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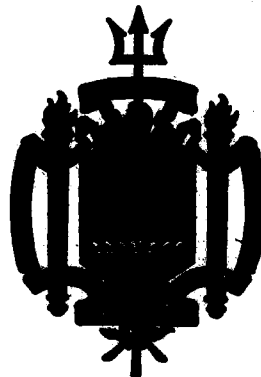
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A TRIDENT SCHOLAR PROJECT REPORT

NO. 118

CAPACITIVE PRESSURE TRANSDUCERS AND
PRESSURE FIXED POINTS



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CAPACITIVE PRESSURE TRANSDUCERS AND
PRESSURE FIXED POINTS

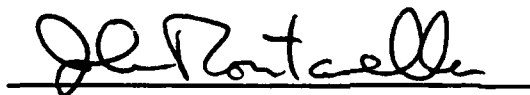
A Trident Scholar Project Report

by

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Annapolis, Maryland



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Physics Department



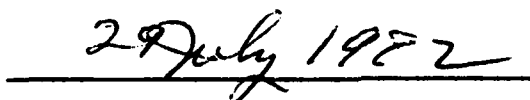
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Accepted for Trident Scholar Committee



Chairman



Date

Abstract

The audio frequency electrical properties of lead fluoride have been studied in order to investigate its possible use in the construction of a capacitive pressure transducer. Previously, the construction of this device has been precluded by lack of materials with both a high pressure coefficient of capacitance and a low coefficient of temperature. Lead Fluoride has been doped with strontium fluoride in an attempt to create a material desirable for such a device. It was found that a material of the desired properties could be approached by increasing the concentration of strontium dopant. However, the crystals with dopants at the desired concentrations could not be grown easily and effort in this area was curtailed in order to pursue the definition of fixed points for lead fluoride at various dopant concentrations.

The pursuit of data on fixed points led to the discovery that PbF_2 will transform from the cubic to the orthorhombic phase at pressures significantly below those previously reported. The trend of the data suggests the possibility that the cubic phase of PbF_2 may be entirely metastable below 600K. Also evidence was found indicating that the phase transformation of PbF_2 is a two stage process, and that the introduction of anion excess materials as dopants may suppress the

first stage of the transition allowing the second stage to proceed immediately.

PbF_2 is a rather good superionic conductor. And, as a result, the increased understanding of its behavior provided by this work may lead to an application as a solid state electrolyte.

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Acknowledgments

Many people were of great assistance to me in finishing this paper. And it is not the least of these many people who were the ones with the encouraging words. Encouraging words are very important, and those words were the drive behind continued effort in difficult times.

Also, not the least of these good people were the ones that gave selflessly of their personal time to help on a problem. These people too I thank.

I also owe a great debt to those people who tolerated my sometimes less than selfless behavior when I was trying to make a deadline I had set for myself. Thank you for understanding and tolerating.

But, most of all I would like to thank my advisors, Dr. John J. Fontanella and Dr. Mary Wintersgill. For they did all of the above things and many more that I cannot even begin to list. They were always patient and ready to help in any way they could. It would be difficult to count all of the hours that they have devoted over the last year in helping. The time that they devoted, more than anything else, made this work a rewarding experience.

Other people who must be mentioned by name are Dr. Allen Chadwick who made all of the crystals used in this work, and Dr. Carl Andeen of Case Western Reserve

University who built the miraculous impedance bridge
that made taking data so easy.

Thank you,
Frank P. Pursel
Midn. USN

1. Introduction

Lead fluoride (PbF_2) has been the subject of intensive experimentation in recent years¹⁻⁵ as it is an example of a superionic conductor. Superionic conductors have shown great promise as solid replacements for the electrolytes in conventional batteries. However, when found with a cubic crystal structure PbF_2 has many anomalous properties. Its dielectric constant is much greater than the dielectric constants of isomorphous compounds such as CaF_2 , SrF_2 , and BaF_2 --about 31 vice 7 for the others. Also, its dielectric constant decreases with increasing temperature which is not the case for any of the other compounds. But, most significantly with respect to the current work, PbF_2 also exists with an orthorhombic structure at room temperature and pressure. It was known that, after transforming from the cubic to the orthorhombic phase, by increasing the pressure to about 4000 atmospheres at room temperature, and then returning the crystal to atmospheric pressure the crystal would remain in the orthorhombic phase. It had previously been thought that the transition from a cubic structure to that of an orthorhombic crystal structure occurred only at these high pressures (see figure 1-1). The main result of the present work is to show that the cubic to orthorhombic phase transition of PbF_2 occurs at

pressures significantly below those previously reported. Also, the trend of the data suggests the possibility that cubic PbF_2 may be entirely metastable below 600K. That is to say, the cubic-orthorhombic phase transition will take place at any pressure if enough time is allowed, as long as the temperature is below 600 degrees Kelvin. It is also shown that the cubic to orthorhombic phase transformation is a two stage process. Finally, the usefulness of PbF_2 in pressure gauges is discussed.

