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CHARACTERIZATION OF P(L)ZT CERAMICS BY MODULATED OPTICAL SPECTROSCOPY

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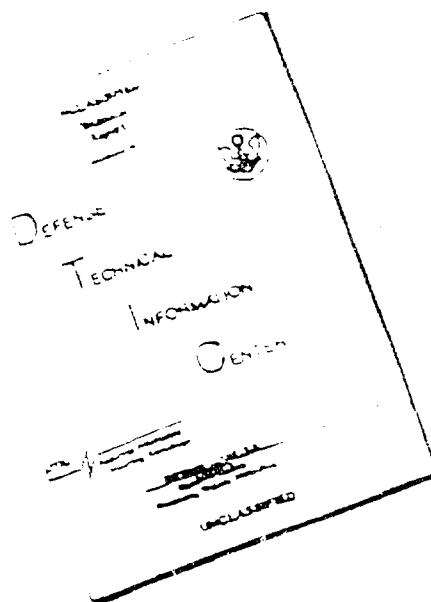
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I. Introduction

The work described in this report was conducted during the period 1 January 1976 through 30 Sept. 1977 under the Office of Naval Research Contract N00014-76-C-0516. The purpose of this investigation is to study and develop non-destructive, simple, and rapid methods for measuring the structural and dynamic properties of ferroelectric ceramics. We have proposed optical modulation techniques, particularly electric field modulated transmission and reflectivity ~~which~~ have been shown to be powerful tools for investigating the electronic properties of solids. By modulating an internal parameter such as electric field (electroreflectance and electrotransmission) it is possible to obtain derivative-like enhancements of optical structures related to interband transitions. The spectra obtained are sharper, more precise and have more structure than those produced by conventional optical techniques.

We present ⁱⁿ Section II characterization of transparent PLZT ceramics by modulated optical spectroscopy ^{and in} Section III ~~describes an~~ electroreflectance study of opaque PZT ceramics ^{as presented} 

An important result of the present study (Section II) is that it is possible, using these techniques, to follow the growth of the polarization with time during poling and its reversal during low field switching. Oscillation observed in the electroreflectance spectra of PLZT are interpreted in terms of space charge effects, and the analysis yields an upper bound for the remanent polarization which is in good agreement with the result of a dielectric hysteresis measurement. The results of opaque, insulating PZT ceramics (Section III) constitute the first observation of hysteresis in these materials by optical means and demonstrate the potential value of this method in studies of the switching and aging of ceramics.

II. Characterization of Transparent PLZT by Modulated Optical Spectroscopy

1. Introduction

Although modulation techniques have been widely used to study the electronic band structure of solids,¹⁻³ their application to ferroelectrics has been very limited, and no studies of ferroelectric ceramics have been reported. The substantial recent interest in the optical and electro-optical properties of transparent, lanthanum-doped lead zirconate/lead titanate (PLZT) ceramics⁴⁻⁷ has led us to consider the possibility that valuable information concerning the electronic and optical properties of these materials could be obtained using the techniques of electrotransmission (ET) and electroreflectance (ER), in which an externally applied electric field is used to modulate the optical constants of the material, and changes in the absorption (ET) or reflectivity (ER) are measured.

2. Experimental

In this work we have used the techniques of Schottky barrier ER (SBER) as well as electrolyte ER (ELER) to investigate the properties of PLZT ceramic material. The experimental techniques of SBER and ELER¹⁻³ have been described in the literature. A block diagram of the ER measurements is shown in Fig. 1.

Hot-pressed lanthanum doped lead zirconate-titanate ceramics, PLZT with relatively high transparency were obtained from Honeywell Inc. via the Naval Research Laboratory. Much of this work was done with reduced samples $10 \times 10 \text{ mm}^2$, with thickness typically 0.24 mm . The transparent gold films of $70 \sim 100 \text{ \AA}$ thick were evaporated on one or both sample surfaces. The reduction of the PLZT platelets could be obtained by annealing at 650°C in a hydrogen stream for 4 hours.

Electrical connections were made to the evaporated gold electrodes with small drop of high temperature conductive epoxy and 1 mil teflon coated silver wire. The reduced samples had resistivity on the order of 3.3×10^8 ohm-cm. Electric fields of up to 10^4 V/cm were used. Electrically, the gold seemed to act as a blocking, non-ohmic contact, so that the field was applied across only a small surface layer of PLZT. The samples were mounted on copper blocks with a hole. The hole and quartz windows allowed the reflected (transmitted) light to pass into a phototube. The copper blocks were held in a high temperature furnace in which the sample was kept in vacuum. For high temperature region, most measurements were taken up to transition temperature ($\sim 230^\circ\text{C}$).

3. Experimental results and discussions

a. Electrotransmission

We have measured ET in lanthanum doped lead zirconate-titanate ceramics (PLZT) from 300 to 500K in the wavelength range 1.2 $\sim$ 3.6 eV for the case of the poling direction of the ferroelectric ceramic perpendicular to the electric field vector of the light. The experimental results for measurements under dc bias are shown in Figs. 2 and 3. We have observed remarkable changes when dc electric field was applied to samples of rhombohedral PLZT ceramics of the composition 7/65/35. This material lies relatively close to the morphotropic (rhombohedral-tetragonal) phase boundary. In the course of these measurements, sign changes were observed in the signal produced by electrically poled samples. In addition, ET lineshape changed during poling. After reversing the electric

field, we observed that the 7/65/35 ceramic sample was first depoled with a change in sign of the ET signal and then repoled to saturation. The dependence of these changes could describe quantitatively the characteristics of domain wall motions in rhombohedral ceramics. Experimental results for the time dependence under applied dc bias are shown in Fig. 2. In this case the effect on the bias is large and easy to observe. When 3.45×10^3 V/cm field was applied on the electrically poled sample, the sign and amplitude of signal was changed, and after 60 minutes, spectrum (2) was obtained without dc bias. Subsequently the phase of the ac modulation was changed by reversing electrodes on the sample. By reversing the dc electric field $E = 2.15 \times 10^3$ V/cm, the sample was depoled at the first stage (spectrum 4) and the re-poled. With $E = 3.45 \times 10^3$ V/cm, spectrum (5) was obtained and after 8 minutes its signal was increased about 20% (spectrum 6). The subsequent measurements with higher electric fields are shown in Fig. 3. The most significant features of the time dependence of the optical signal could be understood on the basis of domain wall motions.

Since the magnitude of the electrotransmission spectrum appears to be proportional to the spontaneous polarization, we have measured electrotransmission up to the transition temperature and on thermally depoled samples. For 7/65/35 composition, the electrotransmission signal decreased with increasing temperature up to 230°C . However, some residual signal could be observed near the transition, and also in the thermally depoled sample, even though the signal becomes much smaller when the sample is cycled through the transition temperature.

According to differential thermal analysis of 6/65/35 PLZT by Keve and Bye⁷, the rhombohedral-cubic transition occurs at 182°C with a relatively small hysteresis on cooling. Hence, the transition temperature of our 7/65/35 sample was expected to be close to 180°C. However, in our results shown in Fig. 4 the transition temperature would appear to be over 230°C. We have taken hysteresis loop measurements as a function of temperature which yielded a nearly identical transition temperature. Since the physical properties of our samples may depend on the source and preparation technique, our samples may differ from those used by Keve and Bye.

b. Electroreflectance

We have also obtained ER spectra of 7/65/35 PLZT in the photon energy range 1.3 - 4.3 eV, at temperatures from 300 to 500K, and under various poling conditions. Fig. 5 shows the ER spectrum at room temperature of a thermally depoled sample. Essentially the same spectrum was obtained above the Curie temperature, but an increase in amplitude of about 60% was observed as the sample cooled to room temperature. A sharp peak at 3.8 eV occurs at an energy corresponding roughly to the lowest direct band gaps in other perovskites⁸, but it is very sharp (full width at half maximum of 160 meV) as any ER peak observed in a perovskite or transition-metal oxide.

In studying the effects of poling on the ER spectra we have concentrated on the large feature near 3.8 eV. In the following discussion a dc bias or poling voltage will be termed position if the front surface of the sample, at which the ER is measured, is

positive with respect to the back surface. When a positive dc bias is applied to the sample, no change in the ER spectrum, other than an approximately 50% increase in intensity, is noted until 120V is reached. Then the sharp peak initially at 3.8 eV shifts suddenly to shorter wavelength (4.0 eV), its width increased substantially, and a series of oscillations appears, extending from 3.6 eV to at least 2.0 eV. (Fig. 6) Removing the dc bias at this point causes no change in the spectrum other than a slight shift in the positions of the oscillations. If the dc bias is increased further to 200V, one obtains the spectrum in Figure 7, where the peak, now located at 4.1 eV, has broadened still more and the oscillations have shifted slightly. Removing the dc bias now results in a spectrum essentially the same as that obtained by removing the field after poling to 120V. If a negative dc bias is now applied, no major changes are seen until a bias of -83V is reached. At this voltage the oscillations disappear abruptly and a broad background emerges, beginning near 2.95 eV and extending beyond 1.57 eV (see Fig.6).

As a first step toward understanding the poling effects, we have performed a quantitative analysis of the oscillations observed for positive dc bias. Our working hypothesis is that these oscillations are interference fringes produced by the superposition of light reflected from the front surface of the sample with the reflection from the back of the space-charge layer. Since our sample has been made semiconducting by reduction and is covered by an evaporated gold film, there exists at the surface a space-charge layer of thickness d given (in the limit of full depletion) by ⁸

$$d^2 = \frac{eV}{2\pi eN}, \quad (1)$$

where ϵ is the static dielectric constant, V is the voltage drop across the space-charge layer, e is the electronic charge, and N is the free-carrier concentration in the bulk. The voltage $V = V_{\text{ext}} + V_{\text{int}}$ is the sum of the externally applied voltage V_{ext} and the internal voltage V_{int} produced by the difference in work function between the metal and the ferroelectric (surface barrier) and by the remanent polarization of the ferroelectric. Since the carrier concentration in the space-charge layer differs from that in the bulk, the layer also has a refractive index different from that of the bulk, and light can be reflected from the boundary of the layer. If we make the crude approximation of representing the space-charge layer by a slab of dielectric of thickness d in which the real part of the refractive index n_r differs from that in the bulk, then interference fringes (reflection maxima) occur at wavelengths λ given by

$$2n_r d = n\lambda, \quad (2)$$

where n is any positive integer. If this interpretation is correct, the maxima in the spectrum should be equally spaced in energy (inverse wavelength) with a separation $(2n_r d)^{-1}$. Exactly this behavior is found in all of our spectra which exhibit oscillations. Fig. 8 shows the positions (in energy) of the maxima in the spectrum of a

sample which was poled at +120V and measured at zero bias plotted as a function of the fringe number n , with n arbitrarily set equal to one for the lowest-energy maximum observed. Assuming a refractive index of $n_r \approx 1.5$, the fringe spacing gives $d \approx 1\mu\text{m}$, which is not untypical of a semiconductor¹.

More detailed information can be obtained by measuring the fringe spacing as a function of the applied voltage V_{ext} . Equation (1) can be re-written as

$$d^2 = d_0^2 + AV_{\text{ext}}, \quad (3)$$

where $A = e/(2\pi N)$ and $d_0^2 = AV_{\text{int}}$ is the space-charge layer thickness for zero applied voltage. Fitting the maxima in the spectra of Figs. 6 and 7 gives values for d of $1.15\mu\text{m}$ with V_{ext} equal to +120V and +200V, respectively. Using equation (3) to find d_0^2 and A , we obtain $V_{\text{int}} = 33\text{V}$. Assuming a static dielectric constant of approximately 1500 for 7/65/35 PLZT at room temperature gives a carrier concentration $N \approx 2 \times 10^{19}/\text{cm}^3$. Finally, if V_{int} is assumed to arise entirely from the remanent polarization P_r of the ceramic, we obtain $P_r \approx 45\mu\text{C}/\text{cm}^2$. Taking into account the surface barrier between the metal and ferroelectric (which has not yet been measured) will reduce our value of P_r and probably bring it into still better agreement with the value $P_r \approx 31\mu\text{C}/\text{cm}^2$ from hysteresis loop measurements on this sample. It is important to note that

this technique not only provides a rapid and accurate measurement of P_r , but does so without reversing the polarization and so altering the domain structure during the measurement as is the case with hysteresis loop measurements. We hope to exploit this fact to gather more detailed information about domain structure and the process of domain switching than can be obtained from conventional techniques.

4. Acknowledgements

The authors would like to thank Dr. R. Pohanka for his valuable assistance and providing PLZT samples. They also wish to thank S. Tsun for his help during the hysteresis measurements and M. Preil for assistance with sample preparation.

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8. M. Cardona, K.L. Shaklee and F.H. Pollak, Phy. Rev. 154, 690 (1967).

Figure Captions

- Figure 1.** Block diagram of experimental arrangement used for electrotransmission and electroreflectance measurements.
- Figure 2.** Electrotransmission spectra of 7/65/35 PLZT which show change in electrotransmission line shape during poling and reverse polarity at $T = 300K$.
 (1) $E = 3.45 \times 10^3$ V/cm
 (2) same as (1) but after 60 min. The same spectrum is obtained at zero bias.
 (3) same as (2) but with sample leads reversed and zero bias
 (4) $E = 2.0 \times 10^3$ V/cm
 (5) $E = 3.45 \times 10^3$ V/cm
 (6) same as (5) but after 8 min. later.
- Figure 3.** Electrotransmission spectra of 7/65/35 PLZT under higher dc bias showing time dependence and phase change during poling and reverse polarity at $T = 300K$.
 (1) same as (6) of Figure 4 but after 6 min.
 (2) 4.29×10^3 V/cm
 (3) $E = 5.83 \times 10^3$ V/cm
 (4) same as (3) but zero bias
 (5) same as (4) but with sample leads reversed
 (6) $E = 2.0 \times 10^3$ V/cm
 (7) $E = 3.45 \times 10^3$ V/cm
- Figure 4.** Comparison of temperature dependence of electrotransmission and hysteresis loop measurements of 7/65/35 PLZT up to transition temperature.
- Figure 5.** Electroreflectance spectrum of thermally depoled 7/65/35 PLZT.
- Figure 6.** Electroreflectance spectrum of 7/65/35 PLZT with 20V ac modulation and +120V dc bias.
- Figure 7.** Same as (6) but with 200V dc bias.

Figure 8. Energy (inverse wavelength) of interference fringe maxima in ER spectrum measured at zero dc bias after poling at +120V.

