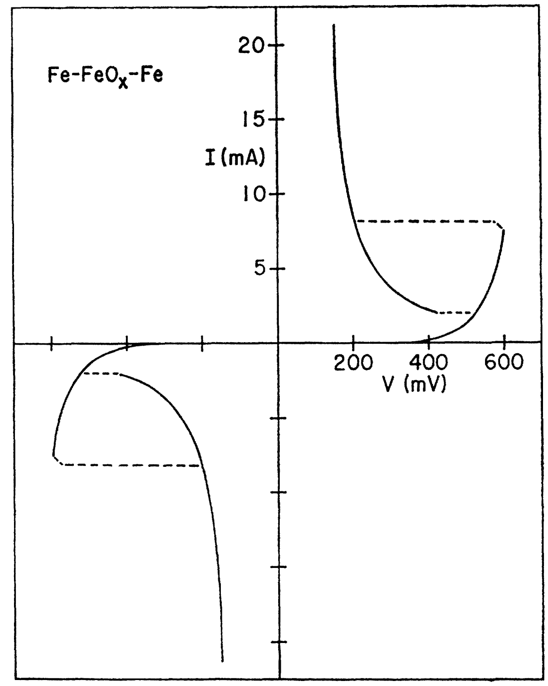


FIG. 3. Examples of various types of dc breakdown behavior of FeO_x sandwiches at 4.2°K.



(a)



(b)

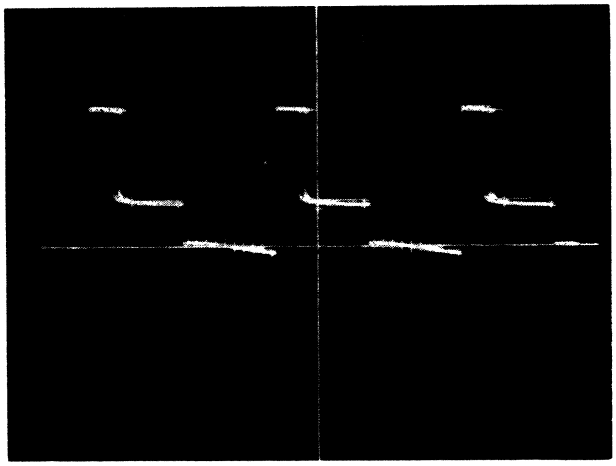
FIG. 4. (a) Voltage-current characteristic for 50-Hz sine wave input of Fe–FeO_x–Fe sandwich at 4.2°K. Scale of x axis is 200 mV per division. Scale of y axis is 5 mA per division. (b) dc voltage-current characteristic of Fe–FeO_x–Fe sandwich at 4.2°K for which ac data are shown in (a).

both sides, which was fabricated by completely oxidizing an iron film plated onto one of the electrodes.

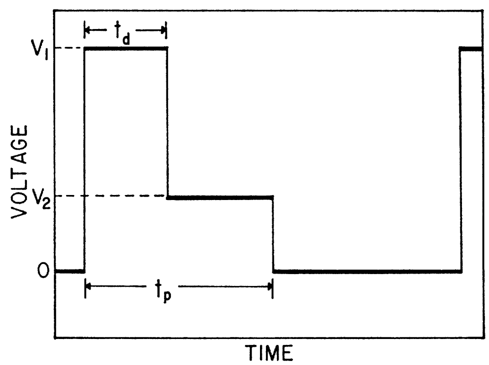
In order to study the basic features of the transition observed in the dc experiments, we have measured the junction response to sine wave and square wave signals of varying frequencies and amplitudes. In a number of experiments we have also used half-wave rectified signals in order to record particular details of the transition. The principal feature observed is again the breakdown of the voltage as the current increases above some critical value. For sufficiently low-frequency signals the I-V curves are essentially identical to the dc I-V curves for the same maximum current amplitude. Figure 4 shows an I-V oscillograph obtained at 50 Hz along with the dc I-V curve for the same junction. However, if the frequency or amplitude of the signal is increased sufficiently, the I-V curves begin to show substantial modifications which result when the period of the applied signal is comparable with the basic time constants describing the transition.

For example the initial voltage breakdown can be conveniently studied by applying square pulses to the junction. If one then measures either junction voltage or junction current as a function of time, the transition can be easily observed when the maximum amplitude is raised above the critical point on the I-V curve. The rise time of the square-wave pulse is less than 2.00×10^{-7} sec so that the maximum-amplitude voltage appears across the junction in this time. The data indicate that the transition to lower resistance which occurs during breakdown is delayed and takes place considerably after the voltage first reaches its maximum value. This is clearly seen in the oscillographs shown in Fig. 5. The transition corresponds to the sharp drop in voltage and rise in current seen in Figs. 5(a) and 5(c), respectively. These occur along the flat portion of the pulse and Fig. 5(b) identifies the critical points for the voltage oscillograph of Fig. 5(a). The current rise during breakdown occurs because the resistance change of the junction changes the total load resistance of the circuit. The delay time observed in these experiments is a function of the amount of overvoltage applied above the critical value required to nucleate the transition. For the junction shown in Fig. 5 the delay time varied from approximately 10^{-2} sec near critical voltage to 3×10^{-5} sec for voltages up to 10% above the critical value.

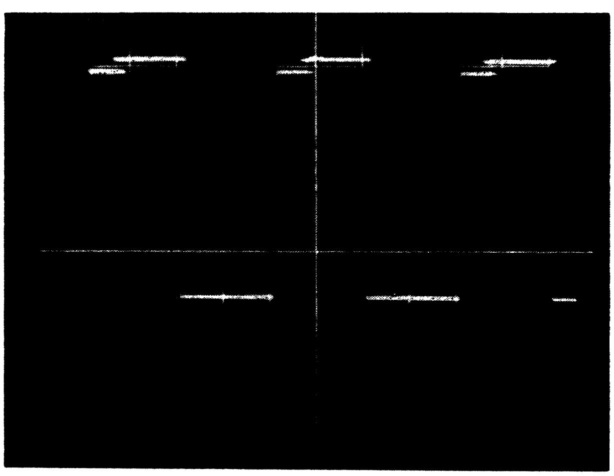
When an overvoltage is applied with a square pulse, the initial voltage and current across the junction attain values that extend the low-conductivity portion of the I-V curve. For example, the oscillograph of Fig. 6(a) shows a multiple exposure corresponding to a series of increasing amplitude pulses. Above the critical current-voltage point the initial overvoltage points are spots due to the delay time in the low conductivity state. The subsequent breakdown jump of voltage for each overvoltage point is also visible. The low-frequency I-V curve for the same junction is shown in Fig. 6(b) for comparison.