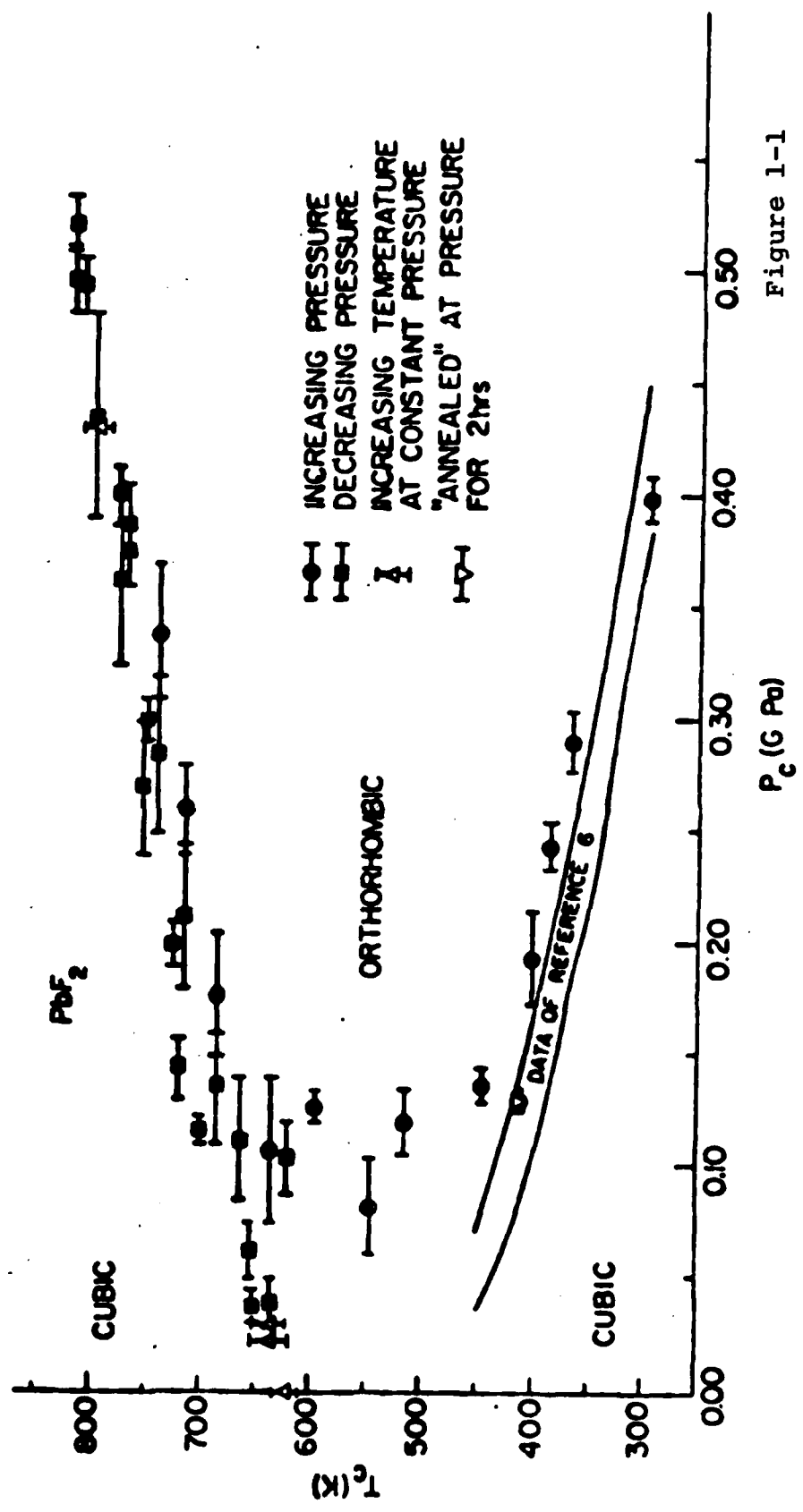


Figure 1-1

Chapter 2 -- Theory

2.1 Conductance and Conductance Mechanisms

Conductance is a very easily measurable quantity that is often very different for different phases of a material. This quality makes the conductance a quantity that changes distinctively when a material changes its structure. It was this fact and the availability of a precision conductance measuring bridge that made the conductance the means by which all the phase transformations in this work were observed. And it is for this reason that the nature of the conductance must be examined.

Conductance is a measure of the ability of a substance to transport charge, and in most materials this charge is transported by electrons. But, in the case of PbF_2 , the dominant charge carriers are ions that move through the lattice. Recent research has indicated that there also exists an electronic contribution to the conductivity, but these contributions are negligible here.⁶ There also exist contributions to the A.C. conductivity from the motion of bound ions; however, these contributions are observed only at relatively low temperatures. For the present work only the free ionic contribution will be considered.

At high temperatures ionic conduction is mediated by either interstitial ions or vacancies. An interstitial ion is an ion that is free within the lattice of the material.

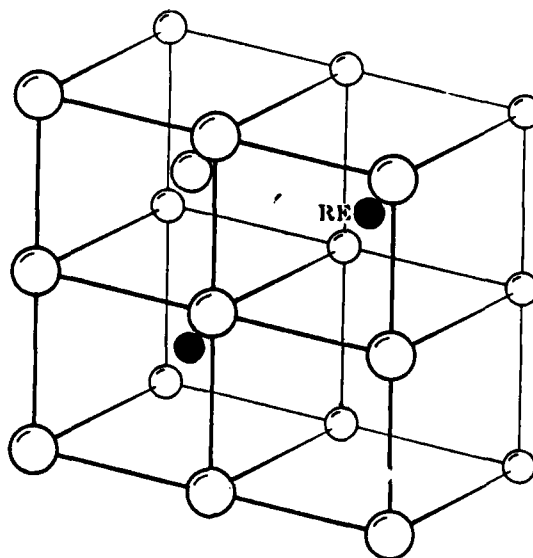


Figure 2-1 shows two interstitial ions in a fluorite type lattice. Here they are rare earths; however, they could be almost anything. (In Crystals with the Fluorite Structure, Oxford: Clarendon Press, 1974, p.105)

A vacancy is the absence of an ion at a lattice point that behaves like an interstitial traveling in the opposite direction. One way to visualize this vacancy as a carrier of charge is to think of two boxes of which one contains a positive charge and the other is empty. The empty box can be thought of as the vacancy. The two boxes represent two lattice points in a crystal. Now, if the positive charge moves into the box that was empty it must, of course, leave the old

box vacant. Hence, the apparent motion of the vacancy and, at the same time, a movement of charge. Since the movements of the charge and the vacancy are directly related to one another, the vacancy is often attributed a charge of its own.

The creation of interstitials and vacancies within the lattice can occur in three ways. In the first two cases ions are jarred loose from their normal lattice positions by thermal excitations creating both an interstitial and a vacancy. Both the interstitial and the vacancy are now able to move within the lattice as long as one does not come into close proximity with another of its counterparts. In which case, the two will recombine. If the interstitial resides in the body of the crystal this defect is called a Frenkel defect. If, on the other hand, the interstitial comes to rest at the surface of the crystal, combining with other ions and forming new layers of crystal the defect is called a Schottky defect.

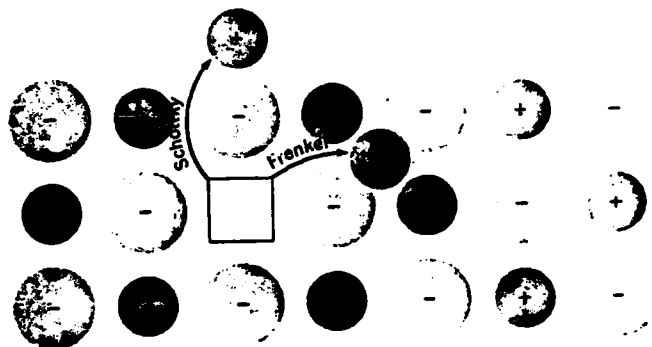


Figure 2-2 shows the difference between a Schottky and a Frenkel defect. (C. Kittel in Introduction to Solid State Physics, New York: John Wiley and Sons, Inc., 1976)

Both the above defects are statistical processes and, as such, they tend to create a relatively constant number of defects. So, in equilibrium, the number of defects being created by thermal excitation is roughly equal to the number of vacancies that are recombining with other interstitials. Another significant point is that these defects are inherently present in the crystal. That is, these defects require no special conditions in order to occur. For this reason conduction due to these mechanisms is termed intrinsic conduction.

There is another method by which interstitials and vacancies may be created, this is by introducing dopants into the lattice. Dopants are ions that may replace the normal ions found within the lattice. When the valence of the substitutional varies from the

valence of the original ion either too many or too few anions will be present to fill the existing lattice points. Excessive anions will become interstitials, and deficiencies of anions will result in the creation of vacancies. For instance, if an atom of valence +3 is substituted for an atom of valence +2 in PbF_2 an extra fluorine ion is also carried into the lattice in order to compensate for the charge imbalance. It is these extra fluorine ions that may dissociate and act as interstitials. Alternatively, the introduction of valence +1 ions as substitutionals for valence +2 ions will create vacancies. This technique that introduces substitutionals into the lattice in order to create additional interstitials or vacancies allows extrinsic conduction to take place. Simply put, extrinsic conduction is the conduction that arises as a result of impurities being introduced into the lattice. The following graph shows the distinct transition that occurs as the dominant contribution to charge carriers shifts from extrinsic to intrinsic mechanisms as temperature increases.

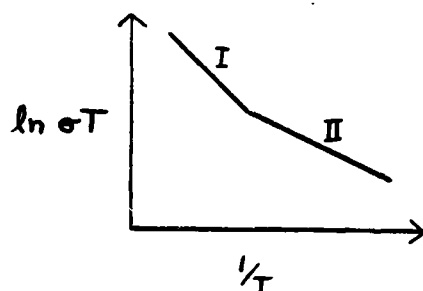


Figure 2-3 demonstrates how intrinsic and extrinsic contributions to conductivity vary with temperature. Region I is intrinsic conduction and region II is the region where the extrinsic contributions to conductivity dominate.

Differences in the conductivities of the two different phases of PbF_2 arise mainly as a result of differences in density that exist between the two phases. The ions simply encounter more obstructions to movement in the more dense material. This makes the more dense material the less conductive. This is clearly reflected by the fact that the conductances vary in roughly the same manner as the densities, with the cubic phase having both a 10% lesser density and a 10% greater conductance.