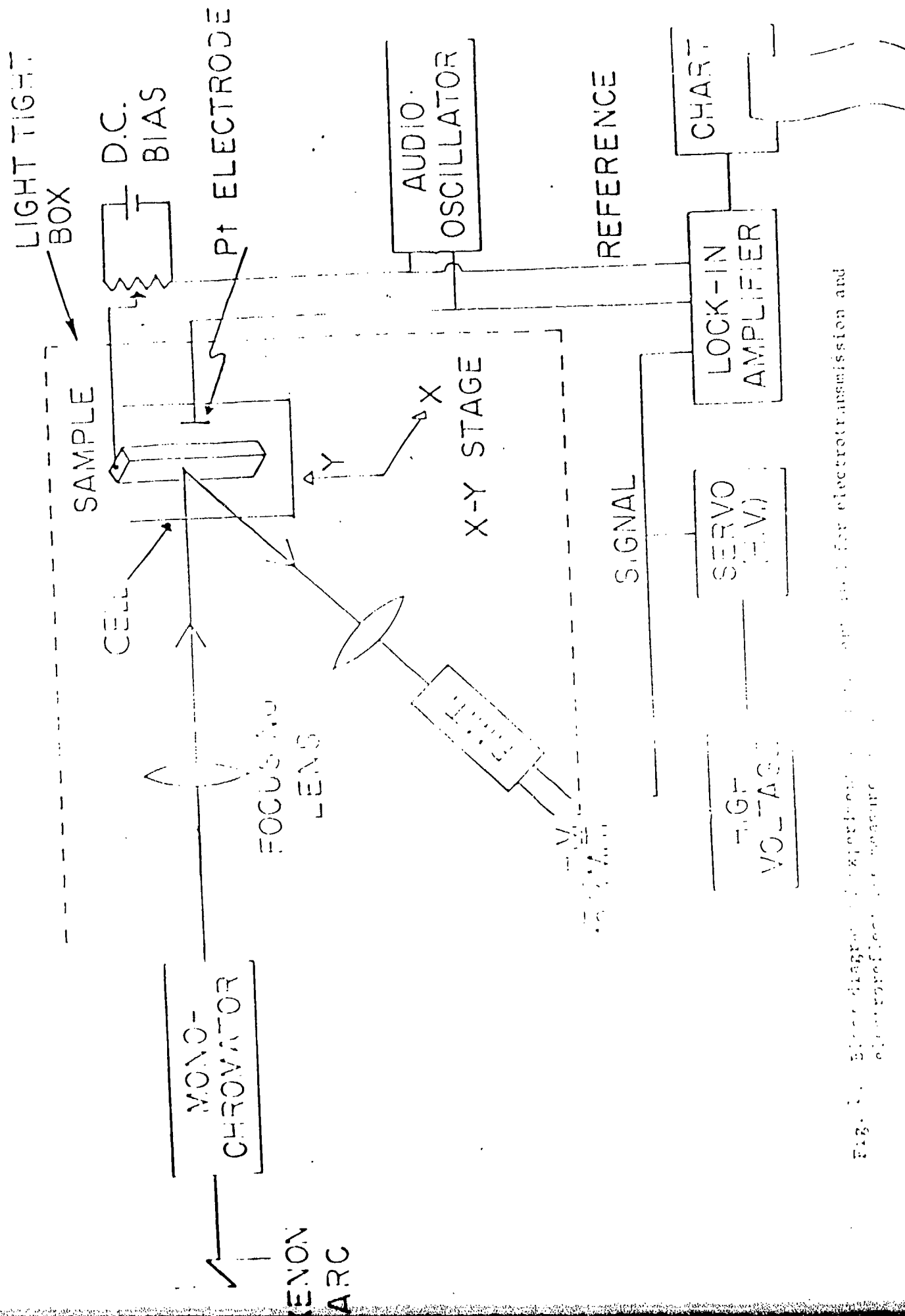


Fig. 1. Schematic diagram of experimental setup for electrotransmission and microphotofluorescence measurements.