(a)



(b)

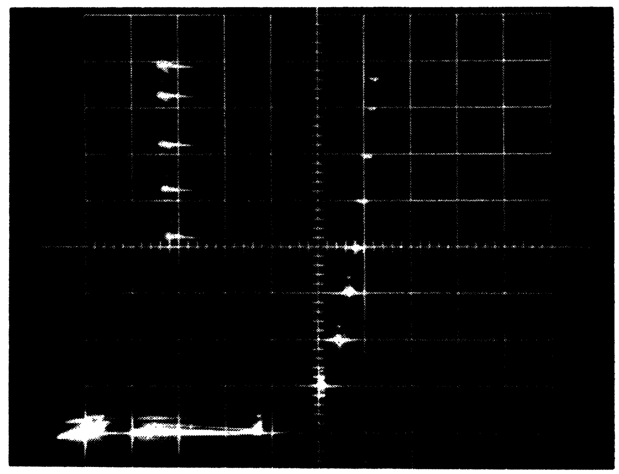


(c)

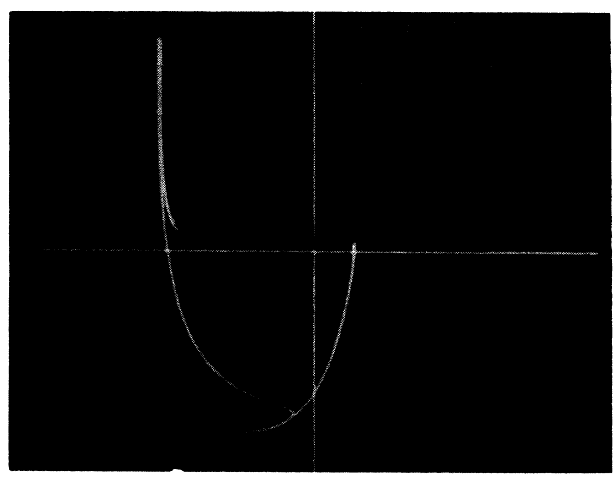
FIG. 5. (a, b) Oscillograph and schematic drawing showing voltage across Fe–FeO_x–Fe sandwich at 4.2°K versus time, for an input square wave pulse of duration t_p. The delay time (t_d) before the junction voltage switches to V_2 is clearly shown. (a) x axis is 0.5 msec per division. y axis is 200 mV per division. (c) Current-versus-time plot associated with voltage plot in (a) of Fe–FeO_x–Fe sandwich and 700Ω series resister. x axis is 0.5 msec per division. y axis is 2 mA per division. Zero is shifted one division below center.

We have also studied the frequency dependence of the complete I-V curve, and find that at higher frequencies there is not a complete recovery of the high-resistance state at zero bias. From these experiments the characteristic relaxation time for decay of the high-conductivity state is on the order of 10^{-4} sec.

A number of the junctions have been observed to go into self-oscillation if a dc bias voltage above critical is applied. An example is shown in Fig. 7. Figure 7(a) shows an I-V plot taken at a drive frequency of 5 Hz. As soon as the applied voltage rises above critical, the junction oscillates rapidly between the high- and low-conductivity state. Time base plots of these oscillations



(a)

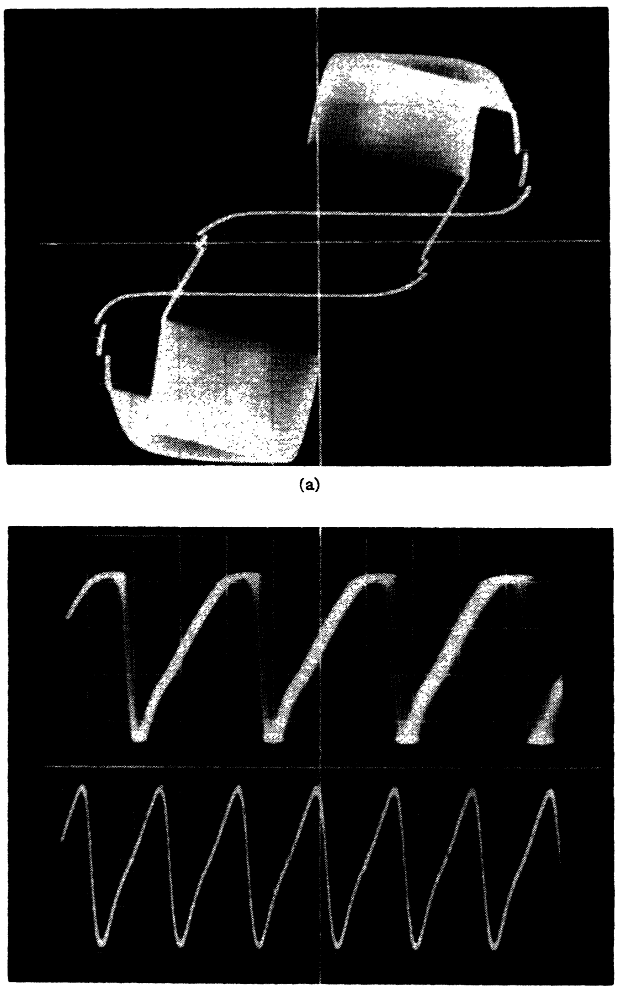


(b)

FIG. 6. (a) Multiple exposure voltage-current plot for Fe–FeO_x–Fe sandwich at 4.2°K showing series of points corresponding to 500-Hz square wave pulses of increasing amplitude. Above a critical voltage-current point two spots are seen. One is due to delay-time holding of the low-conductivity state and the other shows the breakdown jump of voltage to the high-conductivity state. x axis is 100 mV per division. Zero is extreme left. y axis is a 2 mA per division. Zero is one division up from bottom. (b) Voltage-current characteristic curve at 4.2°K for 50-Hz sine wave of Fe–FeO_x–Fe sandwich for which data are shown in (a). Axes and zeros are same as for (a).

for two overvoltages are shown in Fig. 7(b). The frequency is essentially determined by the delay time and in the lower-frequency case this is approximately 5×10^{-6} sec, which appears as a flat top on the upper wave form of Fig. 7(b). As the overvoltage is raised, the frequency increases substantially and the flat top due to delay time is no longer resolved on this time scale.