2.2 Capacitance and Capacitive Pressure Transducers

Capacitance is the measure of a materials ability to store energy. In a capacitor it is defined as the quantity:

$$C=Q/V$$

the case of a parallel plate capacitor (the only type used in this work) the equation for capacitance reduces even further to:

$$C = \epsilon_r A/d$$

Where ϵ_r is the dielectric constant of the material used within the capacitor. (See figure 2-4)

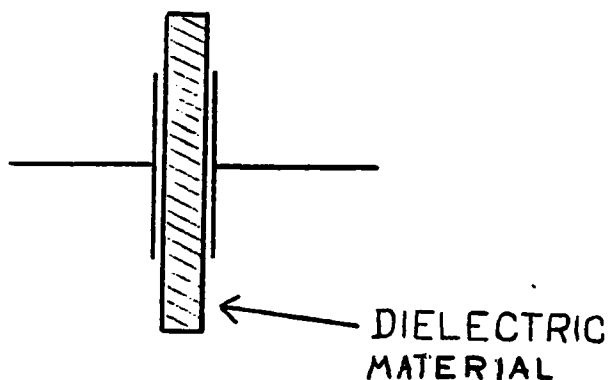


Figure 2-4 depicts a simple parallel plate capacitor utilizing a dielectric material to enhance its capacitance according to the relation $C' = \epsilon_r C$.

It is easily seen that the capacitance of a capacitor varies directly as the dielectric constant of the material it is constructed of.

The concept of a capacitive pressure transducer relies on a material which has a dielectric constant that varies with pressure. Further, in order to be most useful the dielectric constant of the material should not be altered by changes in temperature. Measures of this variability in the dielectric constant with pressure and temperature are called, respectively, the pressure coefficient of capacitance and the

temperature coefficient of capacitance. Materials such as those described above would have large pressure coefficients of capacitance, but zero temperature coefficients of capacitance. The capacitors constructed from this material would change in capacitance with changes in pressure but would not change in capacitance as the temperature changed.

The difficulty has been that the materials known to have a large pressure coefficient of capacitance also have large temperature coefficients of capacitance. The solution to this difficulty lies in the fact that when capacitors are combined in parallel the total capacitance of the system is the sum of the individual capacitances. Hence, the effective temperature coefficient of capacitance may be expressed as:

$$(\partial C/\partial T)_P = (\epsilon_0 A_1/d_1) (\partial \epsilon'_1/\partial T)_P + (\epsilon_0 A_2/d_2) (\partial \epsilon'_2/\partial T)_P$$

or, since,

$$(\partial C/\partial T)_P = (\epsilon_0 A/d) (\partial \epsilon'/\partial T)_P$$

the above is equal to

$$(\partial C/\partial T)_P = (\partial C_1/\partial T)_P + (\partial C_2/\partial T)_P$$

If the temperature coefficient of capacitance is zero then:

$$(\partial C/\partial T)_P = 0 = (\partial C_1/\partial T)_P + (\partial C_2/\partial T)_P$$

or,

$$(\partial C_2/\partial T)_P = -(\partial C_1/\partial T)_P.$$

Physically then, all that is needed is that two materials be found which have opposite temperature coefficients of capacitance. These two capacitors are designed to be of such a size that when connected in parallel their respective temperature coefficients of capacitance cancel each other, creating what is known as a temperature stabilized capacitor. However, the difference between a normal temperature stabilized capacitor and a capacitive pressure transducer is that the materials used to construct it are pressure sensitive. A capacitor of such construction can then be calibrated to measure pressures to a high degree of accuracy.

2.3 Kinetics of Phase Transitions

The transition of PbF_2 from one phase to another phase occurs slowly; the exact rate is dependent on the pressure and temperature. In addition to this the transition does not occur uniformly over the entire volume of the material. Instead, it is a random perturbation of the lattice that gives a small region the activation energy necessary to translate the lattice points from one configuration to another. So, perhaps as small a region as several unit cells may exist in one phase while the entire remainder of the

crystal is in the other phase. However, if the new phase is energetically favored by the pressure and temperature it may trigger neighbors to assume the new configuration; hence, growth of the crystal occurs and nucleation is said to have taken place. This mechanism allows growth to occur in spherical 'domains'. These domains continue to expand as long as conditions are energetically favorable, and if they are given time they will eventually occupy the entire crystal, thus completing the transformation.

The above phenomena can be modeled mathematically.⁷ If v is designated the volumetric growth rate (cm^3/sec) from a nucleated site within the crystal at time t .

$$v(t, T) = \int_t^T v dt$$

where T is the time of nucleation. Assuming spherical growth the volumetric growth rate is just the derivative of the volume of a sphere or $v = 4\pi r^2 dr/dt$. The r represents the radius of the nucleation site. Also constant radial growth may be assumed. So, we let $G = dr/dt$ and $v = 4\pi r^2 G$. Therefore, the radius of the spherulite must be equal to the product of the rate of growth times the time it has been growing or $r(t) = G(t - T)$. Substituting in the equation for v yields the following integral.

$$v(t, T) = \int_t^T 4\pi G^3 (t - T)^2 dt$$

Giving for the volume of a sphere at time t :

$$v(t,T) = 4/3\pi G^3(t-T)^3$$

However, as noted before, it is necessary to consider what happens if several nucleation sites form. The best way to deal with this is to integrate over all nucleation times T . Along with this it is also assumed that the regions of growth remain small and are not impeded in growth by boundaries of other spherulites or edges of the crystal.

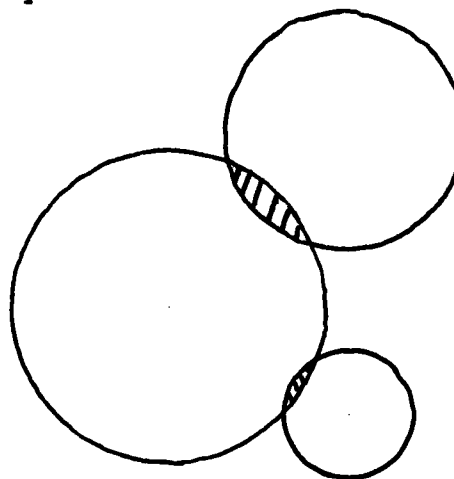


Figure 2-5 shows competing spherulite growth within a crystal.

The variable dn/dt can now be made equal to the number of nucleation sites formed between times T and $T+dT$. So, the mass fraction of all of the transformed crystal at time t is:

$$X(t) = \int_0^t p_c v(t,T) / m_0 (dn/dT) dT$$

The difference in the densities of the two phases can be ignored, and reduction of the above equation gives:

$$X(t) = \int_0^t v(t, T) (dn/dT) dT$$

Letting \dot{N} equal the nucleation rate (nucleations/(cm³-sec)) and assuming that the fractional volume of the new phase is small (so that the nucleation rate is constant over time) the following is obtained:

$$dn/dT = \dot{N}(1-X(t)) \approx \dot{N}$$

So,

$$X(t) = \int_0^t v(t, T) \dot{N} dT$$

Here, a crucial assumption has been made. It is assumed that the nucleation rate is a constant independent of time. This is not always true and will be dealt with later. But, for now, what is called homogeneous, time independent nucleation will be assumed.

The above gives:

$$X(t) = \int_0^t (\pi/4/3) G^3 (t-T)^3 \dot{N} dT$$

and integration yields:

$$X(t) = \pi G^3 t^4 \dot{N} / 3.$$

At this point the assumption can be corrected. In particular as the crystal transforms less and less of the original phase remains to be transformed. Also less and less of the old phase remains to be nucleated. This implies that since the rate of nucleations depends on the volume of the old phase that is present the nucleation rate decreases with time. To make the current expression reflect this non-constant nucleation

rate let it equal $Y(t)$. Now $X(t)$ is the desired quantity (the one with non-constant nucleation) and it is evident that it can be related to the known quantity $Y(t)$ by the following expression.

$$dX(t)/dY(t)=1-X(t)$$

So,

$$X(t)=1-e^{-Y(t)}$$

And the correct expression can be written:

$$X(t)=1-e^{-\pi G^3 t^4 N/3}$$

Letting $k=\pi G^3 N/3$ the expression can be generalized to

$$X(t)=1-e^{-kt^n}$$

The reason that the exponent n is used instead of the explicit value of 4 is that the expression resulting in an exponent of 4 occurs when spherulite growth and homogeneous nucleation are assumed. These are not necessarily so, and if the theory is reworked utilizing different assumptions the resulting equations differ by that exponent n . Therefore, to make the expression most general the exponent n (the so called Avrami exponent) is utilized rather than the explicit value of four.