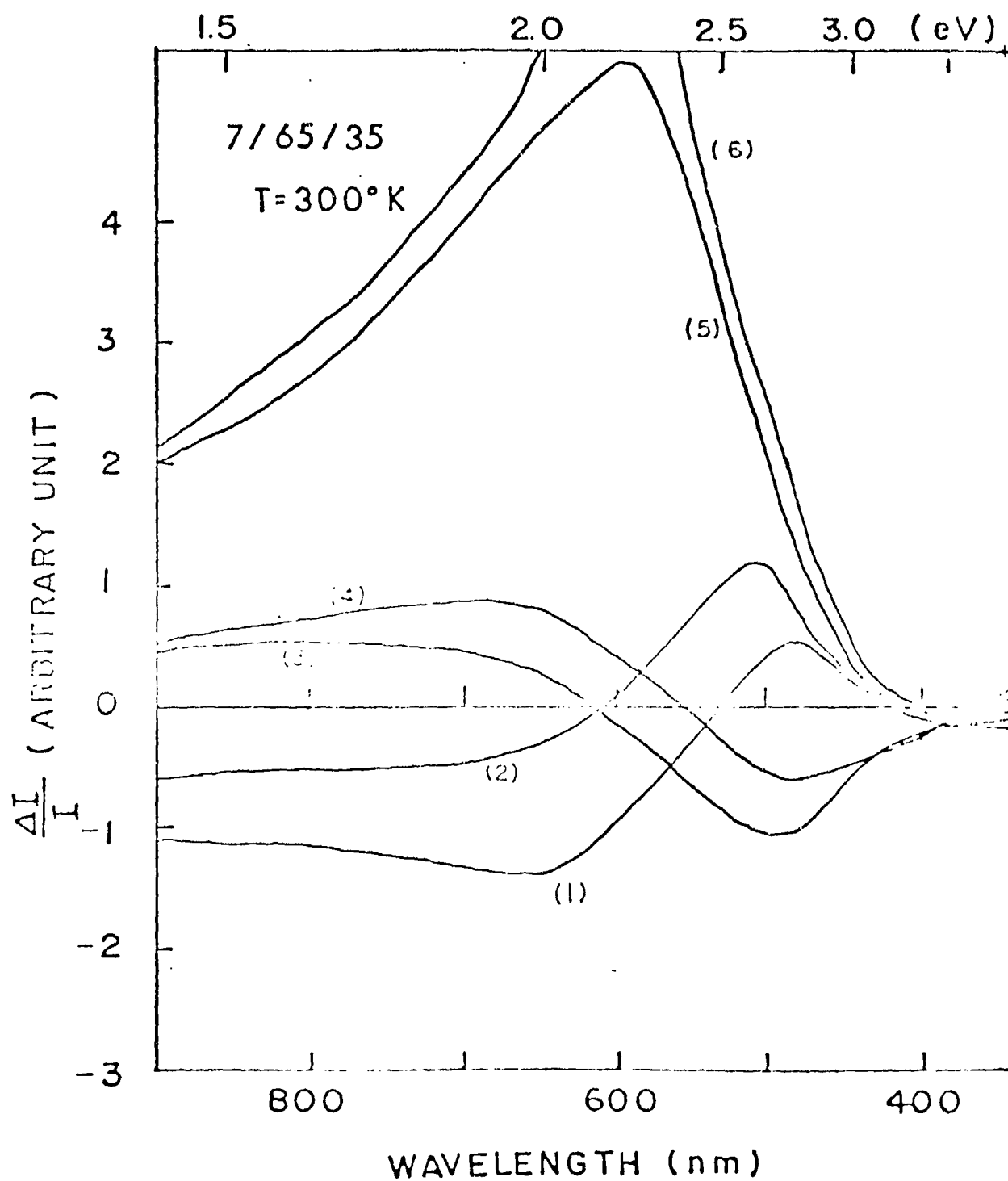


Fig. 2

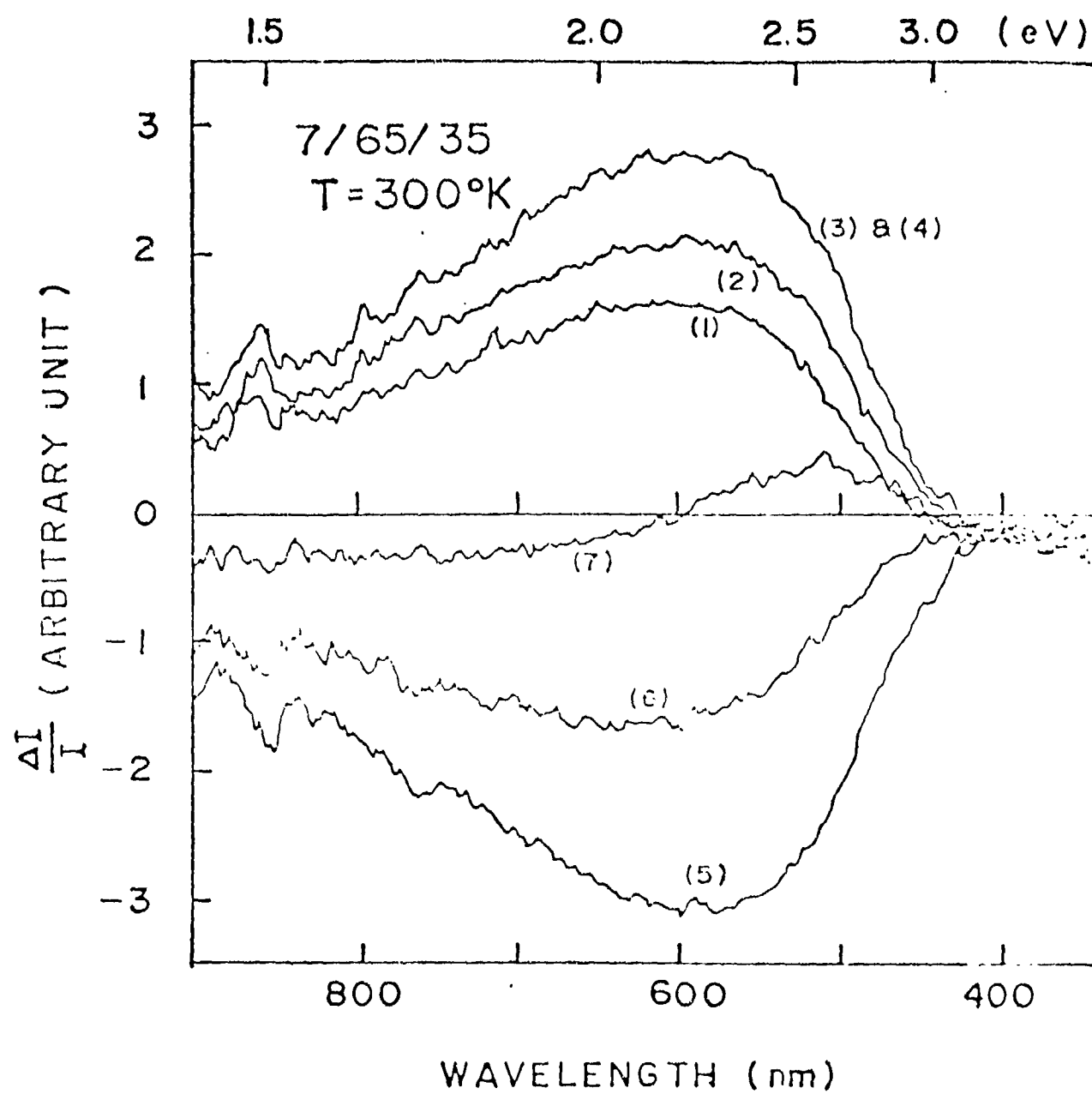


Fig. 3

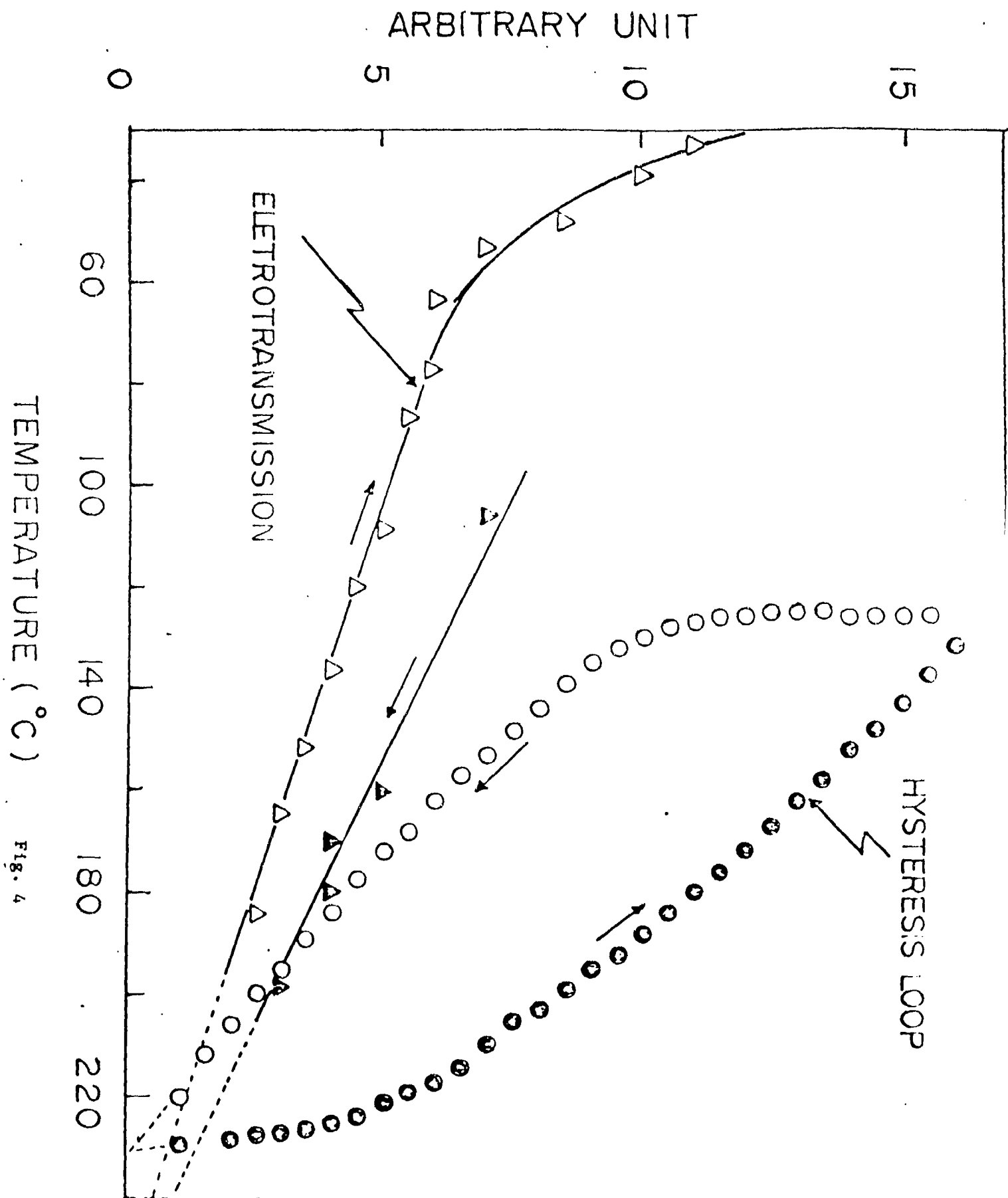


Fig. 4

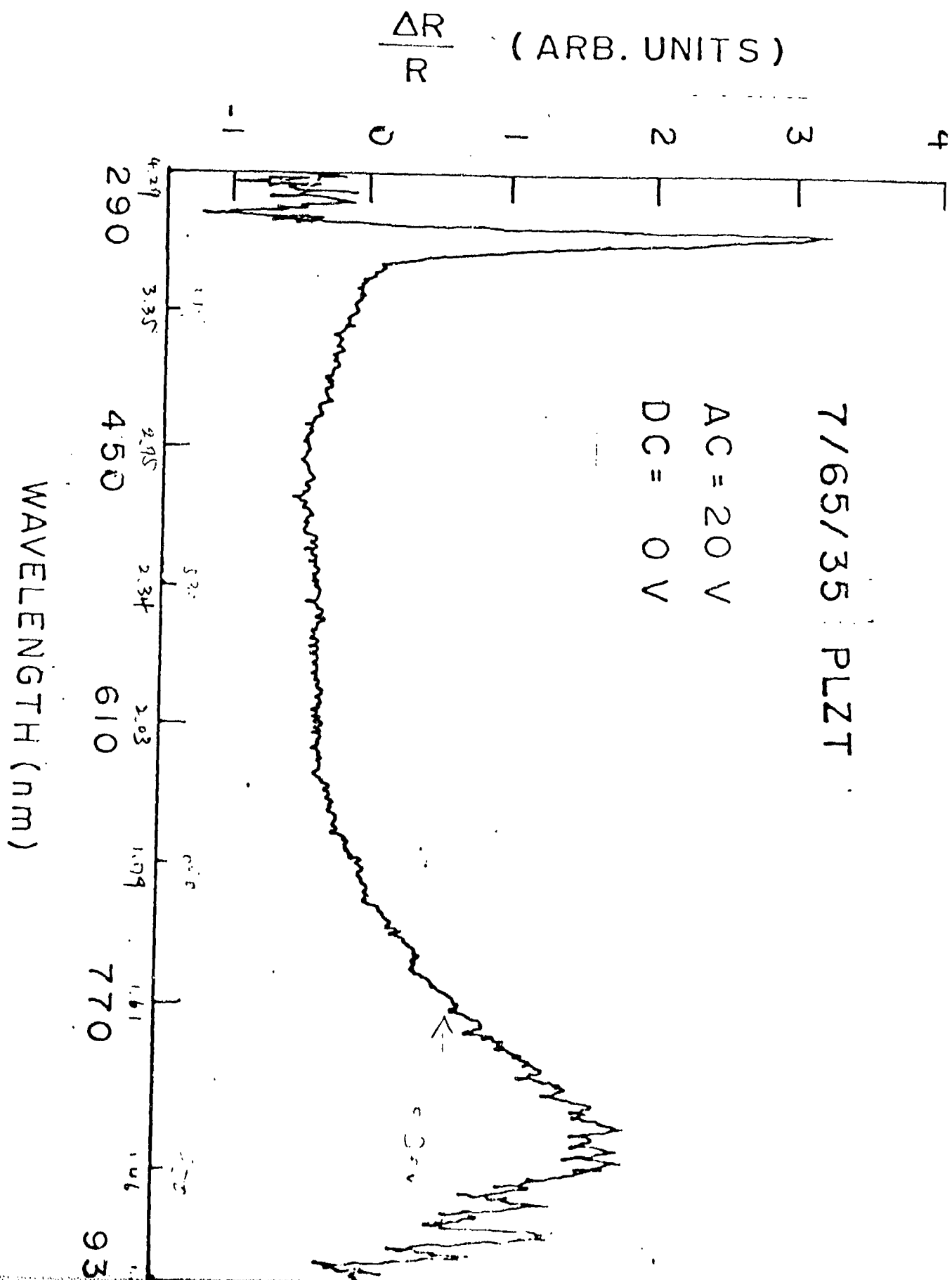


Fig. 5

Fig. 6

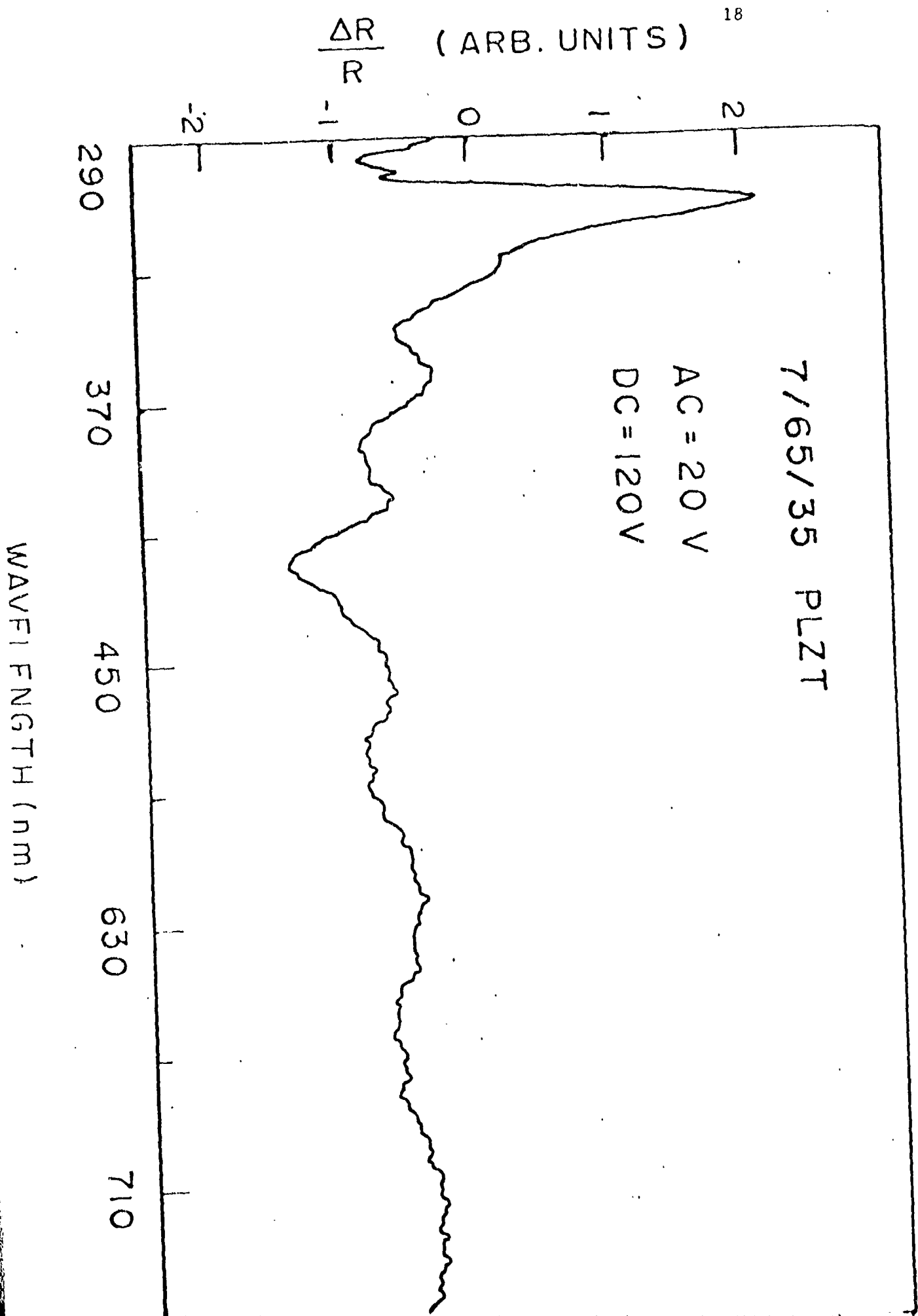
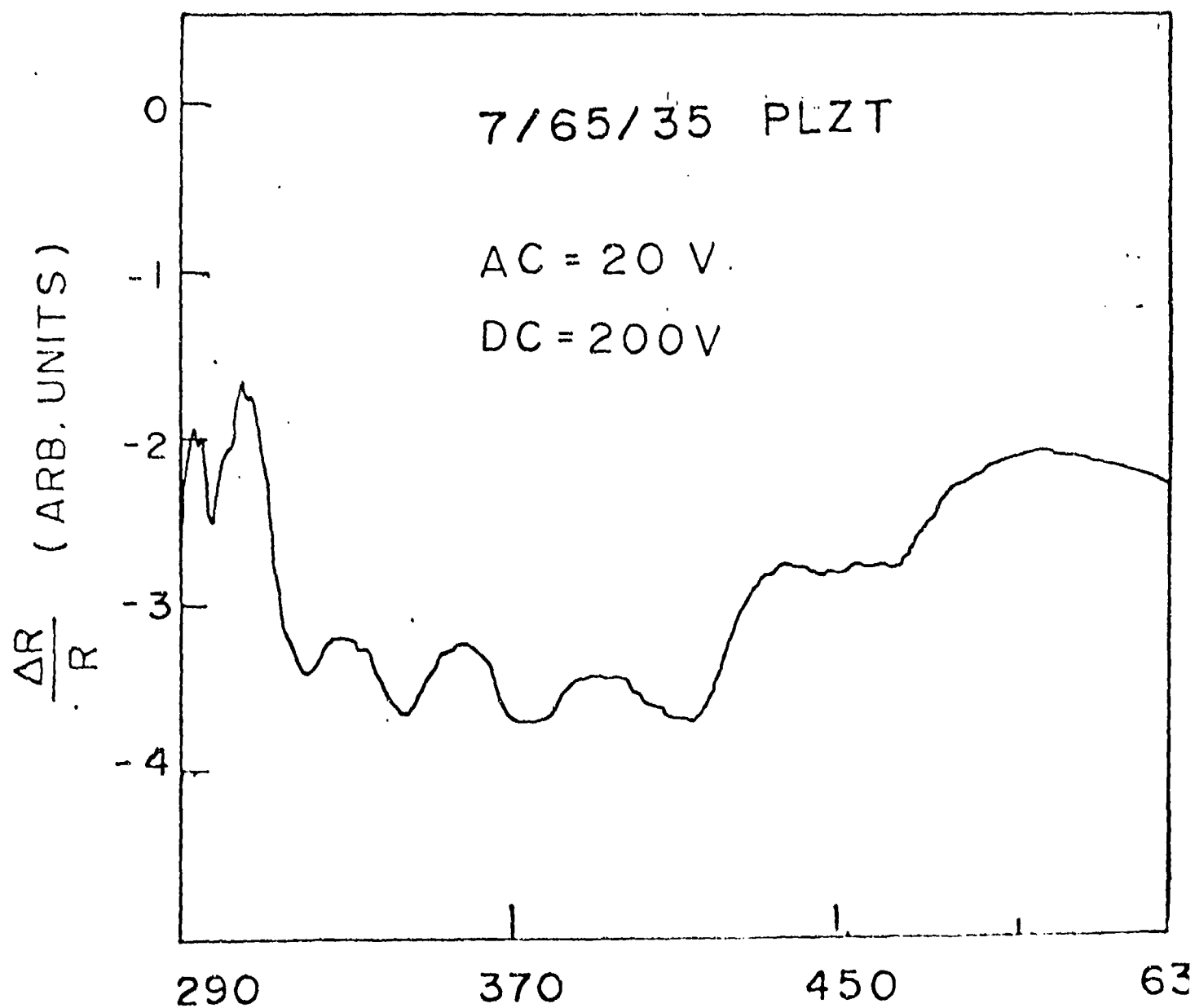


Fig. 7



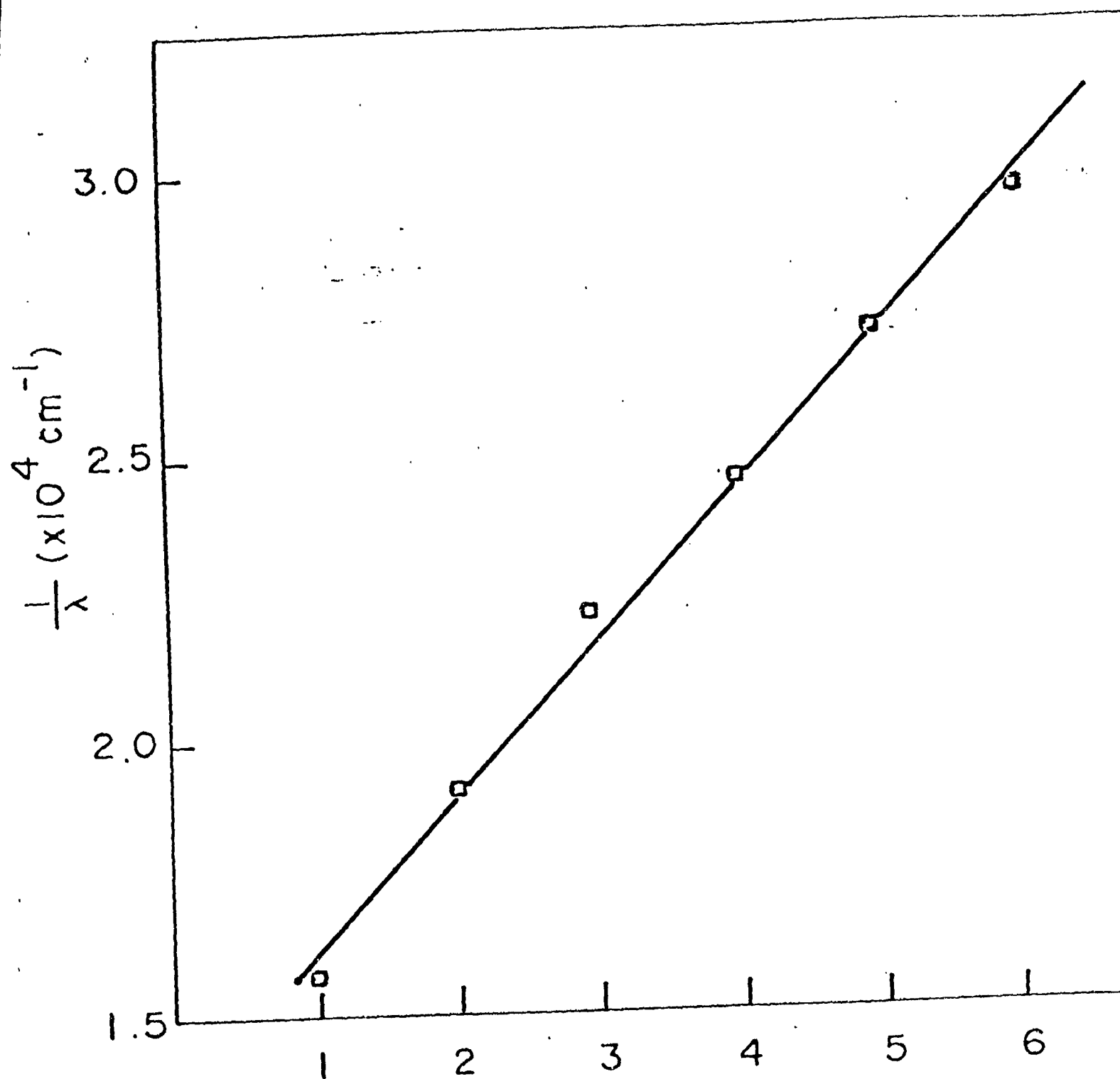


Fig. 8

III. Electroreflectance of opaque PZT ceramics

1 Introduction

Our aim has been to study and develop non-destructive, simple and rapid methods for determining the structural and dynamic properties of ferroelectric ceramics. Optical modulation techniques, particularly electric field modulated transmission and reflectivity, were employed since these methods have been shown to be powerful tools for investigating the electronic properties of solids.¹⁻³ By modulating an internal parameter such as electric field it is possible to obtain derivative-like structures related to interband transitions and hence to gain information concerning the electronic and structural properties of the material.