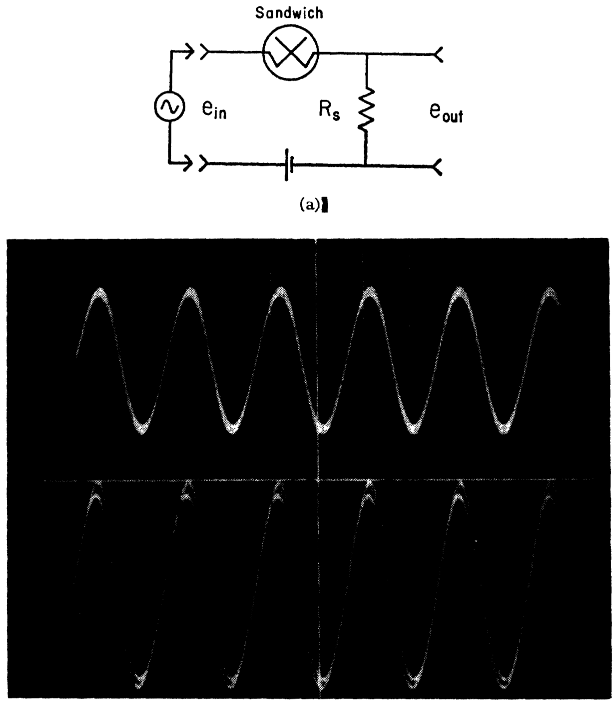
The large negative-resistance region observed on the decreasing leg of the I-V curves has also been utilized as an amplification device. Preliminary data have been obtained using the simple circuit shown in Fig. 8(a). Figure 8(b) shows an input signal of 1000 Hz on the upper trace, and the corresponding output signal across a 200-Ω series resistor is shown in the lower trace. The amplification factor is approximately 1.5.



(a)

(b)

FIG. 7. (a) Voltage-current characteristic curve for 5-Hz sine wave of Fe–FeO_x–Fe sandwich. Oscillations between the high- and low-conductivity states are shown. x axis is 100 mV per division. y axis is 0.2 mA per division. Separation of curves is due to phase shift. (b) Voltage-versus-time plot for oscillations shown on I-V curve in (a), obtained by applying dc bias. Upper curve is for dc bias corresponding to lowest dc overvoltage and lower curve is for dc bias corresponding to highest dc overvoltage. x axis is 5 μsec per division, y axis is 100 mV per division, and zero is arbitrarily set.



(a)

(b)

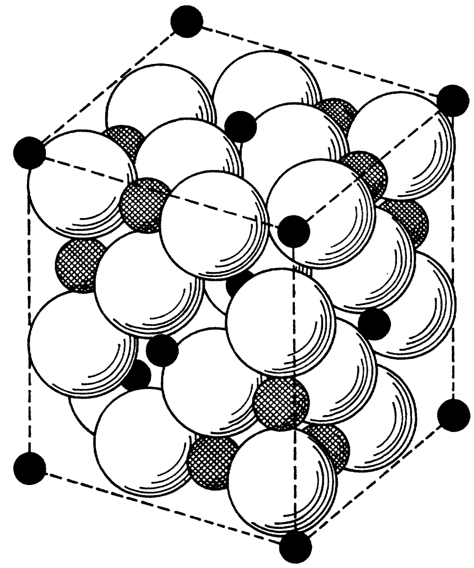
FIG. 8. (a) Circuit diagram for utilization of FeO_x sandwich as amplification device. (b) Input voltage signal (upper) and output voltage signal across 200-Ω series resistor (lower), showing amplification by Fe-FeO_x-Fe sandwich at 4.2°K. x axis is 0.5 msec per division. y axis is 200 mV per division. Zero for two traces was arbitrarily set.

DISCUSSION

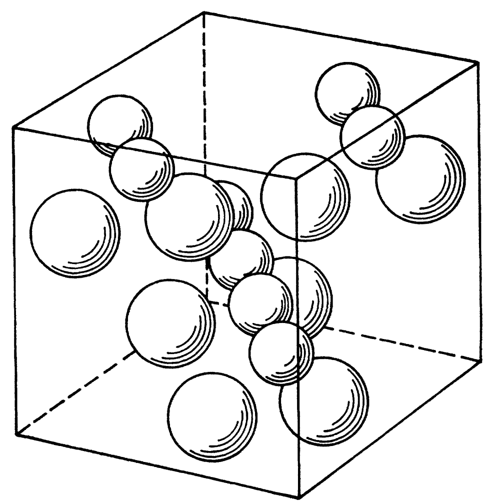
The principal features observed in the electronic response of the iron-oxide junctions described above are associated with an abrupt transition from a low-conductivity to a high-conductivity state. Furthermore, the high-conductivity state, once formed, can be maintained at considerably smaller applied voltages, and the reasonably large negative-resistance regions are observed in the decreasing leg of the I-V curves. For the very thick iron-oxide junctions (>1000 Å in the present experiments) several processes can be considered. These include the tunneling of an electron from the metal electrode through or into the oxide barrier and electronic conduction in the oxide barrier itself. It is probable that at high voltage the conductance of the iron oxide is playing a role, and several possible mechanisms could contribute to the high conductance and breakdown behavior, including a possible phase transition in the iron oxide.