Chapter 3--The Experiment

3.1 Sample Preparation

The samples were grown by Dr. A.V. Chadwick at the University of Canterbury, England, by the Stockbarger technique. The technique utilized a graphite crucible into which the lead fluoride was placed. The crucible was surrounded by a large coil connected to a radio frequency voltage source. When r.f. voltage was applied the oscillating magnetic field caused current flow in the graphite and I^2R losses generated the heat necessary to melt the powder. The crucible was lowered through the coil, at first melting, and then allowing cooling, which produced the desired crystalization. The results of this procedure were exceptionally good single crystals about 2cm long and 1cm in radius. The crystals were cut into slabs using a thin diamond wheel saw and ground with emery and silicon carbide to a thin ($<.062$) plate. In general the finished samples were of odd shapes since cutting and sanding often caused the crystals to fragment. Following another gentle sanding to remove the irregularities in the edges, the samples were placed into a vacuum chamber and the chamber evacuated. Argon gas was then bled into the chamber and a large potential was placed across two posts located inside. The large potential ionized a portion of the gas and the energetic ions then scoured

impurities from the surface of the crystals. Aluminum was then evaporated onto the surfaces of each of the crystals. In subsequent work no chemical interaction or other adverse electrical effects were noted in connection with this bond. Sandpaper was used to remove excess aluminum from the edges of the samples. At this point the samples were ready to be used in the experimental work.

3.2 The Temperature Coefficient of Pressure Experiments

The very first work done was somewhat anomalous in contrast with the bulk of this work. It was the measurement of the effects of divalent dopants on the dielectric constant of PbF_2 . The dopant used was SrF_2 .

Exactly two samples were prepared as stated above. The samples were pure PbF_2 doped with 2.5% and 10% SrF_2 . They were placed in a Cryogenics Associates Cryostat at room pressure. The temperature was then controlled to within .01 degree kelvin. The temperature was then incremented between 5.4 and 310 degrees kelvin. The coolants used to cool the cryostat to these temperatures were liquid nitrogen, from 310 to 80K, and when the temperatures went below 80K liquid helium was used. As the temperature was varied both the capacitance and the conductance were recorded.

After the preliminary data was collected and analyzed, estimates were made of the dopant concentrations that would be needed to get the desired results. However, when attempts to grow these crystals were made they were unsuccessful. In an effort to conserve time it was decided to curtail this effort.

3.3 Experimental Apparatus

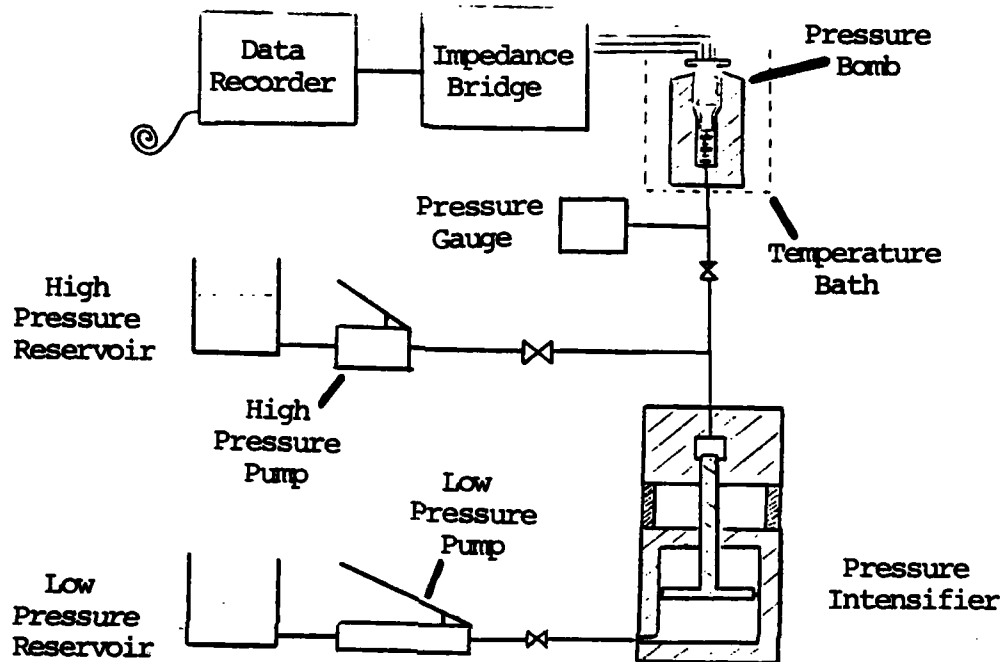


Figure 2-6 depicts the experimental apparatus used.

Figure 2-6 shows the basic elements of the experimental apparatus used in this work. The pressure intensifier required primarily investigation into its correct operation and some engineering to make it work. The piping system, of course, had to be designed and built from scratch. The hydraulic pump was another matter that had to be investigated but in the end proved to be a relatively simple thing. The sample holder and the temperature controlling bath proved to be sources of difficulty.

The sample holder had to hold as many samples as possible in as small a space as possible and not allow the measurements from each sample to interfere with the others. Initially, the samples were to be connected to a common lead. This would have allowed another free lead, which could have been connected to a thermocouple. This would have allowed additional measurement to be made on the generation of heat in the apparatus during a phase transformation. However, this never came to pass, it was discovered in the first two tests of the system that as a transformation of the sample occurred the volume changes of the crystal generated noise that was unacceptable for these measurements. Hence, the sample holder had to be modified to utilize all available leads out of the bomb.

The temperature controlling bath initially consisted of a half of a 50-gal. drum into which was inserted a smaller drum with insulation around it. Into this was placed the temperature controlling fluid (Spinestic 38), a refrigeration coil, a series of heating coils and a sensitive thermostat which turned the heating elements on and off as needed to maintain a constant temperature. The major problem with this setup was that, when the pressure bomb was lowered into the bath, little room remained for the oil to circulate in. This allowed the generation of undesirable thermal

gradients across the pressure bomb. These gradients made the interior temperature unpredictable. The solution was a new, larger temperature bath that was modified to allow good control of the temperature to within about one tenth of a degree celsius.

Another problem came about due to simple lack of experience with high pressure seals. The seal at the top of the pressure bomb was extruding through the seams between the joined pieces of metal. This ruined a number of seals and did not allow pressurization to any useful pressure. The solution to this problem was a simple one; the top of the pressure bomb had to be torqued down with greater force than initially thought. But, along with this discovery came the fact that the sample holder was now too long for the space remaining in the bomb. Corrections were made.

In about the middle of November another difficulty arose; the Harwood A10 pressure intensifier that had been in use suddenly failed. The prospects for getting it repaired quickly were bad, so a new pressure intensifier (Harwood A2.5J) was borrowed from Case Western Reserve University. Cleveland. Ohio. The installation of this intensifier and the decision to upgrade the maximum pressure the system was capable of caused nearly the entire system to be rebuilt.

In all work the pressure fluid used was rather important since it was imperative that it be nonconductive, chemically inert, and a nonviscous liquid at all pressures up to 7000 atmospheres. The mixture used consisted of roughly 80% hexane and 20% spinestic 38, a high grade lubricant; this mixture served admirably. The low pressure fluid was not as crucial and a standard grade motor oil worked well.

Experimental procedure was another aspect of the work that constantly evolved. However, two general techniques typified all the work done. The experiments done utilizing the first technique were all labeled constant rate studies. The constant rate studies were characterized by increases in pressure in specific increments (For instance, if the increment was 50 bars then the pressure would be raised from 100 bars to 150 bars and then 200 bars.) followed by a subjective decision on the part of the experimenter as to when all the temperature fluctuations had settled out and whether or not the conductance or capacitance was changing in a manner that indicated a phase change. Expecting a rapid change of state, as it was initially assumed, this method is sound, since a rapidly changing conductance can be easily seen by the experimenter. However, if the rate of change is slow it becomes increasingly difficult to distinguish between a slow

continuous change indicative of a phase transition, a slow steady change caused by minute temperature fluctuations, and random fluctuations in the conductance or capacitance caused by nothing in particular. Hence, as it was found that the rate of transition occurred more slowly than originally thought, a second technique was used so that the transition would be obvious even if it occurred very slowly.