In a previous report⁴ we have presented detailed electrotransmission (ET) and limited electroreflectance (ER) studies of lead zirconate/lead titanate (PZT) ceramics, which permitted us to make preliminary observations concerning the dynamics of poling and aging. Using certain characteristic features of the ET spectrum which we found to be sensitive to the degree of poling, we could follow the growth rate of the polarization as a function of time during poling and also study polarization reversal (switching). Most of this early work was carried out on initially transparent, lanthanum-doped (PLZT) samples which had been reduced in a hydrogen atmosphere in order to make them semi-conducting. In the present work we show that neither high density (transparency) nor conductivity is necessary for the success of optical modulation techniques: our results were obtained using insulating PZT samples which required no special preparation other than the evaporation of semi-transparent metal electrodes.

In this report we describe an investigation of the ER spectrum associated with the lowest direct optical transition as a function of applied electric field, both ac and dc, as well as time and temperature. We have found that the amplitude and sign of the ER signal is a function of the state of polarization of the sample and follows a hysteresis

loop similar to the conventional D-E hysteresis loops found in dielectric measurements. This represents the first observation by optical techniques of hysteresis in opaque ceramics and hence opens up new avenues of exploration. As a first step in this direction we have used this technique to follow the growth of the polarization during poling and its reversal during switching.

In order to confirm the relation between the ER hysteresis loop and conventional polarization measurements, pyroelectric studies were made using infrared light pulses. Preliminary measurements suggest an equivalence between the pyroelectric coefficient (which is linearly proportional to remanant polarization) and the amplitude and sign of the ER signal.

An effort was made to observe the switching pulses produced by polarization reversal but the long switching times resulted in currents too small to measure accurately.

2. Experimental Approach

In this investigation we have used the technique of Schottky barrier ER (SBER) to investigate the properties of P(L)ZT ceramic materials. The experimental technique of SBER has been described in the literature.¹⁻³

In electric field modulation the application of a periodically varying electric field changes the optical dielectric response of the solid, and a periodic variation in absorption or reflectivity can be observed. Electric field modulation is fundamentally different from other modulation techniques in that the perturbation term for the electric field is not lattice periodic: it represents a net force that accelerates the electron and therefore completely destroys the translational symmetry of the crystal in the field direction. Electric field modulation (either reflection or transmission) produces sharp structure in the region of inter-band transitions. The sharpness of this structure and its dependence on the electric field (both ac and dc) can yield valuable information concerning the material¹⁻³. In general, electric field modulation has been studied most extensively on the diamond, zincblende and wurtzite (DZW) semiconductors although some work has been done on oxide semiconductors.

The technique was originally developed to investigate optical structure associated with interband electronic transitions at critical points in the Brillouin zone. More recently the method has also been utilized to study surface field (i.e. band bending effects) as well as surface states¹⁻³. The optical structure of ferroelectric oxides is substantially different from those of the DZW semiconductors. For example, structure in the reflectance of a ferroelectric shifts markedly

when the material is cooled through its Curie temperature. This indicates that the spontaneous polarization causes band structure effects resulting in the change of the reflectance spectrum. Similar reflectance changes are to be expected when an external field modulates the alignment of the dipoles. Large effects have indeed been observed in the ER of perovskite ferroelectrics such as BaTiO_3 , KATaO_3 , KNbO_3 , and SrTiO_3 . Reflectance changes of up to 45% are distributed over the spectral scale in broad, continuous bands of either sign. Magnitude and lineshape suggest a mechanism other than the Franz-Keldysh effect (electric-field modulation of critical points). This suggests that ER of ferroelectrics is probably not a critical point phenomenon. The relative displacement of the oxygen and metal sublattices responsible for the ferroelectric properties are probably the main cause for the ER optical effect as well. The displacement changes the overlap integrals between pairs which affects the band structure¹. Our work represents a departure from previous studies in that we have utilized ER to investigate the internal fields produced in ferroelectrics by the spontaneous polarization and by space charge effects.

2. Experimental Technique

In our experiments a metal (Au) film is evaporated onto the front surface of the sample in order to apply the electric field which modulates the optical dielectric constants of the material as well as allowing a dc voltage to be imposed. We have studied samples in which the back contact was (a) also a Au contact or (b) a conducting contact made with Viking metal (a liquid alloy of Hg, Tl, and In manufactured by Elmut Corp., Mountainview, Calif.).

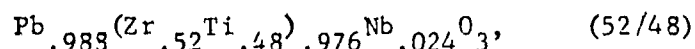
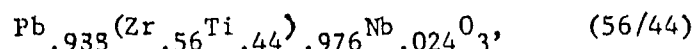
In the present experiments, the ER measurements were carried out with a system including a Xenon lamp, monochromator, focusing and collecting lenses, photomultiplier and the appropriate detection electronics. A block diagram of this equipment is shown in Figure 1. The light from Xenon arc lamp is passed through the Heath monochromator (Model EU-700-56), and focused on the sample surface. The ac modulating voltage (530 Hz) is applied by means of an audio oscillator which also provides the reference signal for the lock-in amplifier. A dc voltage can be superimposed onto the ac voltage by means of the dc control. The reflected light is collected by a lens and focused onto a Hamamatsu S-20 response photomultiplier. The light detected by the photomultiplier contains two signals: a dc signal proportional to the average reflectivity R and an ac signal which is proportional to the modulated reflectivity ΔR . The dc output from the photomultiplier is connected to a servo power supply which varies the high voltage on the photomultiplier so as to keep the dc output constant. Under these conditions the output from the lock-in amplifier, which goes to a strip-chart recorder synchronized with the spectrometer scans, is proportional to $\Delta R/R$.

Hot pressed 1% Nb_2O_5 doped PZT ceramics were obtained from B. Jaffe, Vernitron Piezoelectric Div., Cleveland, Ohio. All of this

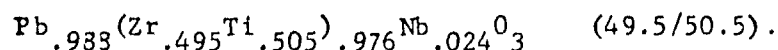
work was done without reduction. After samples were lapped and optically polished, a transparent Au film of $70 \sim 100 \text{ \AA}$ thickness was evaporated on one or both surfaces of the ceramic plates. Therefore a metal-insulator-metal (MM) geometry was used, and the electric field vector $\vec{E}$ of the light was perpendicular to the polarization of the ceramic. The completed samples had a resistance over $20 M\Omega$, and were $10 \times 10 \text{ mm}^2$ in dimension with thickness about $0.1 \sim 0.3 \text{ mm}$.

4. Experimental Results

We have measured ER spectra of 1% Nb-doped lead zirconate/lead titanate ceramics of the compositions



and



These materials lie relatively close to the morphotropic (rhombohedral-tetragonal) phase boundary. For example, 56/44 - 1 wt% Nb_2O_5 and 49.5/50.5 - 1% Nb_2O_5 samples lie in the rhombohedral and tetragonal phases respectively, and 52/48 - 1% Nb_2O_5 lies very close to the phase boundary at room temperature⁵. Shown in Fig. 2 is the ER spectrum of 52/48 PZT ceramic at room temperature in the vicinity of the fundamental gap (305 nm). For this sample both front and back electrodes were Au, the front electrode being semitransparent ($\sim 70\text{-}100 \text{ \AA}$). In studying the effects of poling on the ER spectra we have concentrated on the sign and magnitude of the large feature near 305 nm. In the following discussion a dc poling voltage will be termed

positive if the front surface of the sample, at which the ER is measured, is positive with respect to the back surface.

We have observed dramatic changes of the magnitude and sign of the ER signal as a function of applied dc voltage. Shown in Fig. 3 are some experimental results for 52/48 PZT with different applied dc fields and an ac modulating field (530 Hz) of 3kV/cm. The fields mentioned in this report were determined by dividing the applied voltage (either ac or dc) by the thickness of the sample. Thus the assumption was made that the applied field is uniform across the sample and not confined to a surface (space charge) region as in the semi-conducting samples studied previously. The ER signal of a virgin sample was first measured with no applied dc field (point A in Fig. 3). The sample was then partially poled by applying a field of + 4.0 kV/cm, and after approximately 15 minutes the ER signal was measured (point B in Fig. 3). The ER signal increased somewhat in magnitude but its sign remained unchanged. The material was then switched incrementally from + 4.0 kV/cm to - 7.5 kV/cm, the ER spectrum being measured at each step indicated by the open circles (path 2). At - 7.5 kV/cm (point C) the sign of the ER signal had reversed. The dc field was now changed incrementally from - 7.5 kV/cm to + 8.0 kV/cm (path 3), the ER signal changing in magnitude and sign as indicated. The sample was then cycled around a complete hysteresis loop (paths 4 and 5) and the saturation fields were found to be + 8.0 kV/cm and - 8.0 kV/cm. Figure 3 clearly shows that the ER signal follows the remanent polarization of the ceramic and can be used to measure that polarization without reversing it as is necessary in conventional hysteresis measurements. Although the ac modulating field does have some impact on the measurements it will be shown in the next section that this effect can be taken into account.

Although the ER hysteresis loop of a freshly poled sample is quite symmetric (see Fig. 3), we have observed that a very substantial asymmetry develops with time. A similar effect has been observed in transparent PLZT ceramics and attributed to space charge effects.⁶ Although a detailed study of this behavior is still in progress, the phenomenon itself is clearly evident in the data obtained in two studies of hysteresis and switching reported below.

In order to examine the time dependence of polarization reversal during switching, we have measured the ER signal of a sample of 52/48 PZT as a function of time after the application of a dc field of the appropriate polarity to cause switching. The sample used had been poled several days previously by the application of field whose polarity was positive according to the sign convention described above. At the start of each switching measurement the sample was again poled for 30 min. at a field of +8 kV/cm. First, in order to observe switching toward the original poling direction, the sample polarization was reversed by the application of a field of -8 kV/cm for 30 min. A switching field of +8 kV/cm was then applied and the ER signal measured as a function of time. The results are shown as curve (A) in Fig. 4. Switching away from the original poling direction was then studied by the application of a field of -8 kV/cm to a sample which had been poled as indicated above. The time dependence of the ER signal is given by curve (B) in Fig. 4. It is clear from these results that when switching is toward the original poling direction (A) it proceeds much more rapidly than when the polarization is being switched away from the original poling direction (B). This is consistent with the findings⁶ on PLZT, and we have begun a series of experiments aimed at determining how this

asymmetry develops as a function of time after poling.

Despite the appearance of the curves in Fig. 4, the polarization reversal during switching does not proceed exponentially. This can be seen clearly in Fig. 5 where the polarization reversal for several applied fields has been plotted in the form $\log (AR/R)$ vs. time. The lack of any linear region in these curves rules out an exponential time dependence. The three sets of data shown in Fig. 5 were taken on freshly poled samples and correspond to: (1) instantaneous reversal of the applied field from +8 kV/cm to -8 kV/cm, as in curve (B) of Fig. 4; (2) gradual reduction of the field from +8 kV/cm to zero over several minutes followed by the instantaneous application of -8 kV/cm; and (3) gradual reduction of the field as in (2) followed by the application of -4 kV/cm. Not surprisingly, the results of measurements (1) and (2) are virtually identical. It is interesting to note how dramatically the switching time increases as the field strength is reduced: at -8 kV/cm the switching time (10% to 90% reversal) is about 10s, while at -4 kV/cm it is greater than 200s. This suggests that the "linear resistance" region, in which the switching current (inversely proportional to the switching time) varies linearly with the field⁷, has not been reached, at least at the smaller field. An exponential dependence of switching time on field is to be expected at low fields⁷, and measurements are in progress to determine whether this is the case.

A search of the literature has failed to reveal any theoretical description of the switching process capable of predicting polarization as a function time for comparison with experimental data of type shown in Figs. 4 and 5. However, since it is customary in studies of the aging of ceramics to plot changes in dielectric or piezoelectric

properties as functions of the logarithm of the time since poling⁸ (a linear dependence on $\log t$ is found in most cases), we made similar plots of our switching data. Figure 6 shows the data of Fig. 5 re-plotted in the form $\Delta R/R$ vs. $\log t$. The linear dependence on $\log t$ of measurement (3), obtained with a switching field of -4 kV/cm, is quite striking. Several measurements using switching voltages of magnitude less than 4 kV/cm indicate that as the switching voltage is reduced the linear dependence of $\Delta R/R$ on $\log t$ is preserved while the slope of curve becomes very small. This suggests that as the switching field approaches zero the processes of switching and aging become experimentally indistinguishable. It is obviously important from a theoretical point of view to determine whether the switching rate, when extrapolated to zero applied field, agrees with the aging rate of the remanent polarization (or piezoelectric coupling factor) as determined by other methods.

A second and more detailed study of the ER hysteresis was undertaken in order to understand as fully as possible the dependence of the ER signal on both ac and dc applied fields. Samples of 56/44 PZT, which lies in the rhombohedral phase, were used for this work after it was verified that this material exhibits ER hysteresis loops similar to those seen in the tetragonal phase. Figures 7-11 show the hysteresis loops obtained on a sample of thickness 1.016×10^{-2} cm using various ac modulation fields at a frequency of 530 Hz. As the amplitude of the ac modulation is increased, three major changes can be seen in the ER hysteresis loops: (1) the amplitude of the ER signal at saturation polarization increases so that the loop expands vertically;

(2) the apparent coercive field decreases so that the loop shrinks horizontally; and (3) the loop becomes more asymmetric, with the coercive field corresponding to the original poling direction (positive) decreasing more rapidly than the coercive field for switching in the opposite direction.

The first of these effects can be analyzed with the aid of Fig. 12, which shows the maximum (saturated) value of $\Delta R/R$ as a function of the ac modulation amplitude. The linear dependence seen in this figure can be understood in the following way. Derivative-like modulation methods other than ER (e.g. piezoreflectance, thermoreflectance, or wavelength modulation) are linear in the applied modulating parameter. In contrast, ER is generally not linear but higher order in the electric field since electric field produces an additional effect, the acceleration of the electron (or hole) which amplifies the signal by the reciprocal of the reduced mass in the field direction. This produces a signal which is generally like a higher-order derivative. However, in the oxides the effective mass is generally very large (≈ 1) and hence this latter effect is suppressed. Therefore, in the oxides one would expect the ER signal to be like a first-derivative. In fact, Yacoby and Naveh¹⁰ have measured thermoreflectance and electoreflectance spectra in SrTiO_3 and have shown that these spectra are similar to each other and are also similar to the wavelength derivative of the optical constants.

The apparent decrease in coercive field when the ER hysteresis loop is measured with progressively larger ac modulation is most probably due to the depolarizing effect of the ac field itself. This hypothesis is supported by the data shown in Fig. 13, where the average

coercive field (i.e. one-half the width of the hysteresis loop) has been plotted as a function of the ac modulation amplitude. Once the effects of asymmetry have been removed by this averaging, the relationship between coercive field and modulation amplitude is clearly linear, with no hysteresis observable for modulations exceeding 10 kV/cm and an extrapolated coercive field of 8 kV/cm at zero modulation.