We will first review some of the existing information on the electronic structure of iron oxide and then discuss the possible connection with the characteristic curves observed for the present junctions. This will include discussion of the behavior in relation to internal field emission,[7] to Fowler-Nordheim[8] tunneling theories, to impact ionization processes, to space charge and electrode effects, and to possible phase transition mechanisms. The ac electronic response of the junctions shows a number of special features, and interpretations of these will be given particularly in respect to the breakdown phenomenon.

Several experiments have indicated that the main oxide formed on the iron electrode is Fe_3O_4.[1] There may be small concentrations of other iron oxides present, and the barrier would not be expected to be homogeneous over the entire area of the junction. This fact probably accounts for some of the variation in behavior reported in the experimental section and also for the failure to establish a definite dependence of the *I-V* characteristic on junction area. The Fe_3O_4 form of iron oxide is the only one, however, which shows the unusually high conductivity and other electronic behavior that could account for the observed behavior. A number of experimenters[9–12] have studied the electrical properties of Fe_3O_4, and one of the interesting features is an order-disorder transition that occurs at 119.4°K for stochiometric Fe_3O_4. Above this transition temperature magnetite has an inverse spinel structure and the transition is due to an ordering of the ferrous and ferric ions in the octahedral interstices of the spinel lattice. This ordering requires a transition to an orthorhombic structure and this has been confirmed by x-ray diffraction.[13] It has also been shown[14] that in stochiometric, synthetic, single crystals the transition is marked by a sharp decrease in conductivity amounting to a factor of 90 in a temperature interval of 1°K. From studies of the conductivity both above and below the transition temperature as well as observations of magnetic-field-induced anisotropy in the conductivity below the transition, it has been concluded that the dominant mechanism of conductivity in magnetite is due to the exchange of electrons between the ferrous and ferric ions in the octahedral lattice sites. The phase transition in Fe_3O_4 at 119°K is in fact one of the original examples of the metal-nonmetal transitions considered by Mott.[15] Figure 9(a) shows the inverse spinel structure, and Fig. 9(b) shows the octahedral lattice sites in the ordered phase.



(a)



(b)

FIG. 9. (a) Arrangement and packing of atoms in unit cell of ideal inverse-spinel structure. For Fe_3O_4, large spheres represent oxygen, small black spheres Fe^{3+} on tetrahedrally coordinated sites, and crosshatched spheres Fe^{3+} and Fe^{2+} on degenerate octahedrally coordinated sites which occur above 119.4°K (see Ref. 10). (b) Unit cell showing ordered arrangement at temperatures below 119.4°K of Fe^{2+} (large spheres) and Fe^{3+} (small spheres) in 16-fold octahedrally coordinated positions (see Ref. 11).

In the present experiments the existence of this loosely bound electron offers a possible source for easy excitation of carriers in the oxide by field emission. The existence of a large number of electron states just below the conduction band of the oxide would also lower the barrier height for tunneling from the metal electrode and would make it easy to tunnel electrons into the conduction band of the oxide.

It has been suggested[15] that the low-temperature

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[8] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. (London) **A119**, 173 (1928).
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phase of Fe_3O_4 behaves like a semiconductor, and in addition, measurements of the activation energy for conduction[14] at around 40°K indicate a number of trapped electron levels at approximately 0.03 eV below the bottom of the conduction band. These trapped electron levels could also have a considerable effect on electrons that are actually tunneling through the barrier in addition to providing the easily ionized electron levels in the oxide. For example, the presence of traps could introduce a substantial temperature dependence in the total tunnel current, owing to the temperature variation in the density of ionized traps.

For electrons tunneling through a barrier of height Φ, the tunnel current will be given by a Fowler-Nordheim type of equation when the applied voltage is much greater than Φ.

For a standard rectangular barrier this is of the form

$$J=(BE^2/\Phi)\exp[-(\lambda\Phi^{3/2})/E], \tag{1}$$

where

$B=1.1e^3/4\pi h$,

$\lambda=23\pi m^{1/2}/6he$,

$E=V/s=$electric field in insulating layer.

In the case of field emission from electron traps in the oxide, the theory of Landau and Lifschitz[16] for hydrogenlike atoms has been extended to the case of trapping centers in insulators, and the results have been applied to the basic tunnel equations.[17] The result for the current-voltage characteristic is given by

$$J=\text{const}(E/E_0)^2e^{-E_0/E}, \tag{2}$$

where

$$E_0=\frac{4(2m^*)^{1/2}}{3\hbar e}U^{3/2};$$

U is the depth of trap potential.

Therefore, for junction currents due either to high-voltage tunneling or to internal field emission in the oxide, the I-V characteristics would be given by an equation of the form

$$J=AE^n\,e^{-B/E}, \tag{3}$$

where A and B are constants and n lies between 1 and 3.

In a previous paper[1] we have compared the conductance data on a group of the present junctions to an equation of the Fowler-Nordheim type by plotting $\log_{10}I/V^2$ versus $1/V$. A Fowler-Nordheim behavior would be a straight line on such a plot and the slope would be proportional to $\Phi^{3/2}$ and to the thickness s (see formula 1). By estimating the oxide thickness from rate curves and by taking the best straight line fit of the high-voltage data, we calculated an effective barrier height of 0.025 eV. This average value is in relative agreement with the activation energy for the conduction process in Fe_3O_4 measured by Miles, *et al.*,[14] who obtained 0.030 eV. This suggests that the same electronic levels active in the conduction in magnetite are also playing a role in the I-V characteristics observed for the present sandwiches.

[16] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 257.

[17] Yu. E. Perlin, and A. G. Cheban, Fiz. Tverd. Tela. 4, 3220 [English transl.: Soviet Phys.—Solid State 4, 2358 (1963)].