3.3.1 Constant Rate Studies

The first important result came during pressure run F3. The samples being examined were a pure lead fluoride as a control and a sample of PbF_2 doped with 5% Strontium fluoride. SrF_2 is a compound isomorphous with PbF_2 that is, it has the same crystal shape as PbF_2 . It was found that by repeatedly watching visually for changes in conductance and then incrementing the pressure and waiting for temperature fluctuations to settle out, the pure sample of lead fluoride exhibited rapidly changing conductance which was taken to indicate a transformation. This occurred after the pressure had been increased from 3020 to 3104 bars. The 5% doped sample of lead fluoride was seen to transform between 4942 and 4995 bars. However, upon removal from the sample holder it was seen that this sample had only partially transformed in the short period of time it had remained at that pressure, and since the pressure was at the

limit of the available system's capability it was decided to work at lower dopant concentrations. This was the primary consideration in selecting the samples for F4. The two samples examined in F4 were a pure PbF_2 and a PbF_2 doped with 2.5% SrF_2 . The same procedures were followed on these samples as the previous ones except that the pressure intervals were smaller, allowing greater accuracy. The pure sample's capacitance and conductance were noticed changing when the pressure was incremented from 2889 to 3010 bars. In an effort to conserve time the pressure was then immediately increased to 3.7KB, about 300 Bars below where an educated guess had put the transition. Upon reaching this pressure the conductance and capacitance seemed to be rising slightly; however, it was so slight that it was initially attributed to a slow pressure leak and the pressure was incremented to 3.9kB. At this pressure the changing in capacitance and conductance was very rapid and could not be attributed to the effects of a pressure leak; a transition was apparent. Now the question arose whether or not the earlier rises in conductance were really a pressure loss, or rather an actual transition. Looking back at the data it was seen that the conductance at that lower pressure was lower than previous experience would have expected. Hence, it is believed that the transformation was

observed taking place between 3757 and 3921 bars. As will be emphasized later, this observation made it apparent that the time frame that could be involved in a phase transformation of this type might be much longer than previously anticipated.

The next data to be taken was an attempt to see if trivalently doped compounds influenced the phase transition pressure in a manner similar to the divalent dopant SrF_2 . The representative trivalent dopant chosen was Erbium. In order to see the influence of the dopant best, two doped samples were used. One sample was doped with .1% Erbium and the other 3%. The .1% sample transformed in the 3053 to 3158 bar range. The 3% sample could not be transformed even at 5.2kBar. F6 began as any previous pressure run. The pressure was increased in intervals of 100 bars and at each pressure, after a time to allow settling, data was taken. The first sample was a PbF_2 very lightly doped with Sodium Chloride. The signs of a phase transformation were observed between 3211 and 3303 bars. The pressure was increased to 3.4kBar and then 3.5kBar; data were collected for both of these points. Here the system was allowed to remain overnight. The next day the capacitance and conductance were observed to have changed dramatically from the previous evening, yet the temperature and the pressure were the same. However,

the capacitance and conductance appeared steady. When the pressure was then increased to 4.5 kbar the capacitance and conductance refused to steady out--a transition was occurring.

The next materials to be tested were a vacancy doped sample and another Erbium sample. This time the Erbium was doped only to the 1% level; the vacancy dopant was NaCl. The vacancy doped material transformed at the 3211 to 3303 pressure level. At this point the remaining sample was allowed to remain at 3.5 kbar for roughly 8 hours. Upon returning, the previously untransformed sample displayed radically different values of capacitance and conductance. Further it was noted that the conductance was creeping. A transition was again taking place at an unexpectedly low pressure.

Previous work done on PbF_2 had advocated the view that the phase transformation was metastable and could occur over a relatively wide range of pressures. And here it was decided to test that idea more thoroughly. Two identical samples of PbF_2 were inserted into the pressure bomb for testing. It was reasoned that the transformations should occur at different pressures for each sample in accordance with the previous work. However, when the samples were placed under pressure and scrutinized, they both transformed at identical

pressures as far as could be discerned by the fluctuations in the conductance. They both transformed at between 2952 and 2997 bars. Here the pressure had been incremented in 50 bar steps until the slightest change in conductance became apparent. This was the most accurate determination of a transformation pressure in the work to that point

At this point the size of fluctuations in conductance that seemed to be indicative of the beginning of a phase transition were very small. In fact, the size of the fluctuations were becoming so small as to be difficult to distinguish from random noise inherent in the detection system. This began to become a nagging problem and one more simultaneous experiment was proposed that would utilize a larger amount of time in order to assure that a transition was not going undetected at lower pressures. This experiment proceeded in a regular fashion up to a pressure of 2552 bars. No sign of a transformation was seen at any pressure even though the criterion for stability were the strictest yet imposed. However after making certain of the stability of the sample at 2552 bars and allowing it to remain undisturbed overnight, a large change in the conductance was observed for both samples. This was entirely unexpected.