The growing asymmetry of the hysteresis loops shown in Figs. 7-11 is probably not due to the increasing ac modulation but rather to the passage of time and the resulting development of a space-charge field as described above. The measurements were performed over a period of two weeks and in order of increasing ac modulation. Measurements, now in progress, of the asymmetry as a function of time after poling will determine whether the observed asymmetry can be accounted for in this way.

In order to confirm that the ER results are compatible with other measurements of the dielectric hysteresis, we have studied the pyroelectric coefficient of a 52/48 PZT ceramic sample as a function of applied dc field. When a poled sample in the form of a parallel-plate capacitor is subjected to a temperature change and a low-impedance path is provided between the two electrodes, a current i will flow in the external circuit given by

$$i = A \frac{dP}{dt} = A \frac{dp}{dT} \frac{dT}{dt},$$

where A is the electrode area, t is the time and T is the temperature. The pyroelectric coefficient p is defined as

$$p = - dp/dT.$$

In order to avoid spurious currents produced by the irreversible release of charge injected during poling or by the decay of space charge built up during aging, a dynamic measurement technique was used in which the sample was exposed to chopped infrared radiation.¹¹ Since the sample was alternately heated and cooled, and only the current which changed sign at the chopping frequency was measured, the true reversible pyroelectric current was obtained. Details of the method employed can be found in the literature.¹²

Samples of 52/48 PZT ceramic of area $4 \times 4 \text{ mm}^2$ were polished to a thickness of $4 \times 10^{-3} \text{ cm}$, and a transparent gold film about $70 \text{ \AA}$ thick was evaporated on one surface and a thicker film (about $1000 \text{ \AA}$) deposited on the other. Teflon-coated silver wires (about 40 Ga) were attached to the electrodes using silver paste. Figure 14 shows preliminary measurements of the pyroelectric current as a function of the dc electric field applied to the sample. Further measurements will be necessary before a detailed comparison of pyroelectric and ER hysteresis loops will be possible, but it is interesting to note at this stage that the coercive field of the pyroelectric loop agrees well with the extrapolation of the ER results to zero modulation field. We should point out, however, that the pyroelectric loop does not appear to be saturated at fields of $\pm 8 \text{ kV/cm}$, and limitations of our present apparatus prevent us from applying larger dc fields. A simple modification of the detection electronics, to be completed shortly, will eliminate this difficulty.

An attempt was made to measure directly the current pulse produced by the polarization reversal,⁷ but the long switching time in these ceramics makes it impossible to obtain a well-defined switching pulse

of sufficient amplitude to measure accurately. It would seem that in this situation the ER and pyroelectric methods, which measure the sample polarization directly, have a significant advantage over techniques such as switching current measurements which respond only to the time rate of change of polarization.

5. Conclusions

We have measured electrorreflectance (ER) in the vicinity of the fundamental gap (wavelength approximately 310 nm) of PZT ceramics having compositions near the morphotropic phase boundary. Our results constitute the first observation of hysteresis in these materials by optical means. Studies aimed at establishing the validity of the technique have shown that the ER signal follows the sample polarization and that a reliable value of the very-low-frequency coercive field can be obtained from ER measurements. Efforts were begun to exploit the new technique in obtaining information on the hysteresis and switching behavior of these ceramics, and three major findings can be reported at this time. First, the ER hysteresis loops of poled PZT ceramics become increasingly asymmetric with time after poling, probably as a result of space charge effects similar to those reported in PLZT ceramics.⁶ The time dependence of this phenomenon is now under study. Second, the switching (polarization reversal) of these ceramics becomes similarly asymmetric after poling and aging. Substantially longer switching times were found for switching the polarization away from the original poling direction than for switching toward that direction. Finally, the polarization change produced by small switching fields (one-half or less of the very-low-frequency coercive field) was found to have a logarithmic time

dependence similar to that reported for the aging of dielectric and piezoelectric properties. This observation may prove quite important in the development of badly needed theoretical models for switching and aging. Unsuccessful attempts to observe switching in these ceramics by conventional methods ⁷ clearly demonstrate the value of the ER technique, without which these studies could not have been performed.

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Figure captions

- Fig. 1. Block diagram of experimental arrangement used for electroreflectance measurements.
- Fig. 2. Typical electroreflectance spectrum of 52/48 PZT at $T = 300\text{K}$ with 3 kV/cm ac modulation and 8 kV/cm dc field.
- Fig. 3. Electroreflectance peak intensity in 52/48 PZT (using an ac modulation of 3 kV/cm at 530 Hz) as a function of the applied dc field as the sample is taken around the hysteresis loop.
- Fig. 4. Polarization reversal as determined by the electroreflectance signal measured at $T = 300\text{ K}$ for 52/48 PZT ceramic samples;
- (A) poled by $- 8\text{ kV/cm}$ for 30 min. and then instantaneously switched to $+ 8\text{ kV/cm.}$
 - (B) same as (A), but from $+ 8\text{ kV/cm}$ to $- 8\text{ kV/cm.}$
- Fig. 5. Polarization reversal characteristic of 52/48 PZT samples measured at $T = 300\text{ K}$ after poling under various conditions;
- (1) same as Fig. 4 - (B).
 - (2) poled by $+ 3\text{ kV/cm}$ for 30 min. and decreased to zero field slowly during for several minutes, and then switched to $- 8\text{ kV/cm.}$
 - (3) same as (2), but switched to $- 4\text{ kV/cm.}$
- Fig. 6. Same as Fig. 5 but plotted as $\frac{\Delta R}{R}$ vs $\log t$ (t in seconds).
- Fig. 7. Hysteresis in electroreflectance of 56/44 PZT (rhombohedral phase) with 2 kV/cm ac modulation.
- Fig. 8. Same as (7) but with 4 kV/cm ac modulation.
- Fig. 9. Same as (7) but with 6 kV/cm ac modulation.
- Fig. 10. Same as (7) but with 8 kV/cm ac modulation.

- Fig. 11. Same as (7) but with 10 kV/cm ac modulation.
- Fig. 12. Dependence of the maximum (saturated) electroreflectance signal on the amplitude of the ac modulation field (derived from Figs. 7-11).
- Fig. 13. Dependence of the averaged coercive field (one-half the width of the electroreflectance hysteresis loop) on the amplitude of the ac modulation field (derived from Figs. 7-11).
- Fig. 14. Hysteresis in pyroelectric current in 52/48 PZT ceramic.