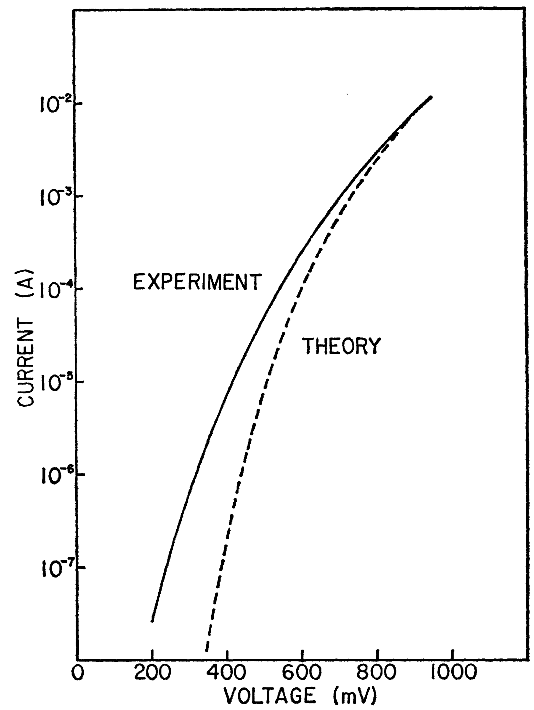

FIG. 10. Logarithm current versus voltage for typical FeO_x sandwich (solid line). Also plotted is Fowler-Nordheim type curve (dashed line) obtained by using a barrier height of 0.034 eV and fitted to highest-voltage experimental point by treating effective junction area as parameter.

The current-voltage data for a representative junction is plotted in Fig. 10 and plots the log of current against applied voltage. A theoretical Fowler-Nordheim type of curve as given by Eq. (1) is also shown, where the previously calculated barrier height of 0.034 eV has been used. The theoretical curve has been adjusted to coincide with the highest-voltage experimental point by treating the effective junction area as a parameter. The required area for fitting is in fact very much smaller than the actual physical area of the junction and indicates that the main tunneling and conduction may be occurring through well-localized filaments in the barrier. For the above junction the total area was 10^{-2} cm^2 while the required total cross section for conducting filaments was approximately 10^{-5} cm^2.

The experimental and theoretical curves are of the same general shape, but certainly do not agree over the entire voltage range. The extent of agreement is, however, similar to that observed for tunnel emission devices, for example, Ta-Ta_2O_5-Au.[18] In addition, the

[18] C. A. Mead, J. Appl. Phys. 32, 646 (1961).

high-voltage data on the Fe-FeO_x-Fe junctions is limited by the onset of breakdown and, at lower voltages, tunneling and internal field emission may be occurring simultaneously and would require different constants even though the voltage dependence should be the same.

After the present paper was submitted, Mattis[19] published a paper proposing a model based on a modified Zener tunneling theory. He assumes that the tunneling barrier is a decreasing collective function of electronic excitation and shows that this model can describe behavior observed in iron oxide.

Alternatively, the rapid temperature dependence of conductivity and the jump in conductivity at the 119°K phase transition when combined with rapid heating effects offers a possible explanation for the behavior observed. However, several checks of the experimental data indicate that the possibility is rather remote. The electrical conductivity at breakdown assuming filament formation is approximately that of Fe_3O_4 at the phase transition and therefore requires heating of at least 115°K. We have varied the average power input by a factor of 10^5 by applying 2 μsec pulses with times between pulses varying from 200 μsec up to one minute and no change in characteristic behavior has been observed. In order for the instantaneous power of a single pulse to heat the filament to 119°K, a thermal conductivity of the oxide is required, which is much poorer than is probable. Calculations of the worst geometrical case require a thermal conductivity, an order of magnitude poorer than the poorest known materials in the helium temperature range, and several orders of magnitude poorer than most oxides. The only remaining possibility might be some type of thermal runaway generated by a very unusual and anomalous temperature dependence of the thermal conductivity of iron oxide.

The breakdown phenomena introduces a number of special features into the ac response of the junctions, and in the remaining sections of the discussion we will emphasize this behavior.

One possible process which produces a many-order-of-magnitude increase in conduction current for electric fields above some critical value is impact ionization of impurity states. This occurs at the point at which the impact ionization rate exceeds the recombination rate. In some cases this breakdown is also accompanied by a fairly large negative-resistance region, for example, experiments on conduction in compensated germanium by McWhorter and Rediker.[20] The impact ionization process alone does not, however, explain the negative resistance, because the sudden current increase would not be accompanied by a sudden voltage drop. McWhorter and Rediker suggest in addition that in compensated germanium two nearby donors form a hydrogenlike molecule-ion which has a high cross section for scattering. Following impact-ionization breakdown, the donors in a filamentary path are all ionized, and this scattering mechanism is effectively removed, which leads to the voltage drop. A similar type of process is a possibility in the Fe_3O_4, with the Fe^{++} sites becoming ionized in filaments through the FeO_x barrier. A specialized scattering process analogous to that proposed for compensated germanium is not at all obvious, however. In addition the breakdown in compensated germanium does not show the large hysteresis effect observed in the present experiments.

The breakdown voltage observed for the present junctions is a function of the oxide thickness and would therefore indicate that the breakdown is determined by the electric field throughout the oxide layer. However, the voltage observed after breakdown is not correlated with oxide thickness and might therefore indicate that space charge is playing some role in the high-conductivity state. Possible space charge formation and its relation to delay time and negative resistance in the iron-oxide junctions is not established by the present experiments. However, space charge effects alone cannot explain the range of experimental behavior observed.

The presence of hysteresis suggests that the FeO_x barrier may be exhibiting some type of phase transition and that superheating of the low-conductivity phase occurs before the actual transition takes place. Superheating is suggested because the increasing voltage cycle shows the sharpest and often unstable transition while the decreasing cycle is always smooth and stable with a reproducible negative-resistance region. The superheating would be consistent with the nucleation process required to initiate the growth of a filament of the high-conductivity phase. The rate of critical nucleation will be proportional to $e^{-\text{const}/\Delta\mu}$, where $\Delta\mu$ is the change in chemical potential describing the superheating of one phase with respect to the other. $\Delta\mu$ will in turn be proportional to the overvoltage applied to the junction. The delay time would be inversely proportional to the rate of critical nucleation, and would therefore be expected to follow a relation of the form $t_d \sim A e^{B/(V-V_R)}$, where $V-V_R$ is the overvoltage and .' and B are constants. In the present experiments V_R would correspond to the highest voltage reached on the negative-resistance portion of the I-V curve (see Fig. 2). We have made a preliminary fit to the data on delay time as a function of voltage with an expression of the form $t_d \sim A e^{B/(V-V_R)}$ and the results are shown in Fig. 11, where the log of t_d is plotted as a function of $1/(V-V_R)$. The data falls reasonably close to a straight line on such a plot, indicating that the suggested exponential expression may have some validity. Considerably more detailed measurements will be necessary, however, in order to make a thorough check on such a comparison.