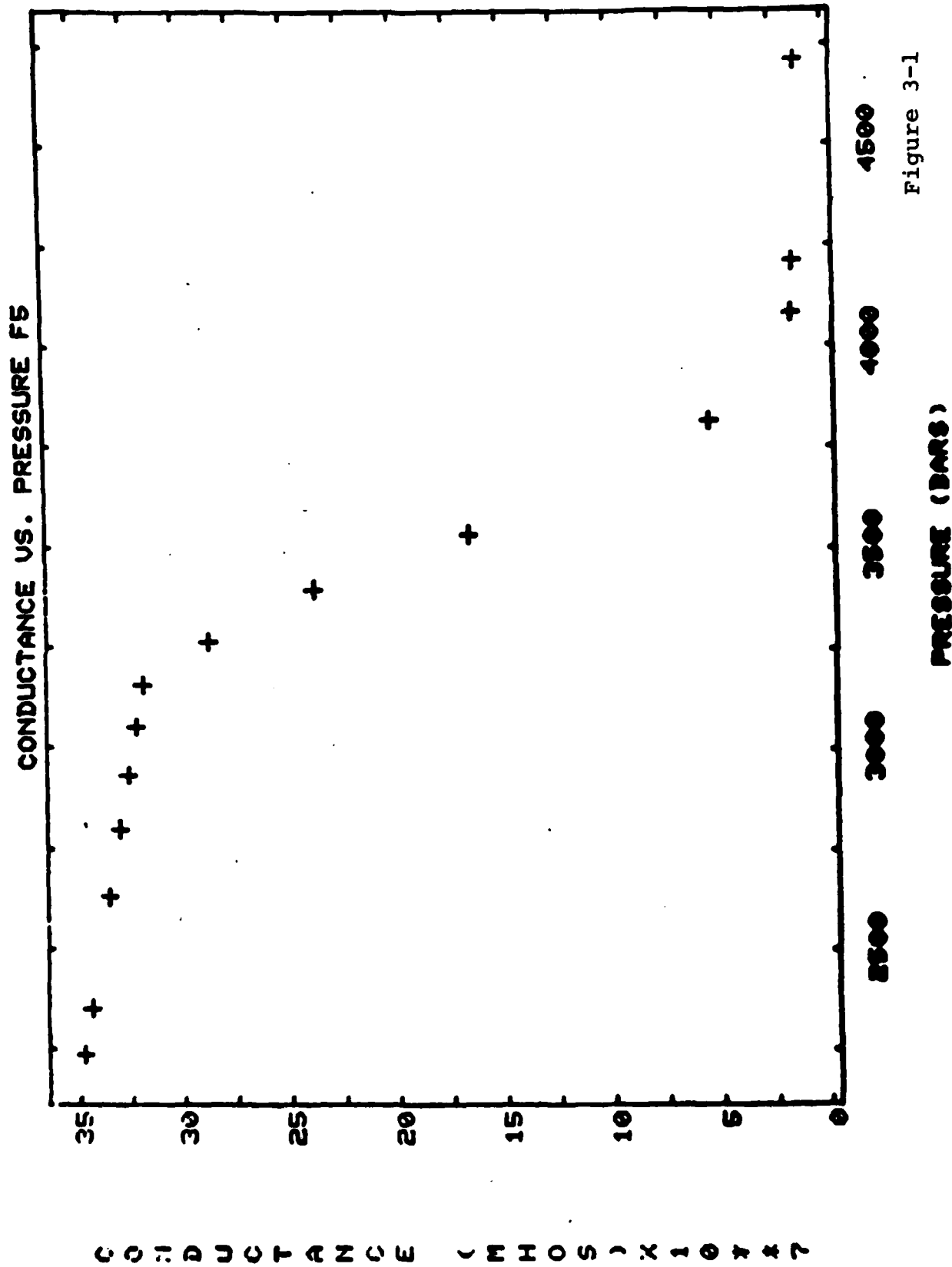


Figure 3-1

Pure PbF_2 had never previously been observed transforming at such a low pressure.

It was thought that since the transformation now appeared to be occurring rapidly, good information could be derived by lowering the pressure until the transformation stopped. However although lowering the pressure did slow down the rate of transformation to a crawl it never stopped it entirely even when the pressure was depressed as far as 2165 bars.

This result made it apparent that the transition could not be easily detected using the previous procedures. A new technique had to be used in order to be able to detect at what pressure PbF_2 would transform.

3.3.2 Constant Pressure Studies

The series of experiments that attempted to pin down the transformation pressure of PbF_2 were called constant pressure experiments because the pressure applied to the samples was indeed a constant value. By observing the conductance of the PbF_2 for an extended period at a single pressure the certainty that a transformation was or was not occurring was much improved. Also by printing this data onto paper tape which was subsequently read into a computer these studies allowed an insight into the kinetics

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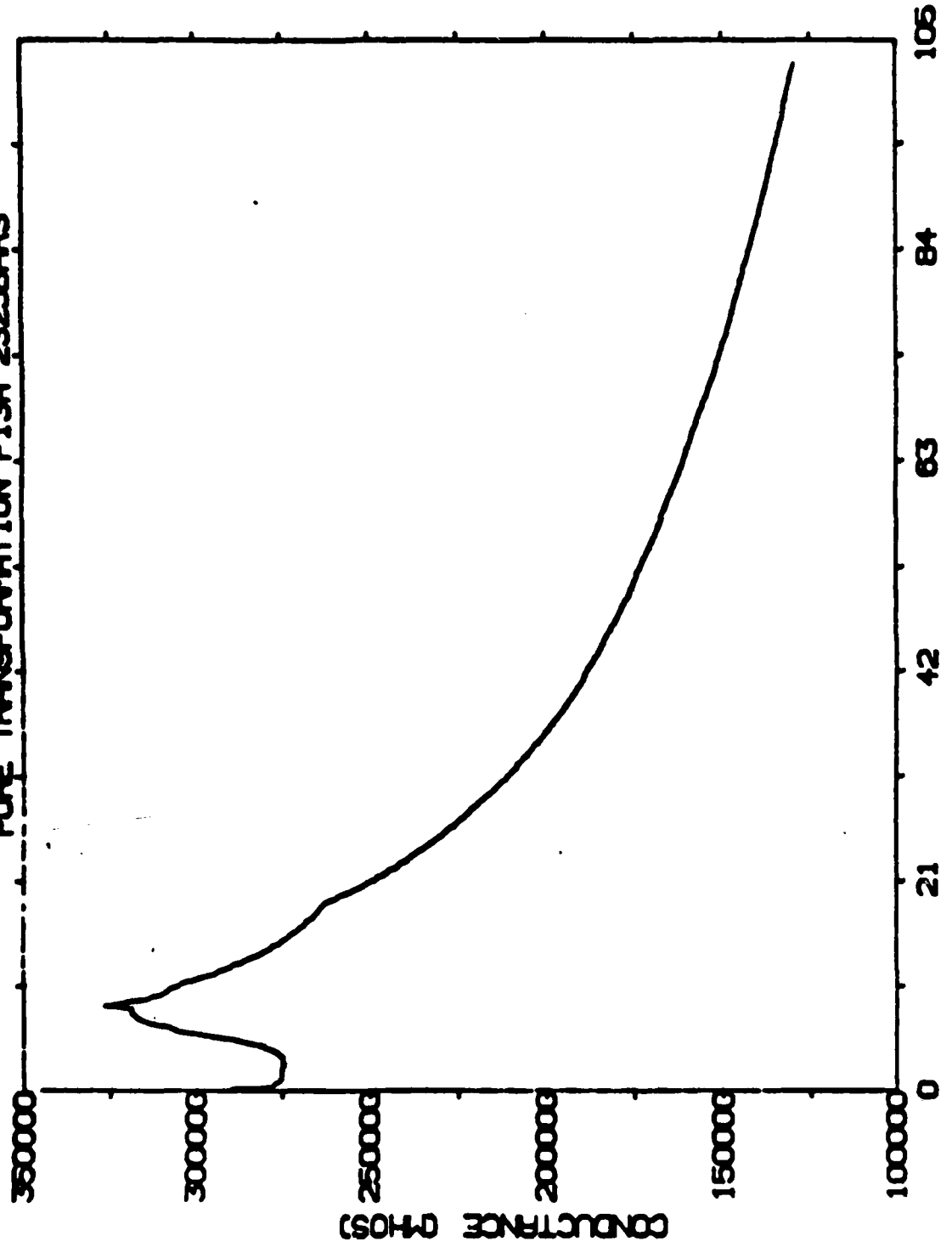