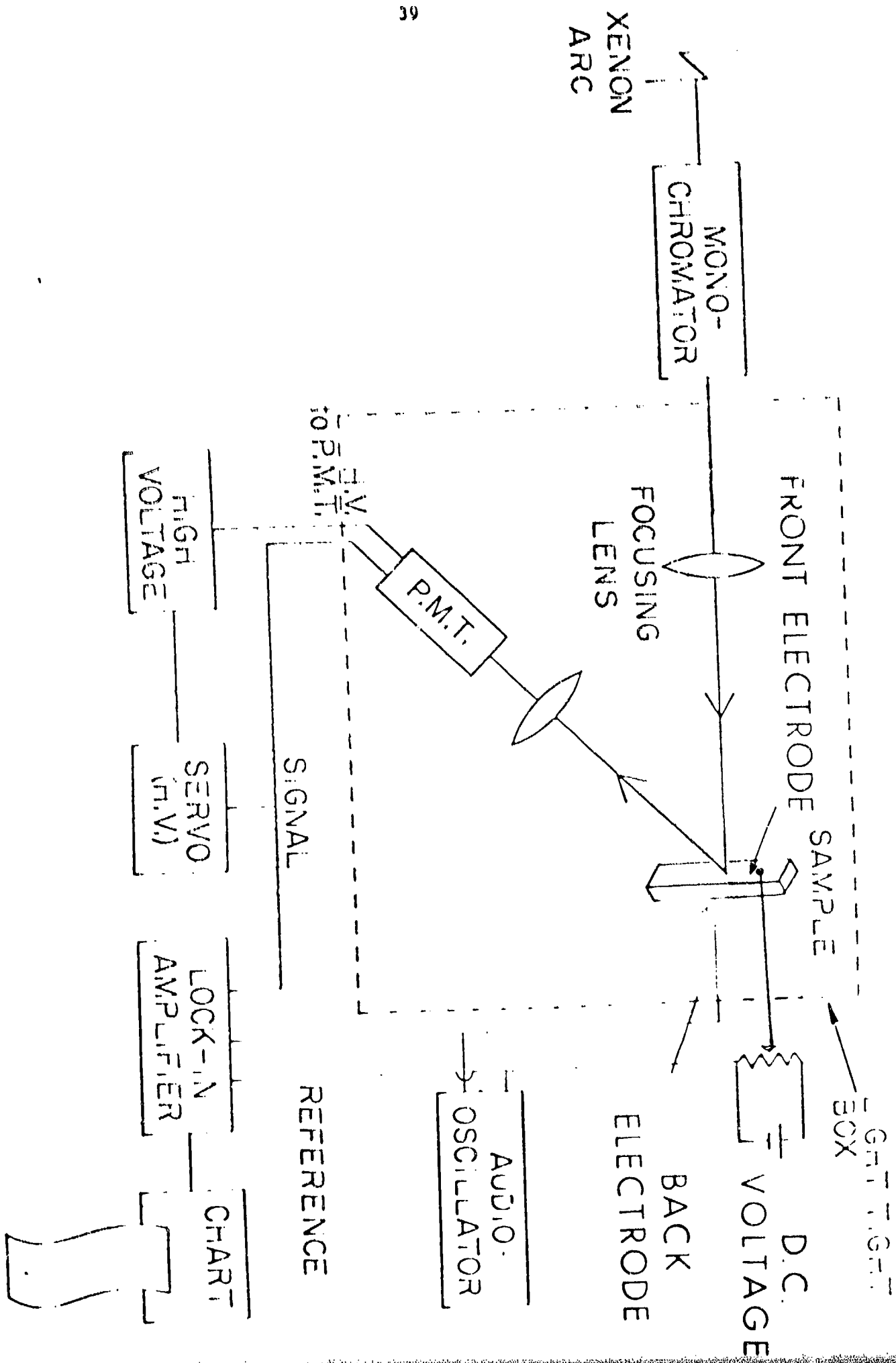


Fig. 1

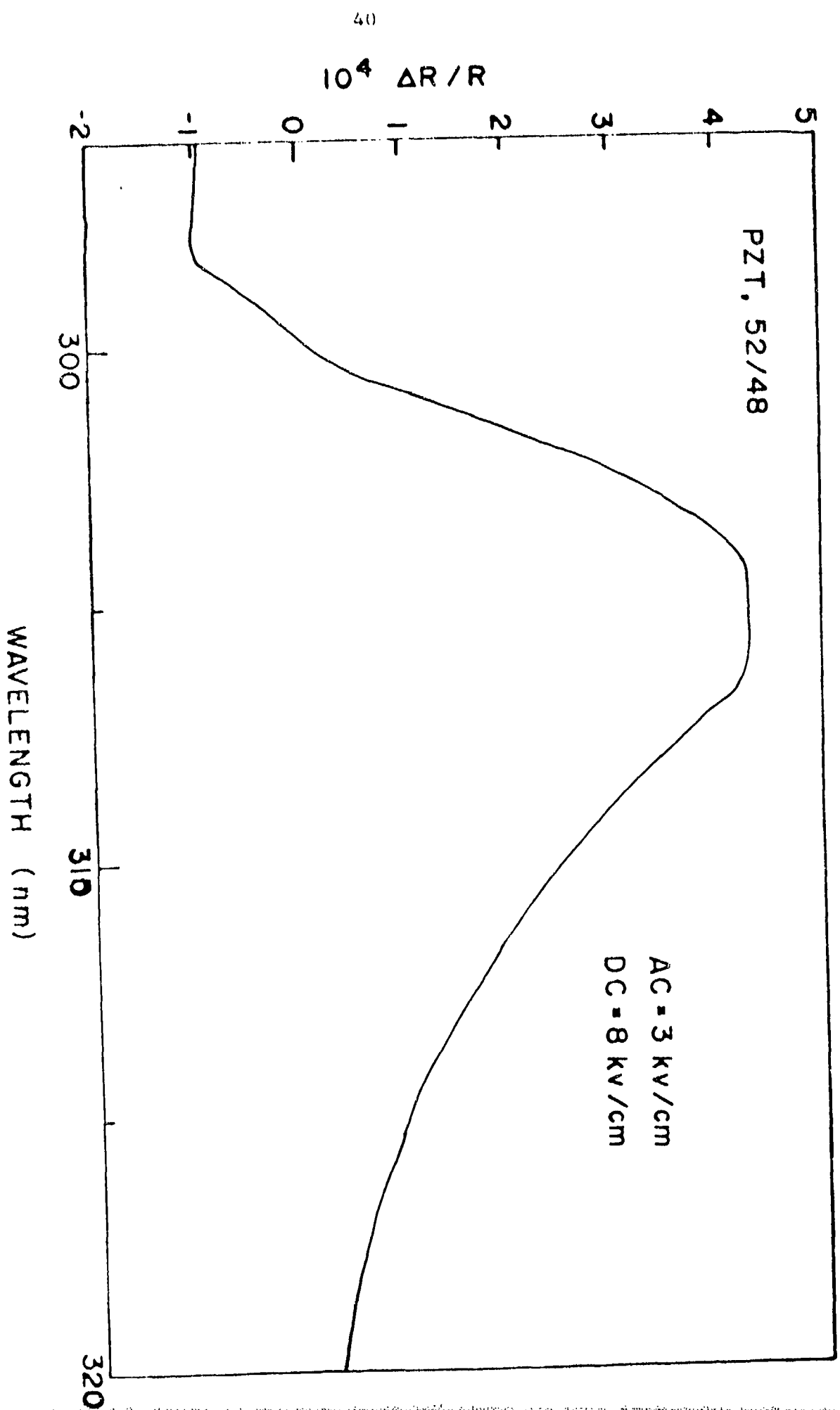


Fig. 2

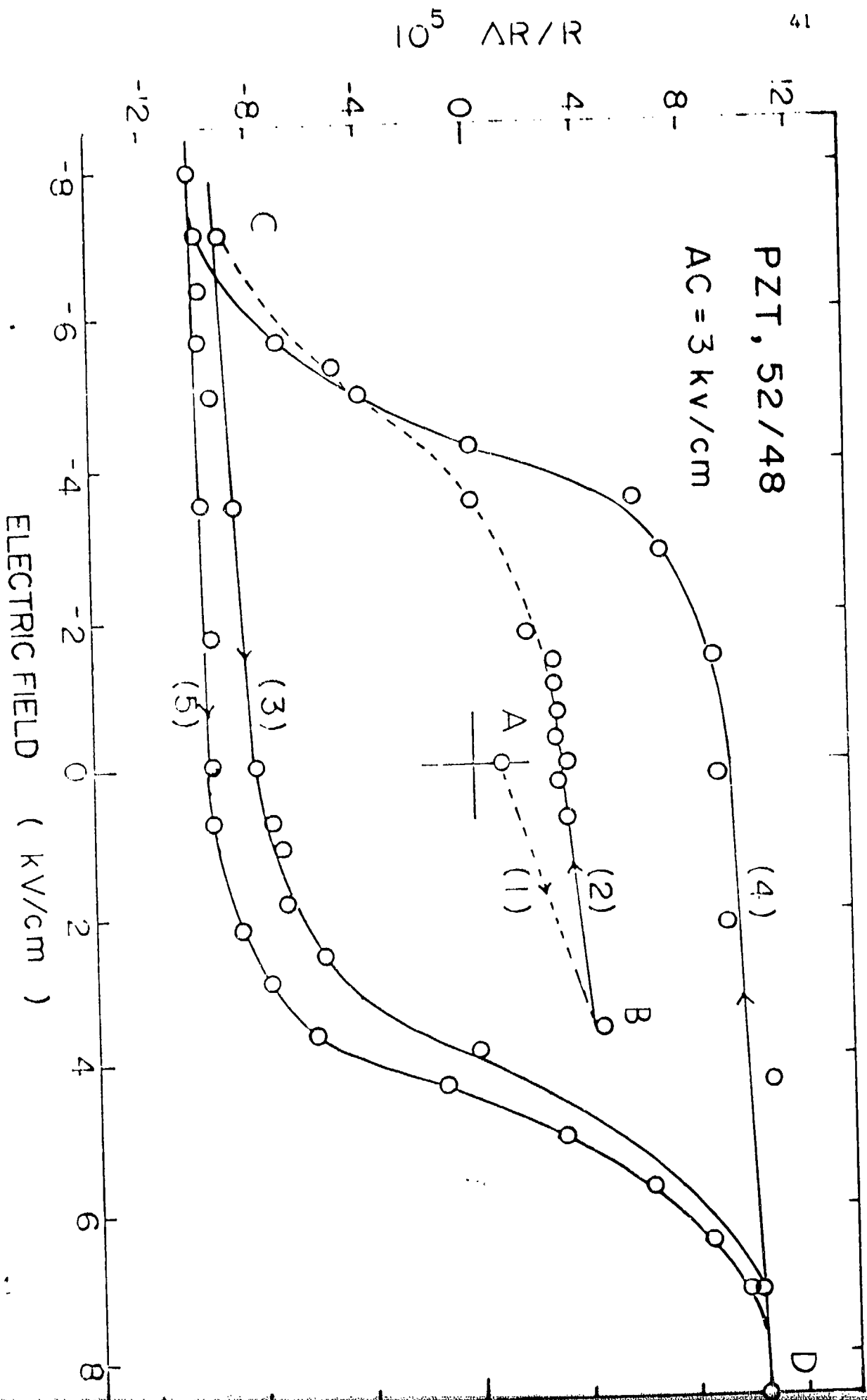


Fig. 3

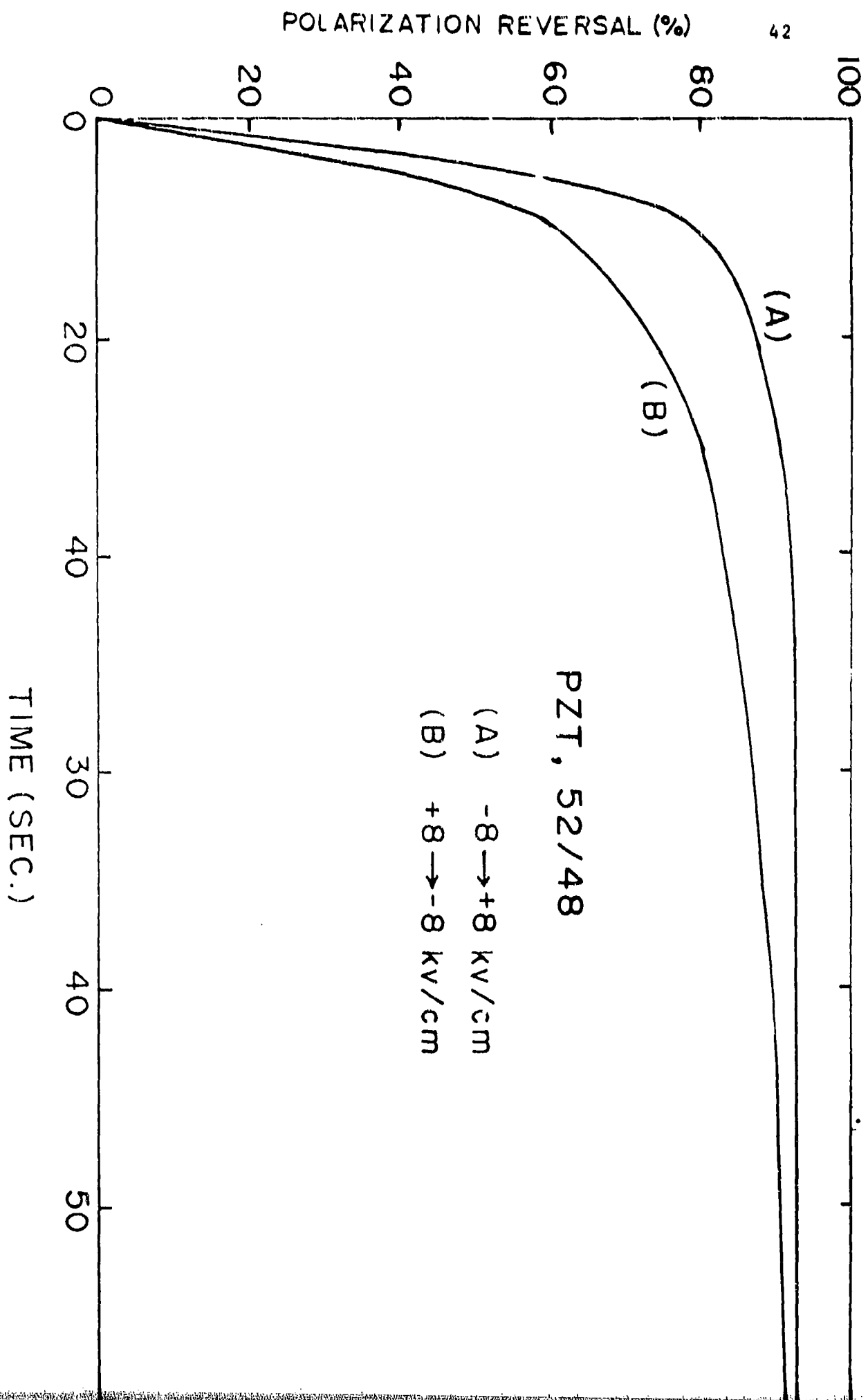


Fig. 4

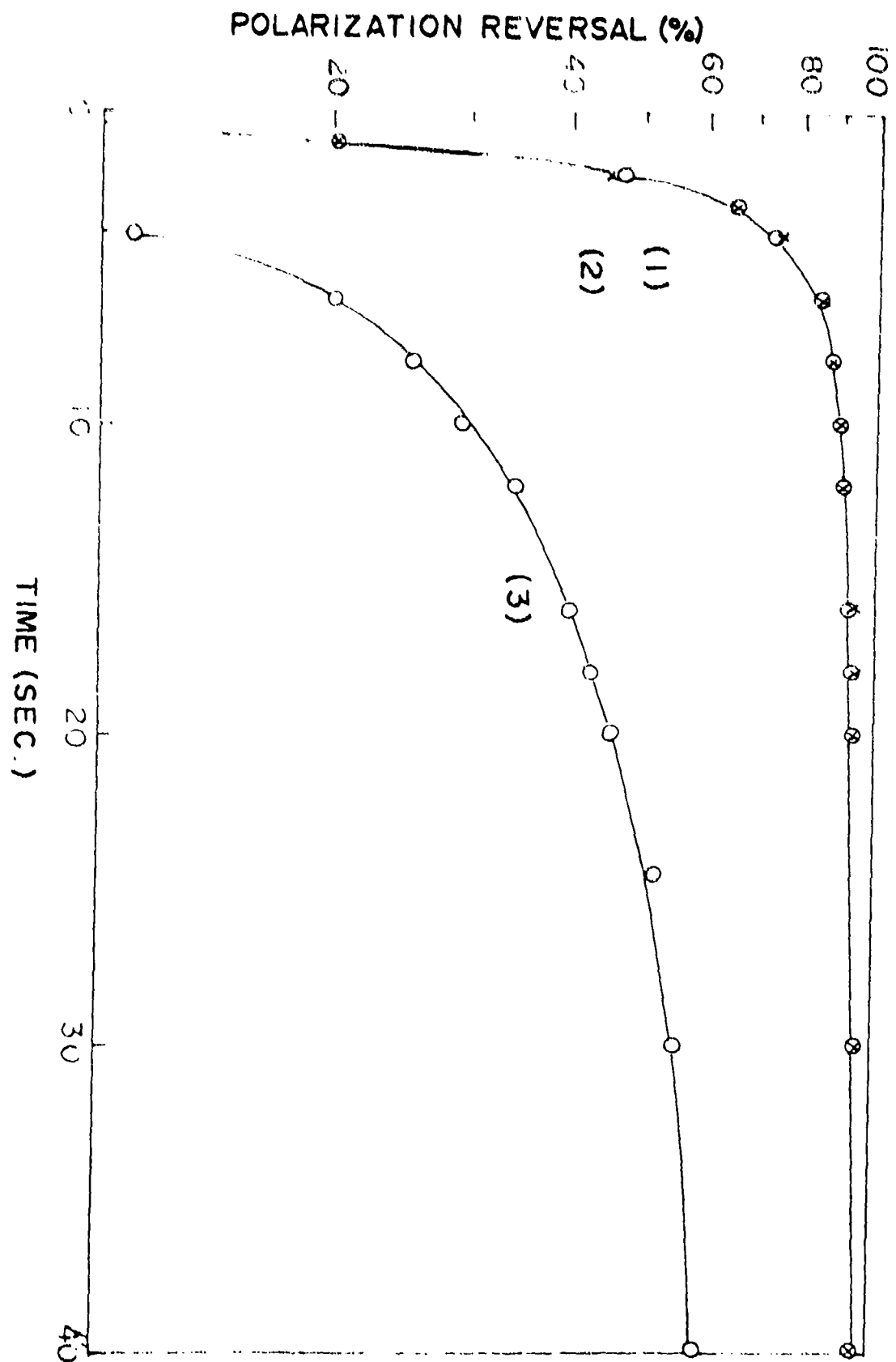


FIG. 5

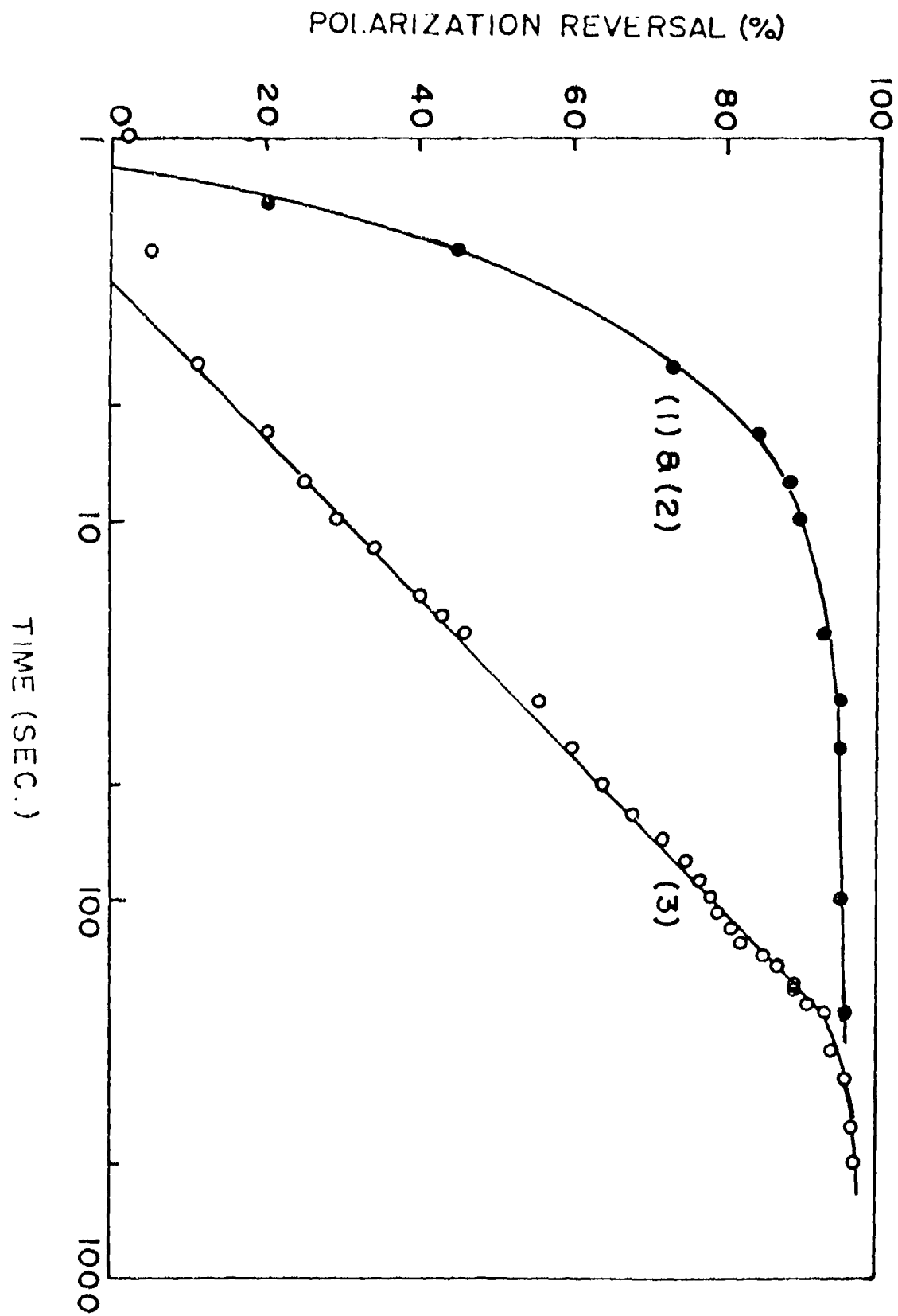


FIG. 6

6- PZT, 56/44

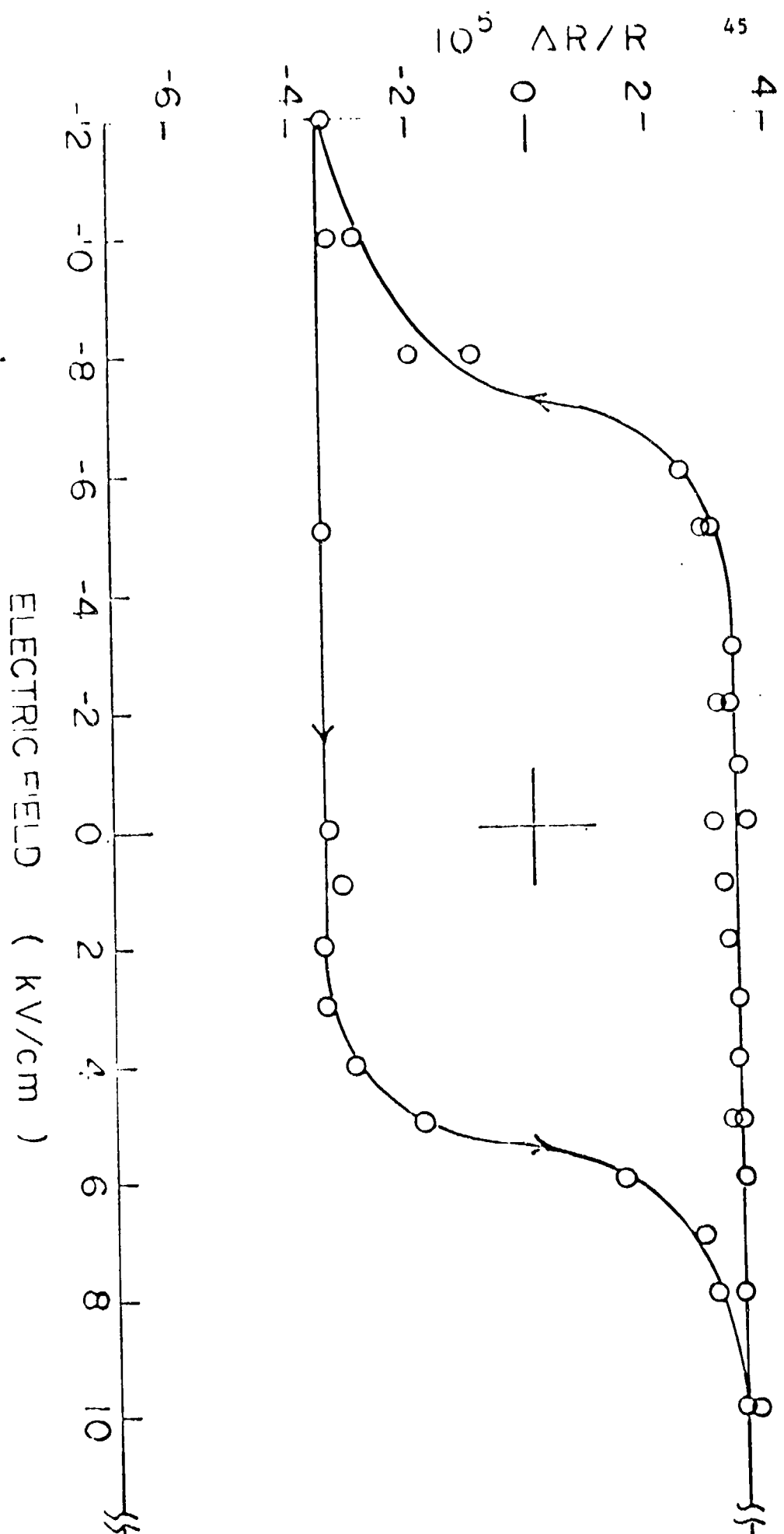


Fig. 7

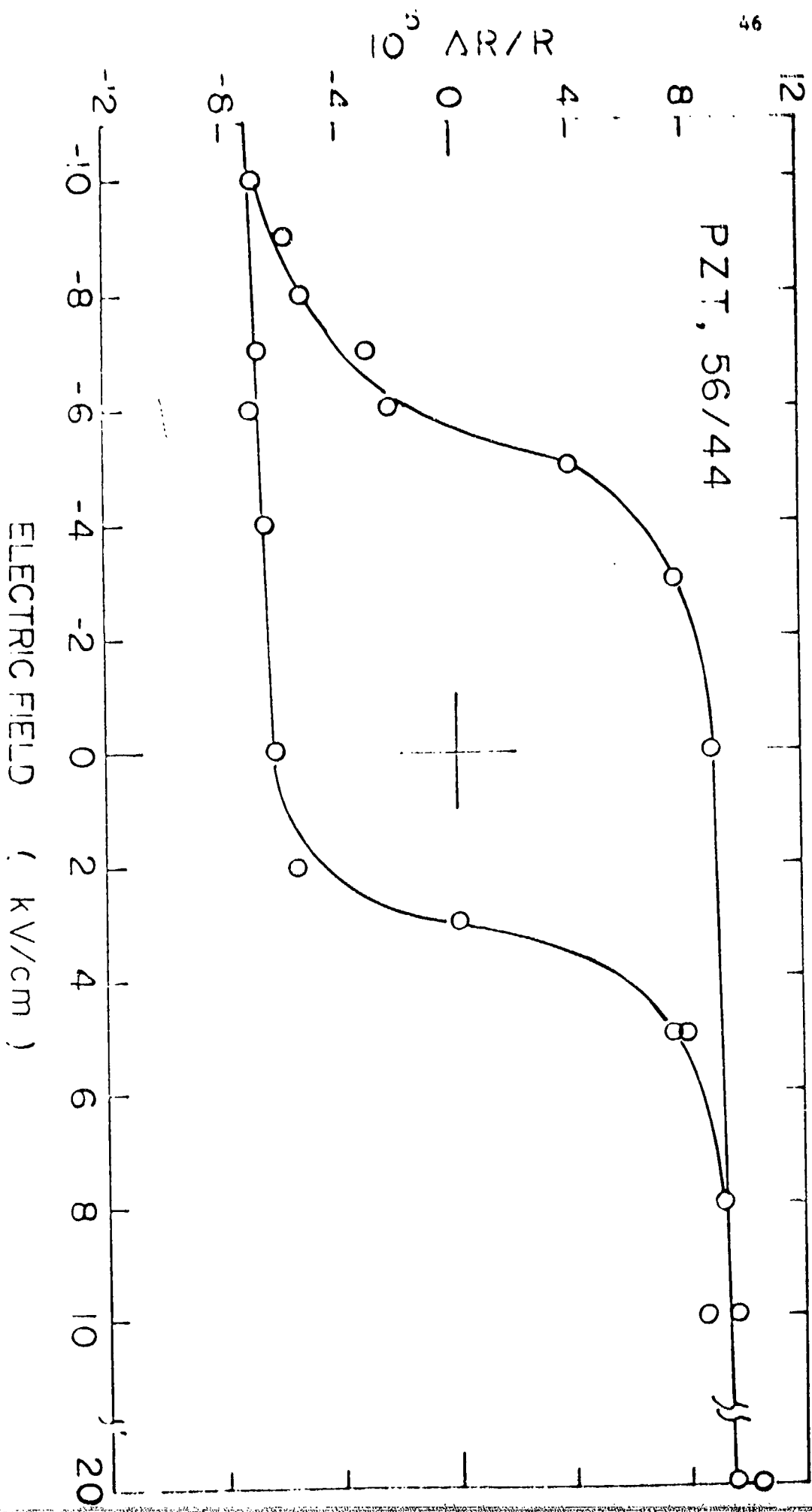


Fig. 8

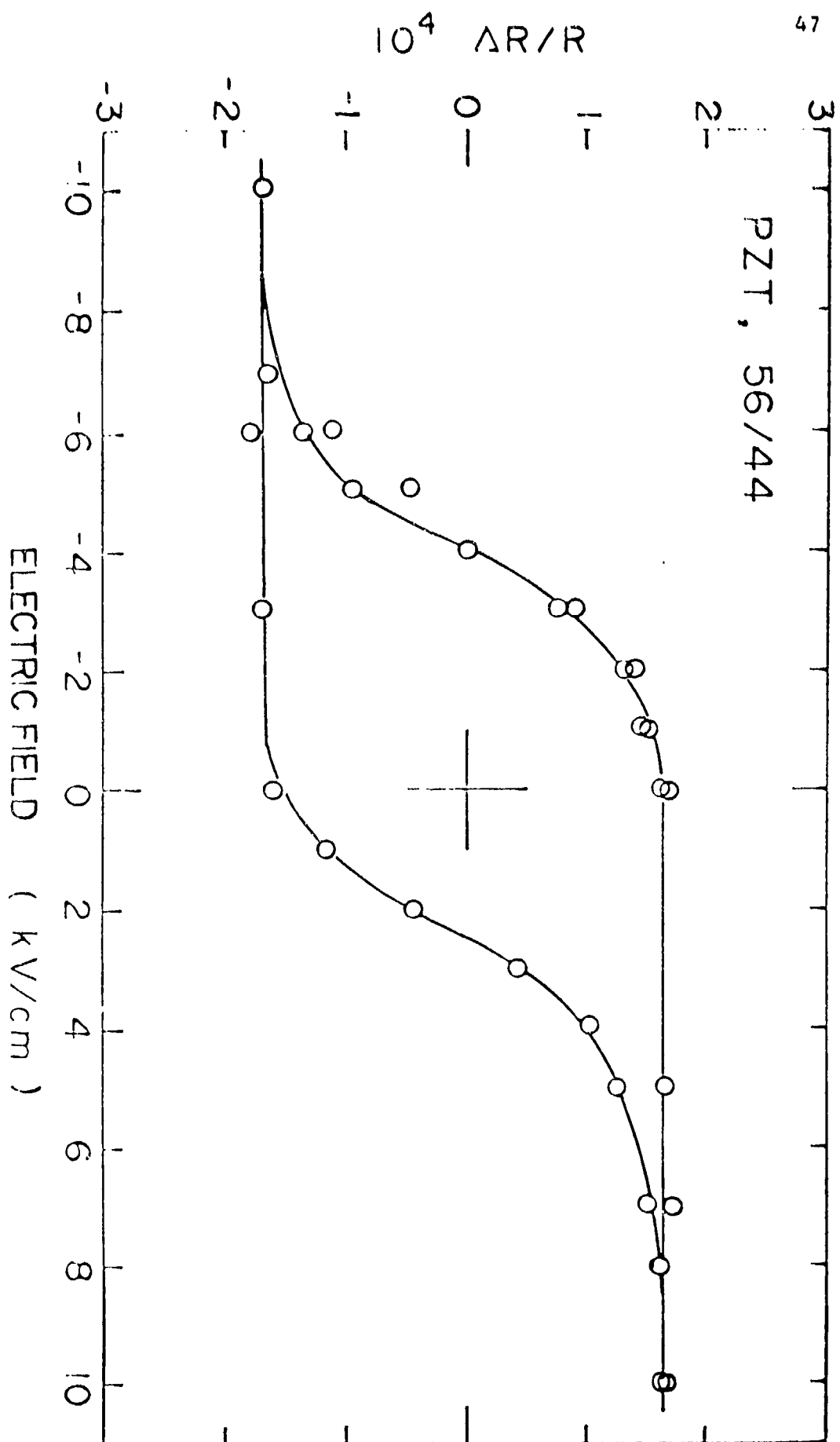


Fig. 9

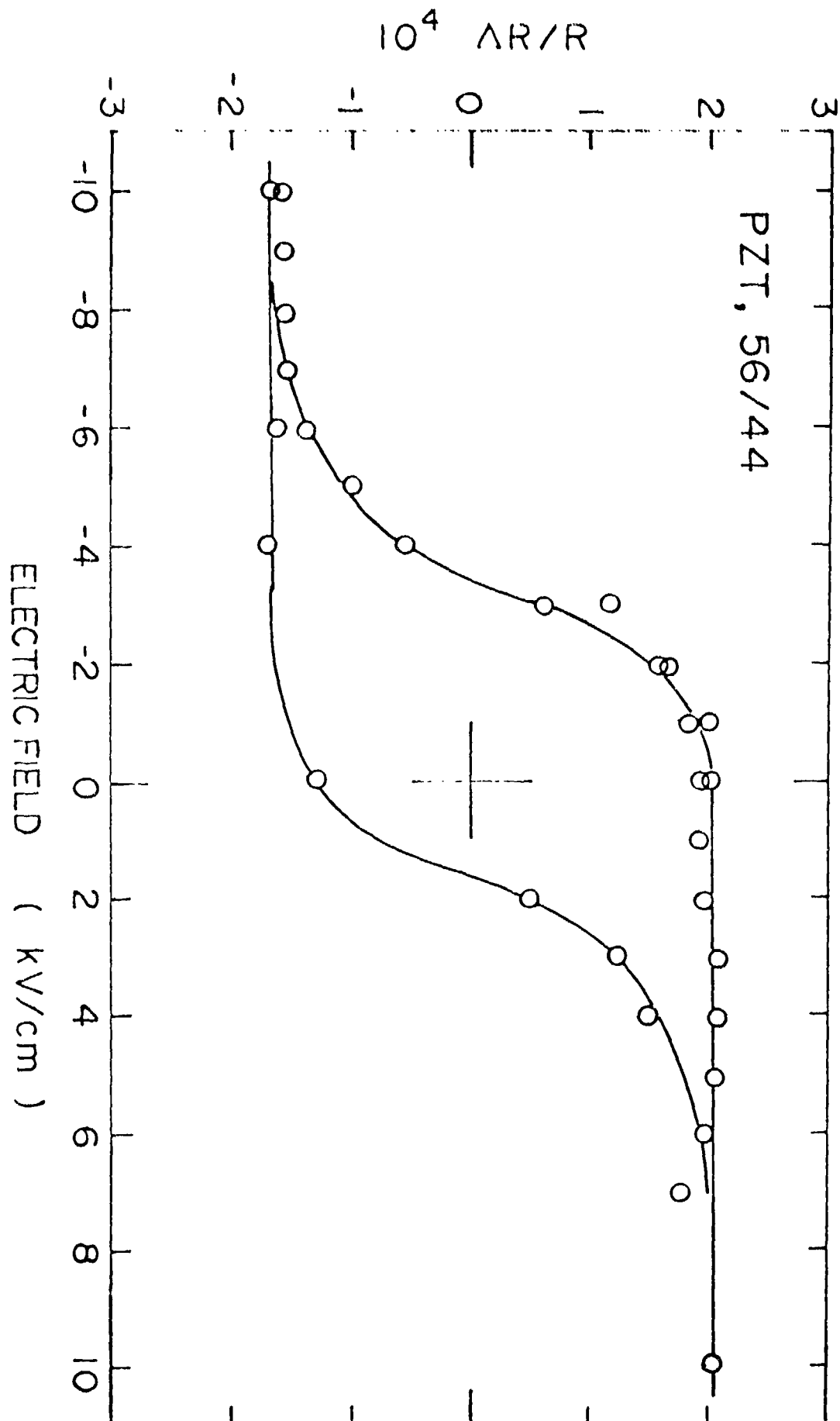


FIG. 10

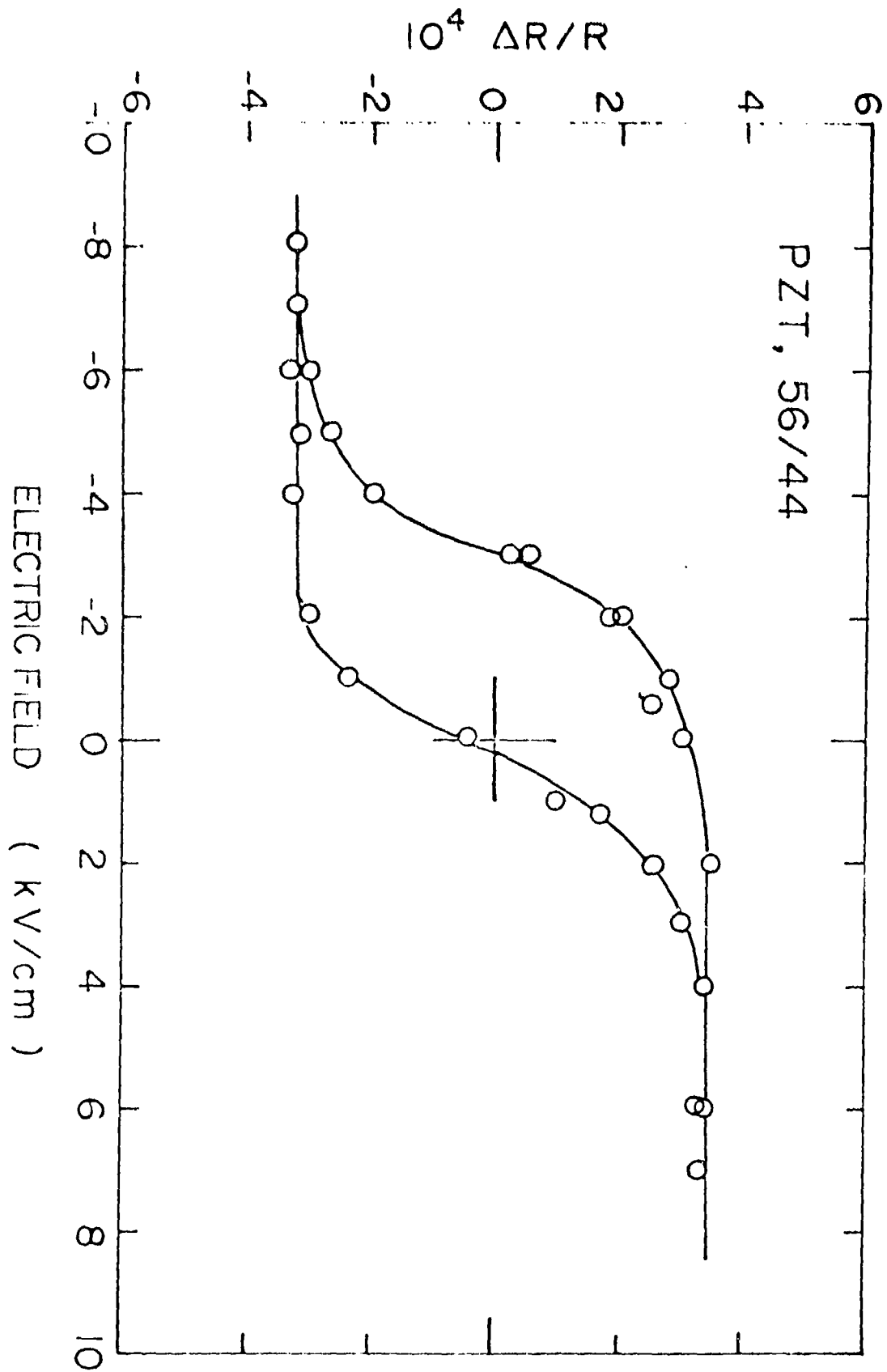


Fig. 11

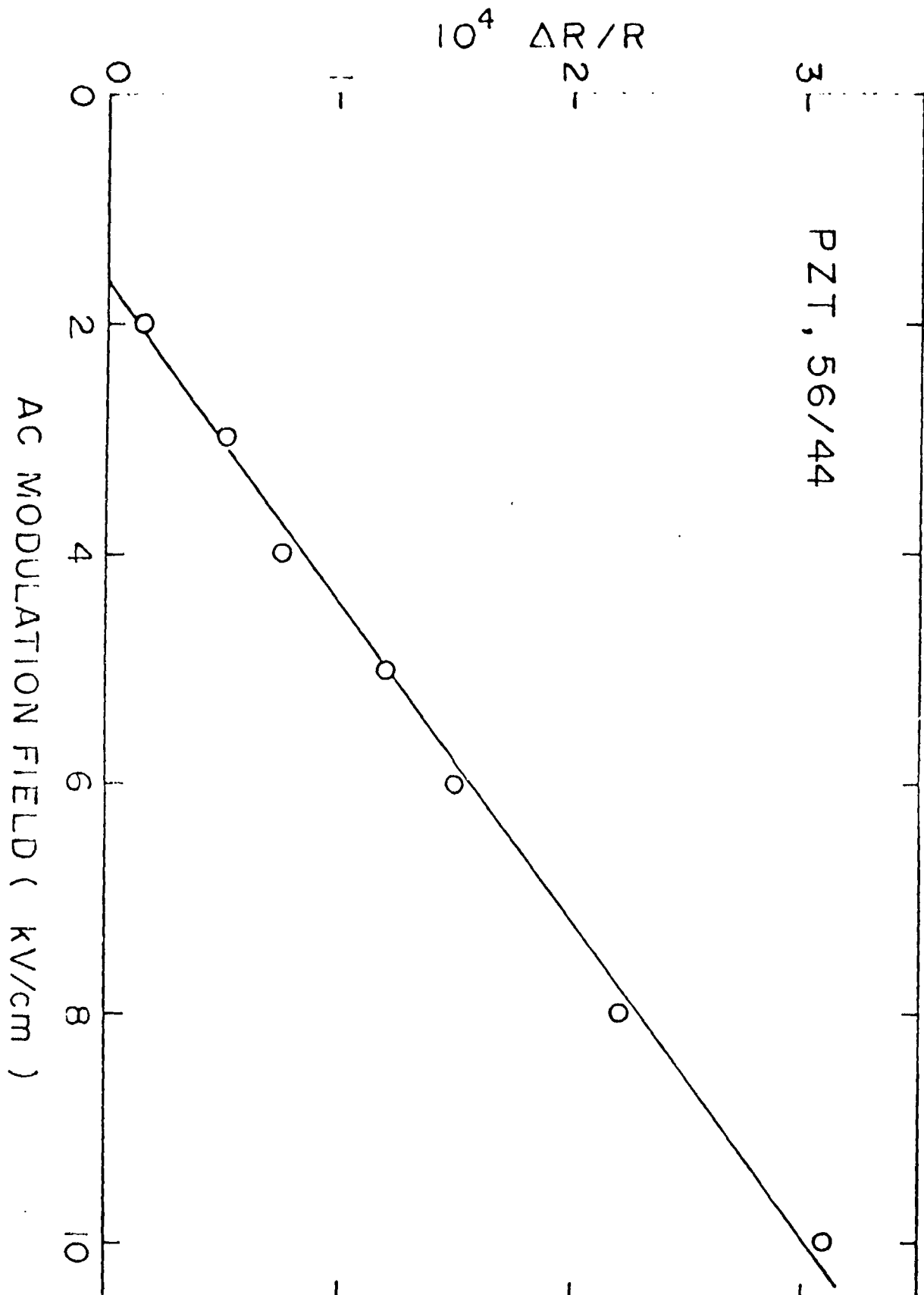


Fig. 12