On the decreasing cycle of the I-V curve, the filament would transform back into the low-conductivity phase

[19] D. C. Mattis, Phys. Rev. Letters 22, 936 (1969).
[20] A. L. McWhorter and R. H. Rediker, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 134.

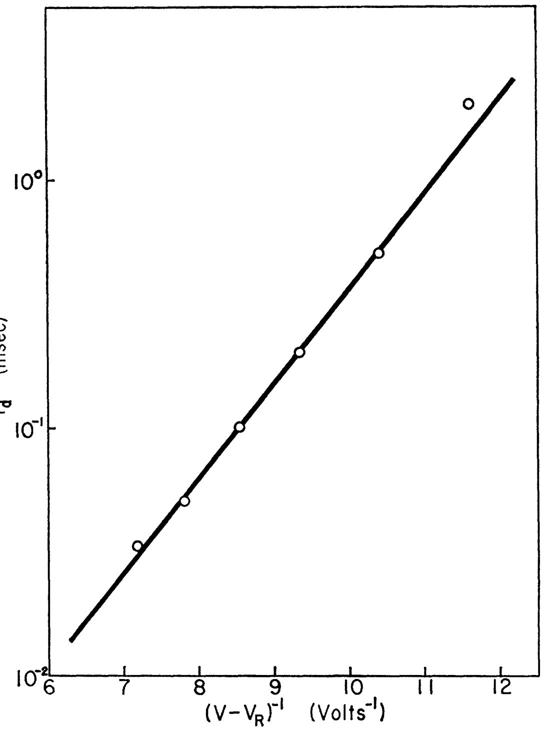

FIG. 11. Logarithm of delay time (t_d) versus $(V-V_R)^{-1}$ for Fe–FeO_x–Fe sandwich at 4.2°K, where V is voltage applied across sandwich before breakdown. V_R is the highest voltage reached on the negative-resistance portion of *I-V* curve.

by domain growth from the edges of the filament where the initial low-conductivity phase is still present. This would not require any nucleation process so that the decreasing cycle of the *I-V* curve should follow some type of equilibrium curve describing the gradual decrease of high-conductivity filaments embedded in the low-conductivity phase.

A possible phase transition that fits the above picture could be produced by the ionization of the Fe^{++} ions in the ordered Fe_3O_4 lattice. The critical values of voltage and current could be identified with a critical ionization density in a filament of Fe_3O_4 such that the ordered orthorhombic phase becomes unstable and a transformation back to a cubic structure of predominately Fe^{+++} ions takes place. If the cubic phase had a much higher conductivity, a sudden breakdown in voltage would be observed. The delay time would be due to the critical nucleation process required to initiate the cubic phase once the critical ionization density was achieved. This is essentially a field-induced Mott transition, which has also just been suggested by Mattis.[19] In addition to field-induced ionization, localized heating processes could be playing a role, including thermal activation of the phase transition. At the present time, however, we do not feel that this is the major cause of the transition. On the decreasing leg of the *I-V* curve the filament cross section and conductivity would change smoothly and in the proper combination to produce the negative-resistance section of the curve. The detailed model for the decrease of the filaments and correlation with the negative resistance appears rather difficult at the present time, however.

CONCLUSIONS

In this paper we have reported the results of studies on the *I-V* characteristics of metal–iron-oxide–metal sandwiches at helium temperature. The *I-V* curves for these sandwiches show a breakdown phenomena and a negative resistance which we conclude is associated with the electronic properties of iron oxide. We have identified this breakdown with a possible phase transition in the iron oxide and have proposed a model based on the order-disorder transition known to occur in Fe_3O_4. Application of square pulses to the junctions have shown that a delay time exists for the onset of this transition and that substantial overvoltages can be applied prior to breakdown. The detailed functional form agrees fairly well with that predicted by nucleation theory.

The negative-resistance features have been utilized to produce amplification of electronic signals and various aspects of the frequency dependence have been studied. Under certain conditions the sandwiches can be induced into self-oscillation at frequencies in the neighborhood of 100 kHz and this frequency can be varied over a considerable range by adjusting the external circuit parameters.

We have also carried out studies on vanadium oxide sandwiches and find a similar breakdown behavior at helium temperatures. Vanadium oxide was tried because it has phases which show transitions similar to that observed in Fe_3O_4, and which also exhibit high electrical conductivity. For example V_2O_3 shows an order-disorder transition at 150°K. When oxides are formed on metals such as iron and vanadium, for which numerous oxide phases exist, it is possible that highly disordered or amorphous regions may form. These could also be playing some role in the behavior observed here, and further study will be necessary to sort out all the possible effects.

The basic behavior observed in these junctions has many similarities to the behavior observed in a number of glassy semiconductors[21] at higher temperatures where transitions from a high- to a low-resistance state are observed. Various types of phase transitions have also been suggested for the glassy-semiconductor behavior, and the present experiments may help us to understand some aspects of this transition behavior.