Figure 3-2

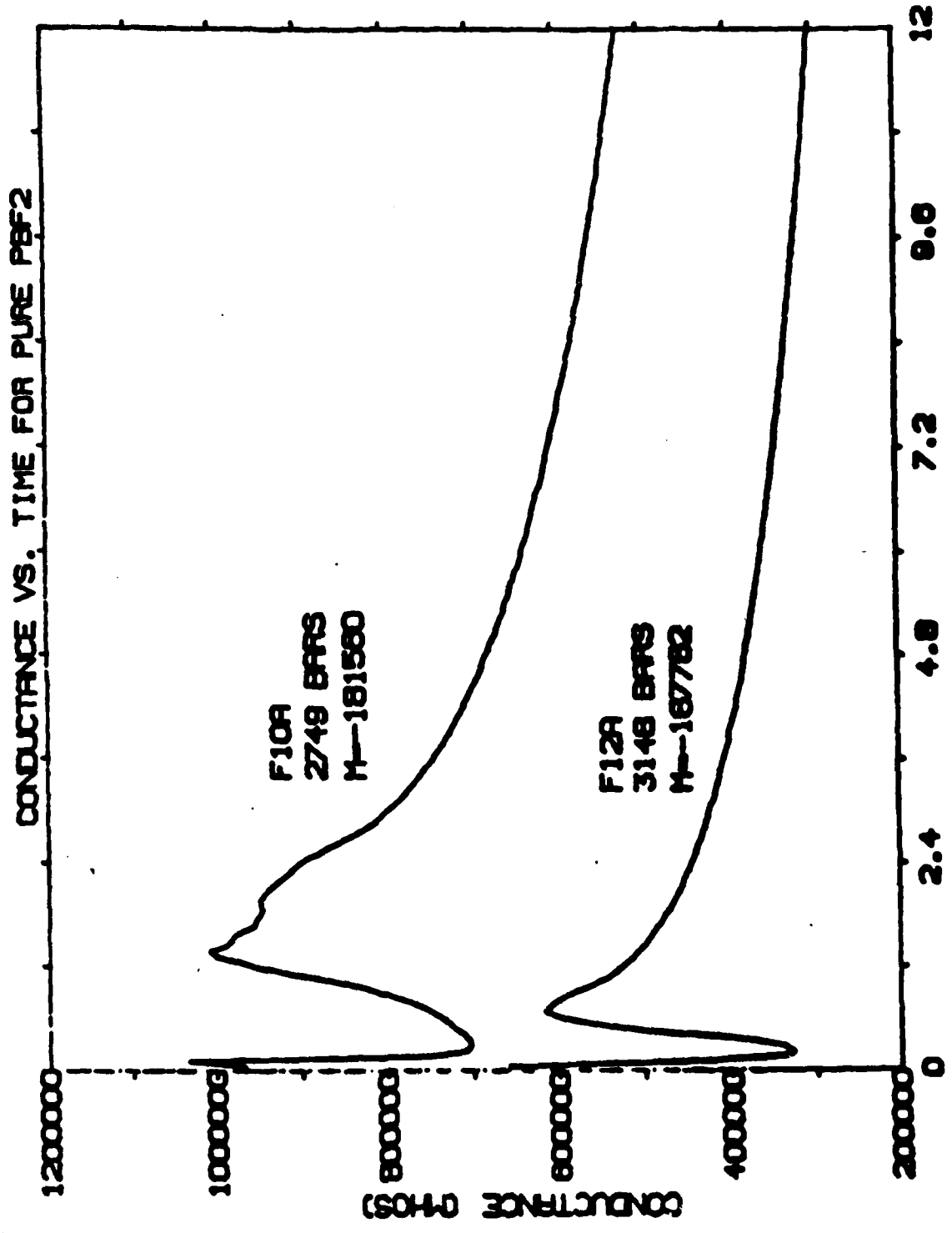


Figure 3-3

of this phase transformation. This information on the kinetics of the transition not only allowed the determination of the occurrence of a transformation but also gave a glimpse of the mechanisms by which materials are able to change structure.

The work in this area began with two identical samples of PbF_2 both doped with .2% holmium. The intent was to clarify the questions concerning stability and reproducibility of a particular transformation at a particular pressure. The technique used was simple--the samples were placed into the pressure system and the pressure increased to the desired level. Then, after a period of time in which thermal gradients were allowed to settle out the complex impedance bridge was turned on and programmed to take data at a specific rate. All this data was printed to paper tape and subsequently fed into the computer for further analysis. The measurements continued in this fashion until either the sample transformed and the conductance appeared to be settling out in the new phase or it appeared that the sample was not going to transform in a reasonable period of time. In general, the period of time allowed per sample was one or two days although some samples were allowed to remain for an entire week. The samples of Ho doped PbF_2 were allowed to remain under pressure for 13 hours and 56 minutes.

The next samples to be transformed in this manner were a pure sample of PbF_2 and a PbF_2 doped with 1% Erbium. The pressure to which they were initially subjected was 1500 bars. This pressure was much lower than any pressure at which a transition had previously been seen. No transformation was seen at this pressure after 12 hours and it was decided that to look longer was futile. Accordingly, it was decided to increase the pressure to 3500 bars and watch for the phase change. At this point the pure sample rapidly transformed. However the doped sample showed only a very slight change in the capacitance that occurred only after many hours and it was not believed to be transforming. Yet, when it was removed from the pressure chamber and examined closely a small corner region had changed from a clear to a milky white crystal indicating a phase transition occurring.

The next samples were pure and holmium doped (.2%) pieces of PbF_2 . The pure sample transformed at 2749 bars, but the doped sample required a pressure of 3500 bars before it quickly transformed.

In all the other samples tested both samples transformed at the same pressures; hence, since no special treatment was accorded to any of these no special narrative is required here and all necessary information is conveyed in the following table.

Table 3-1

Sample Code	Composition	Temperature degrees Kelvin	Pressure Bars
F7B	PbF ₂ :Ho .2%	58.9	2952
F10A	PbF ₂ 'pure'	58.9	2749
F10HB	PbF ₂ :Ho .2%	58.9	3500
F12A	PbF ₂ 'pure'	58.9	3148
F12B	Pbf ₂ :Ho .2%	58.9	3148
F13A	PbF ₂ 'pure'	58.9	2323

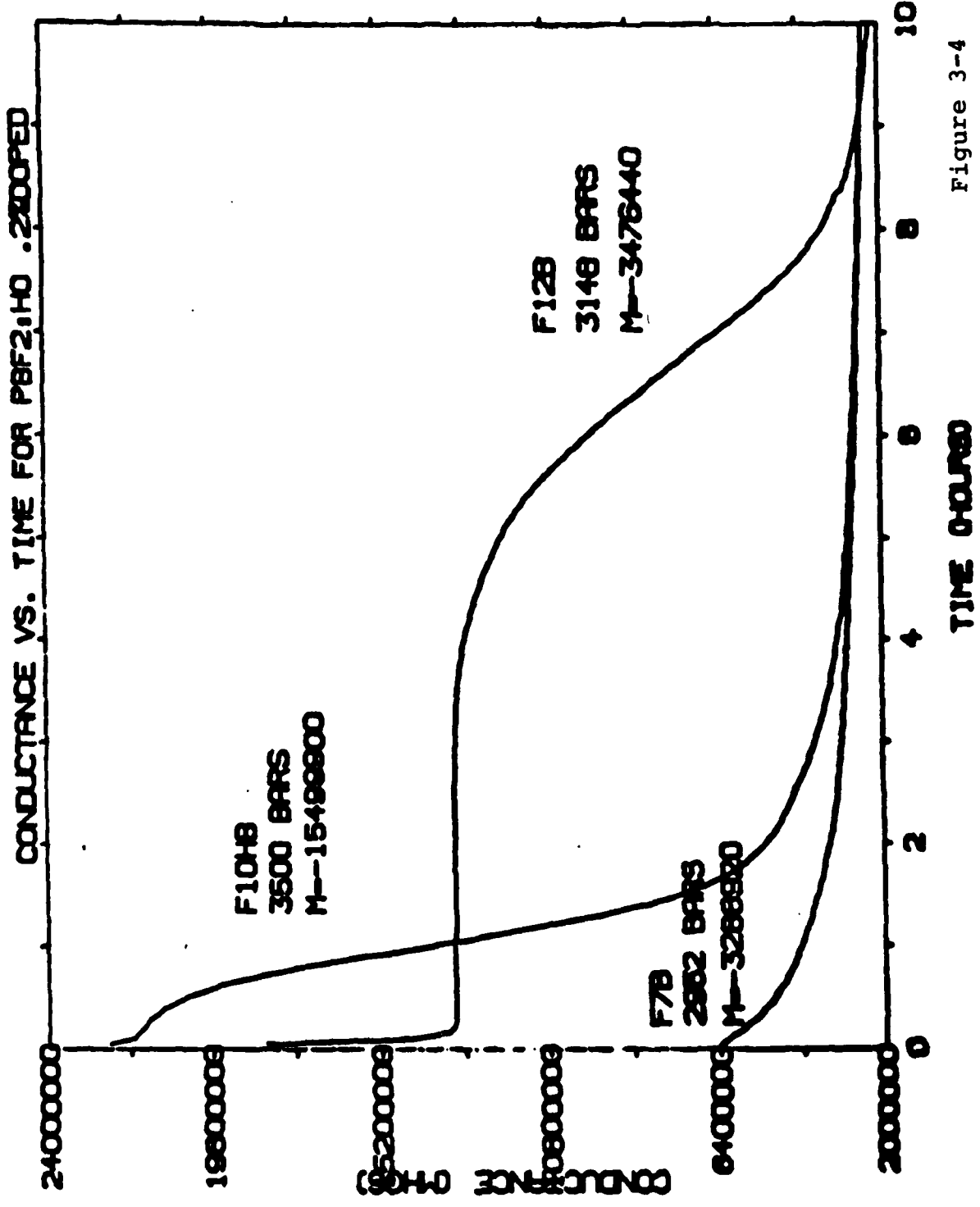


Figure 3-4

Chapter 4--Results and Conclusions

4.1 Results

A plot that is representative of the data taken in the constant rate studies is shown in figure 5-1. This data, as was later shown, yields little true information about the phase transformation; however, it was results of this type that eventually led to the results depicted in figs. 5-2 through 5-4. Several important points may be gleaned from this data. First, the pure lead fluoride samples all displayed irregular changes in conductance in the first several hours of their transformations. This irregular period is then followed by an extended period of orderly transformation. This is indicative of a two-stage transition. The absence of this initial irregular behavior in the anion excess doped materials all depicted in figure 5-4 indicates that the initial irregular behavior of the transformation may be suppressed by doping the original material so as to generate interstitials.