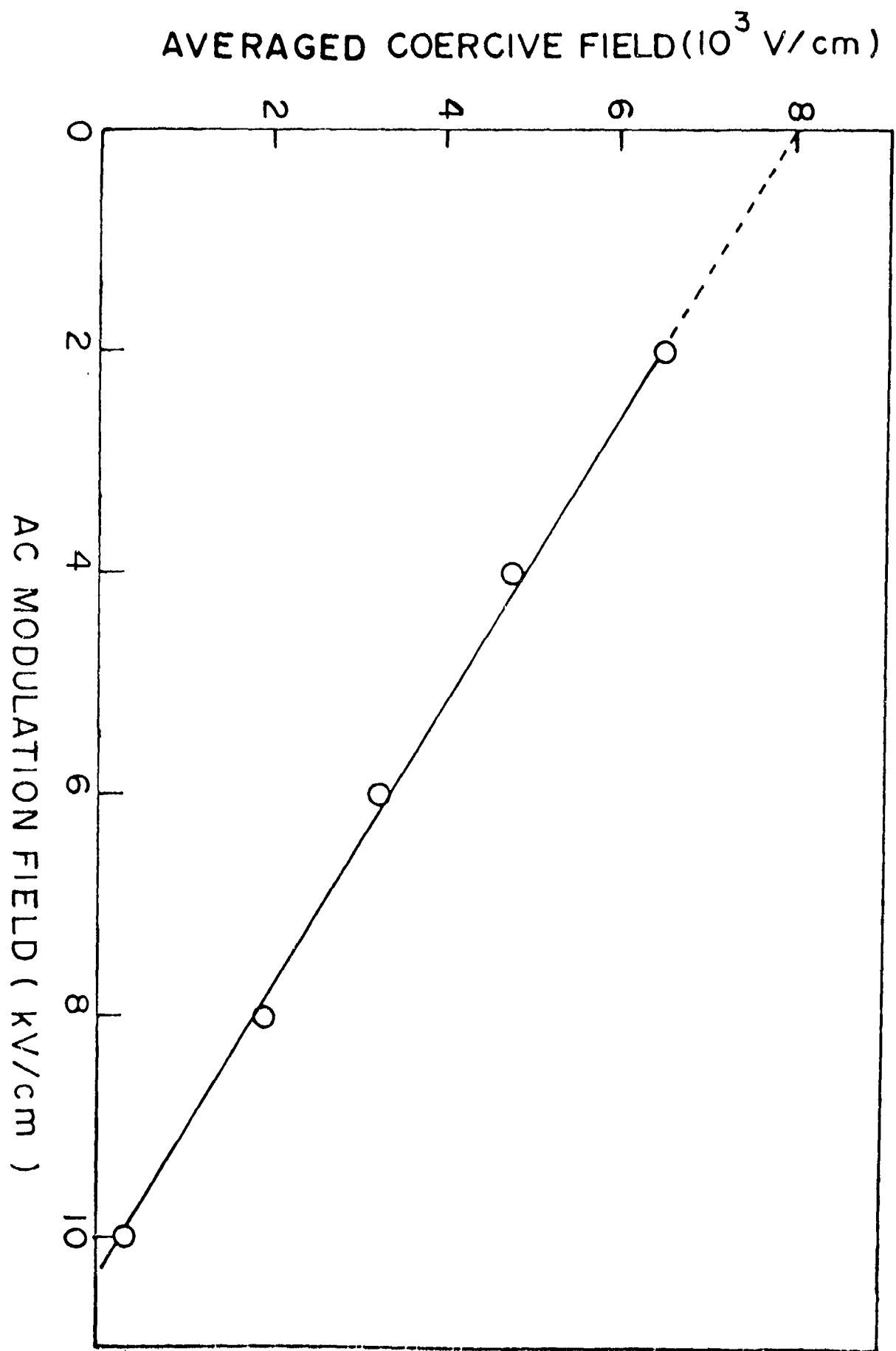


Fig. 13

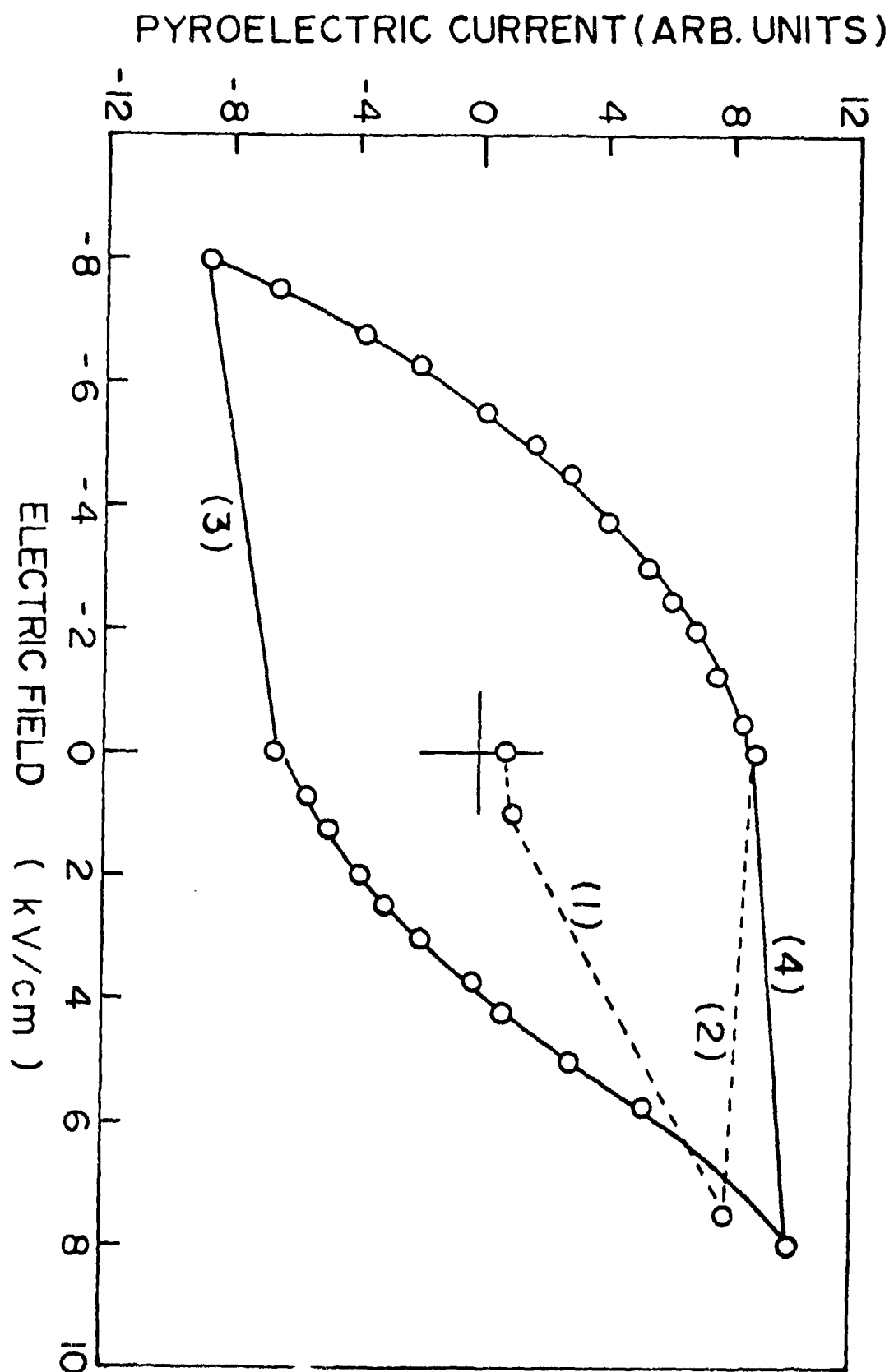


Fig. 14

IV. Summary and Conclusion

Electrotransmission and electroreflectance measurements were performed on lanthanum-doped lead zirconate/lead titanate (PLZT) ceramics. The results show that it is possible, using these techniques, to follow the growth of the polarization with time during poling and its reversal during low-field switching. Oscillations observed in the electroreflectance spectra are interpreted in terms of space charge effects, and the analysis yields an upper bound for the remanent polarization which is in good agreement with the result of a dielectric hysteresis measurement.

Application of the technique of surface barrier electroreflectance to opaque, insulating PZT ceramics is reported. The results constitute the first observation of hysteresis in these materials by optical means and demonstrate the potential value of this method in studies of the switching and aging of ceramics. Asymmetric hysteresis and switching behavior is described, which is apparently related to the growth of space charge fields during aging. The time dependence of the polarization during low-field switching is shown to resemble closely that of the dielectric and piezoelectric properties during aging.