ACKNOWLEDGMENTS

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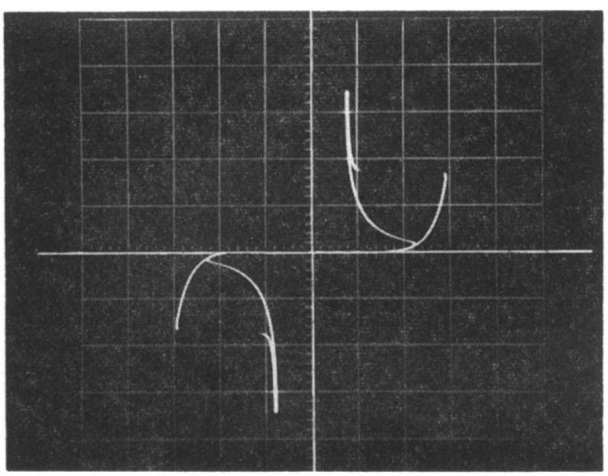
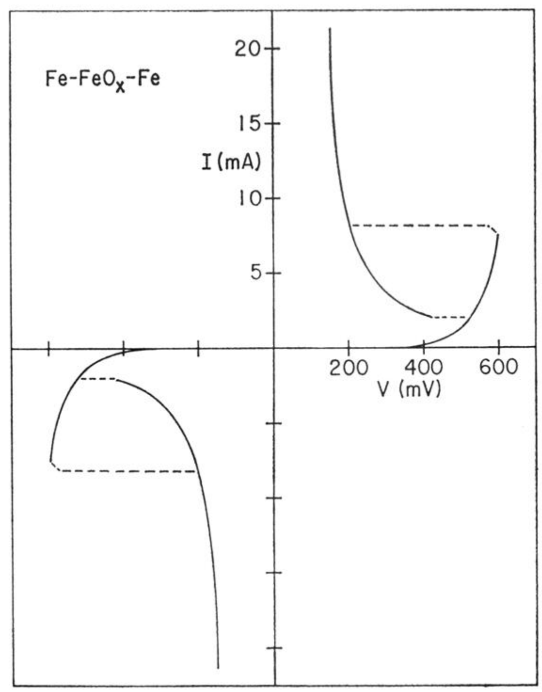
[21] Phys. Today 22, No. 1, 63 (1969).

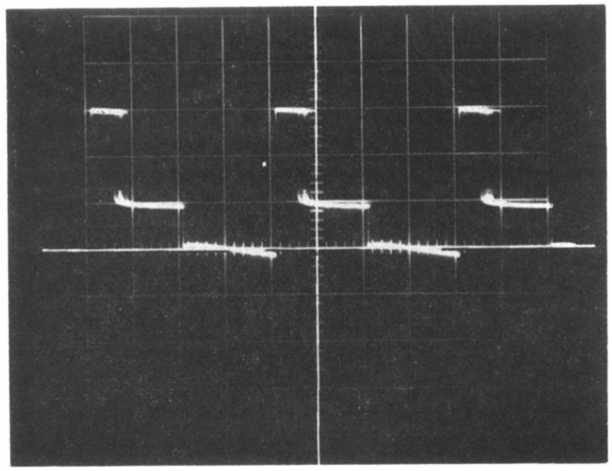


(a)



(b)

FIG. 4. (a) Voltage-current characteristic for 50-Hz sine wave input of Fe–FeO$_x$–Fe sandwich at 4.2°K. Scale of x axis is 200 mV per division. Scale of y axis is 5 mA per division. (b) dc voltage-current characteristic of Fe–FeO$_x$–Fe sandwich at 4.2°K for which ac data are shown in (a).



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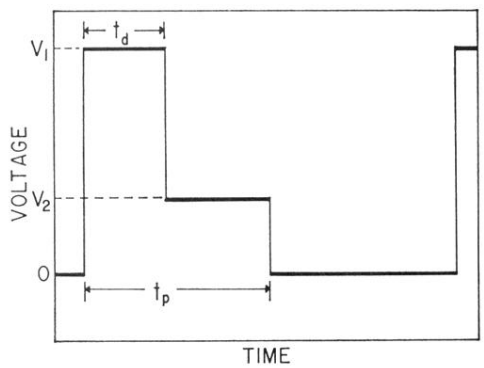

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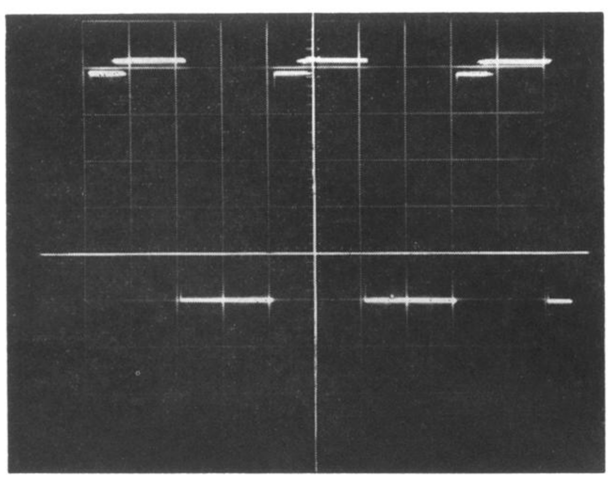
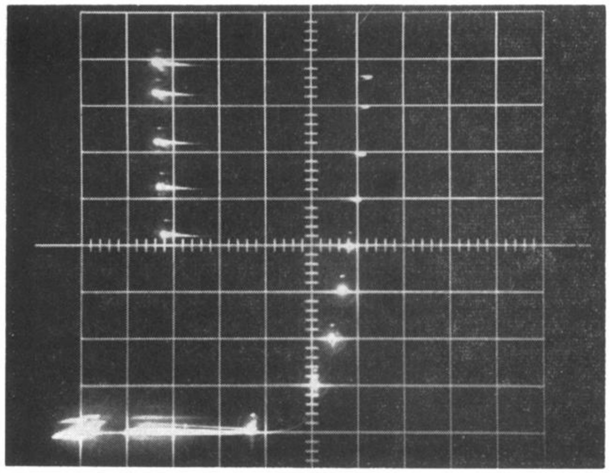
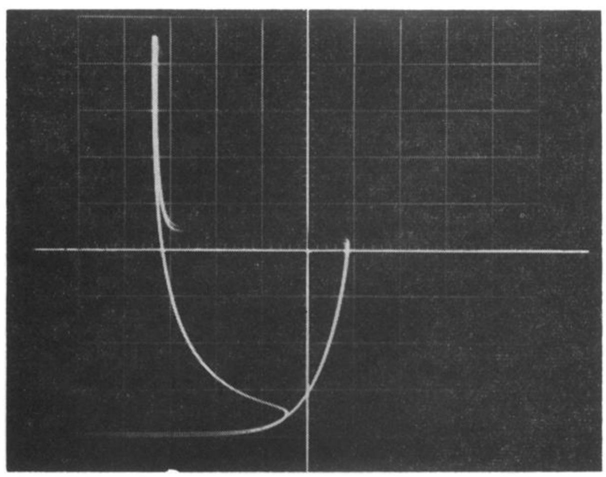


(c)

FIG. 5. (a, b) Oscillograph and schematic drawing showing voltage across Fe–FeO_x–Fe sandwich at 4.2°K versus time, for an input square wave pulse of duration t_p. The delay time (t_d) before the junction voltage switches to V_2 is clearly shown. (a) x axis is 0.5 msec per division. y axis is 200 mV per division. (c) Current-versus-time plot associated with voltage plot in (a) of Fe–FeO_x–Fe sandwich and 700Ω series resister. x axis is 0.5 msec per division. y axis is 2 mA per division. Zero is shifted one division below center.

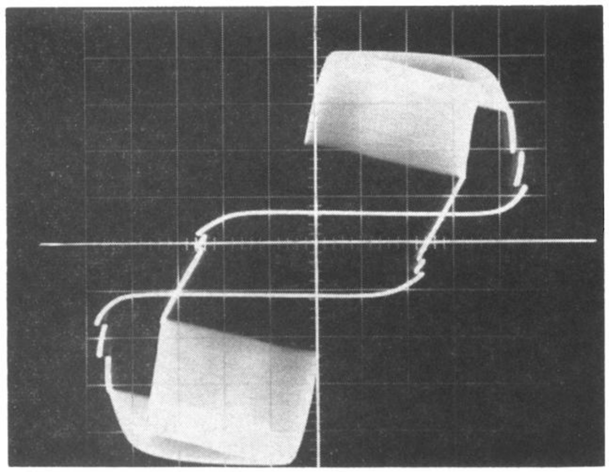


(a)



(b)

FIG. 6. (a) Multiple exposure voltage-current plot for Fe–FeO_x–Fe sandwich at 4.2°K showing series of points corresponding to 500-Hz square wave pulses of increasing amplitude. Above a critical voltage-current point two spots are seen. One is due to delay-time holding of the low-conductivity state and the other shows the breakdown jump of voltage to the high-conductivity state. x axis is 100 mV per division. Zero is extreme left. y axis is a 2 mA per division. Zero is one division up from bottom. (b) Voltage-current characteristic curve at 4.2°K for 50-Hz sine wave of Fe–FeO_x–Fe sandwich for which data are shown in (a). Axes and zeros are same as for (a).



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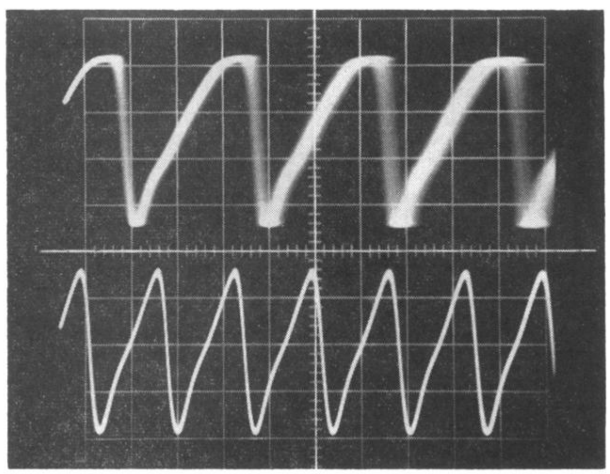
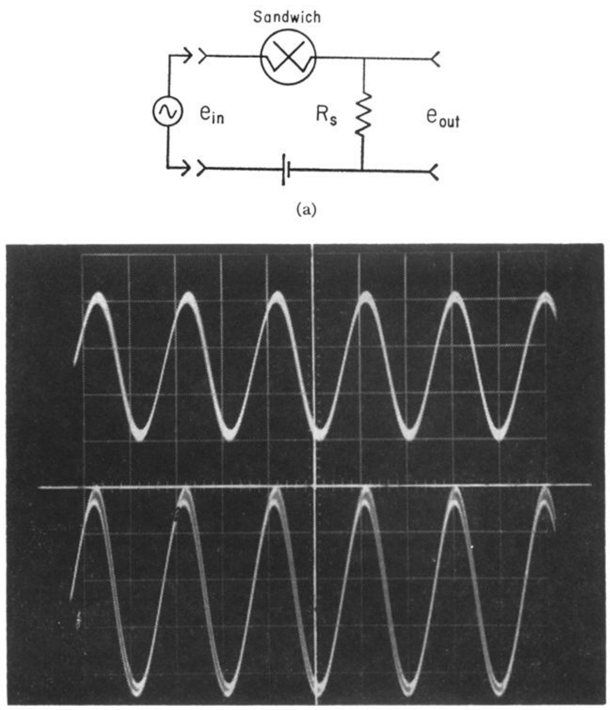


(b)

FIG. 7. (a) Voltage-current characteristic curve for 5-Hz sine wave of Fe–FeO_x–Fe sandwich. Oscillations between the high- and low-conductivity states are shown. x axis is 100 mV per division. y axis is 0.2 mA per division. Separation of curves is due to phase shift. (b) Voltage-versus-time plot for oscillations shown on I-V curve in (a), obtained by applying dc bias. Upper curve is for dc bias corresponding to lowest dc overvoltage and lower curve is for dc bias corresponding to highest dc overvoltage. x axis is 5 μsec per division, y axis is 100 mV per division, and zero is arbitrarily set.



(a)

(b)

FIG. 8. (a) Circuit diagram for utilization of FeO_x sandwich as amplification device. (b) Input voltage signal (upper) and output voltage signal across 200-Ω series resistor (lower), showing amplification by Fe-FeO_x-Fe sandwich at 4.2°K. x axis is 0.5 msec per division. y axis is 200 mV per division. Zero for two traces was arbitrarily set.