A third point that may be made is that the phase transformation occurs at a slow rate at pressures far below those determined by previous experimenters.^{2,5}

The final point is illustrated by figure 4-2. Divalent dopants, such as SrF_2 , may be used to alter the temperature dependence of the dielectric constant of the material. This effect may be used to advantage

in the creation of a zero temperature coefficient capacitive pressure transducer. Figure 4-1 depicts the change in the dielectric constant of two types of lead fluoride, one doped with 2.5% SrF_2 and the other with 10% SrF_2 . Both sets of data are normalized to the value of the dielectric constant of the material at 103K.

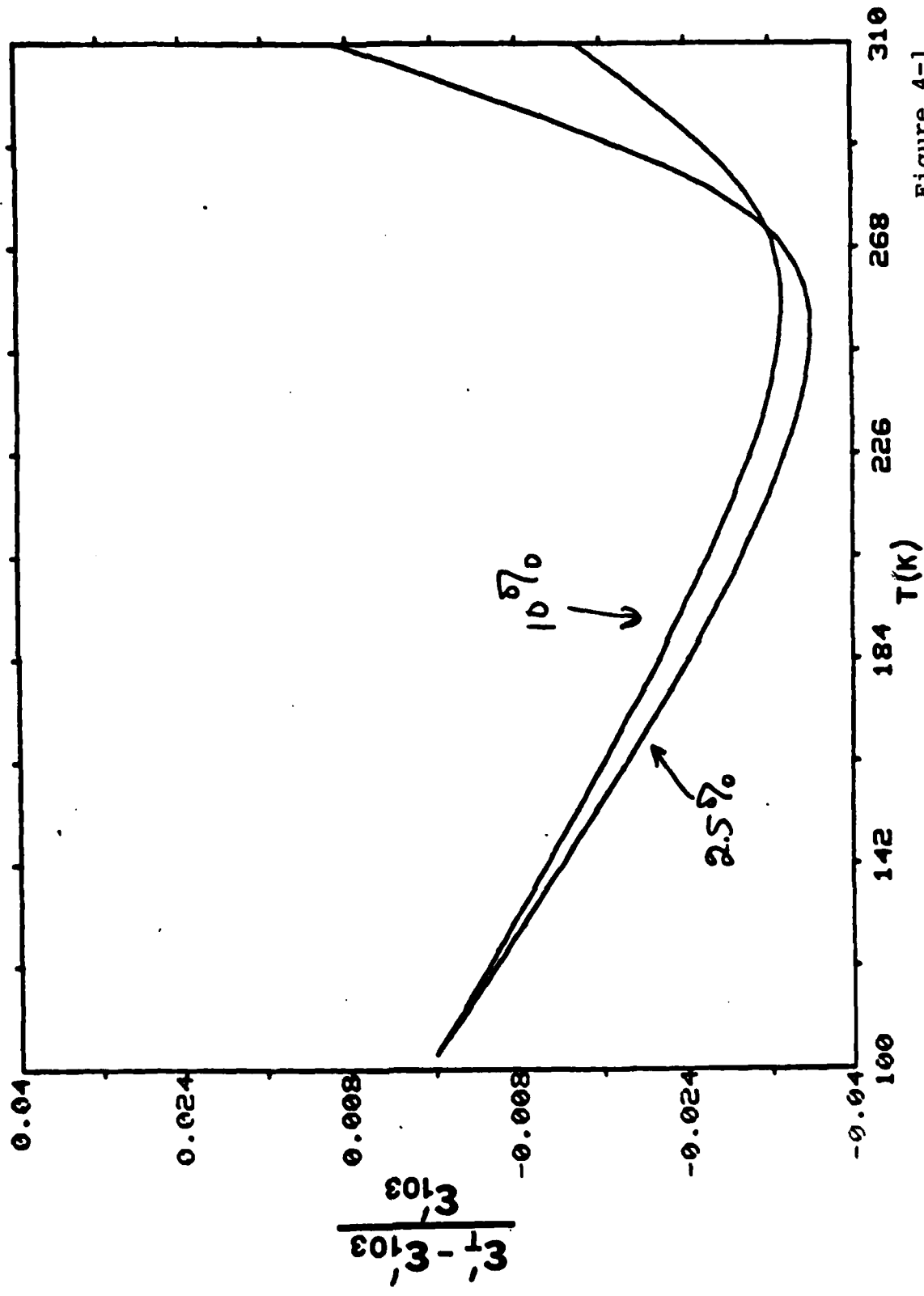


Figure 4-1

$\frac{3}{103}$
 $\frac{3}{103}$

4.2 Analysis

The large quantity of data collected required the use a computer for analysis. The computer was found to be the most efficient means by which the data could both be sorted and numerically manipulated

Upon receipt of the raw data the computer was programmed to sort the data by sample frequency type data desired (capacitance or conductance), and then to convert from the standard output format of G/w to straight conductance.

At this point, the data was plotted directly by the computer. The use of irregularly shaped samples made measurements of of the area and thickness of the samples nearly impossible. Since the data consisted of the geometrically dependent quantity conductance rather than the intrinsic conductivity, there was no easy comparison.

An attempt was made to fit an exponential to the curves. It was hoped that a time constant could be derived from this that might allow a fair comparison of the rates. However, it was soon determined that the curves were not truly exponential except near the end of the transition. It was not felt that the fit in this region of the curve was truly representative of the rate and so the results were discarded.

A second attempt to find a rate parameter was more successful. The reasoning behind the second attempt was as follows. The relation between the conductance and the conductivity is this

$$G = \sigma A/d$$

The derivative of this quantity is

$$dG/dt = (A/d) (d\sigma/dt)$$

Dividing by G gives the desired expression that is not dependent on the geometry of the sample--

$$(1/G) (dG/dt) = (1/\sigma) (d\sigma/dt)$$

The point at which it was believed this quantity had the greatest validity was the point at which the transition was occurring most rapidly (most rapidly in the second stage of the transition). A computer program was written which calculated this value for each curve; the results of this work are tabulated in table 4-1.

Table 4-1

<u>Sample</u>	<u>Pressure (Bars)</u>	<u>(1/G) (dG/dt)_{max}</u>
PbF ₂ 'pure'	2749	.212298
PbF ₂ 'pure'	3148	.332463
PbF ₂ 'pure'	2323	.0377245
PbF ₂ :Ho .2%	3500	1.28128
PbF ₂ :Ho .2%	3148	.611374
PbF ₂ :Ho .2%	2952	.574362

These results reflected the expected results for varying pressures on each type of material. However a better relation was found along with a theory that

reflected the same type of behavior observed in these transformations--the Avrami expressions (as discussed in detail in section 2.3).

When the data was fit using this expression with $n=4$, a fit with good agreement through most of its length was found.

This fit is shown in figure 4-1. The exact expression used in this fit was,

$$G(t) = G_0 - C(1 - e^{-k(t-T_0)^4})$$

Here G_0 is the conductance of the cubic PbF_2 and $G_0 - C$ is the conductance of the orthorhombic phase after the transformation. T_0 is a factor inserted that defines the time the transformation begins and k is the number that defines the rate of the transformation.

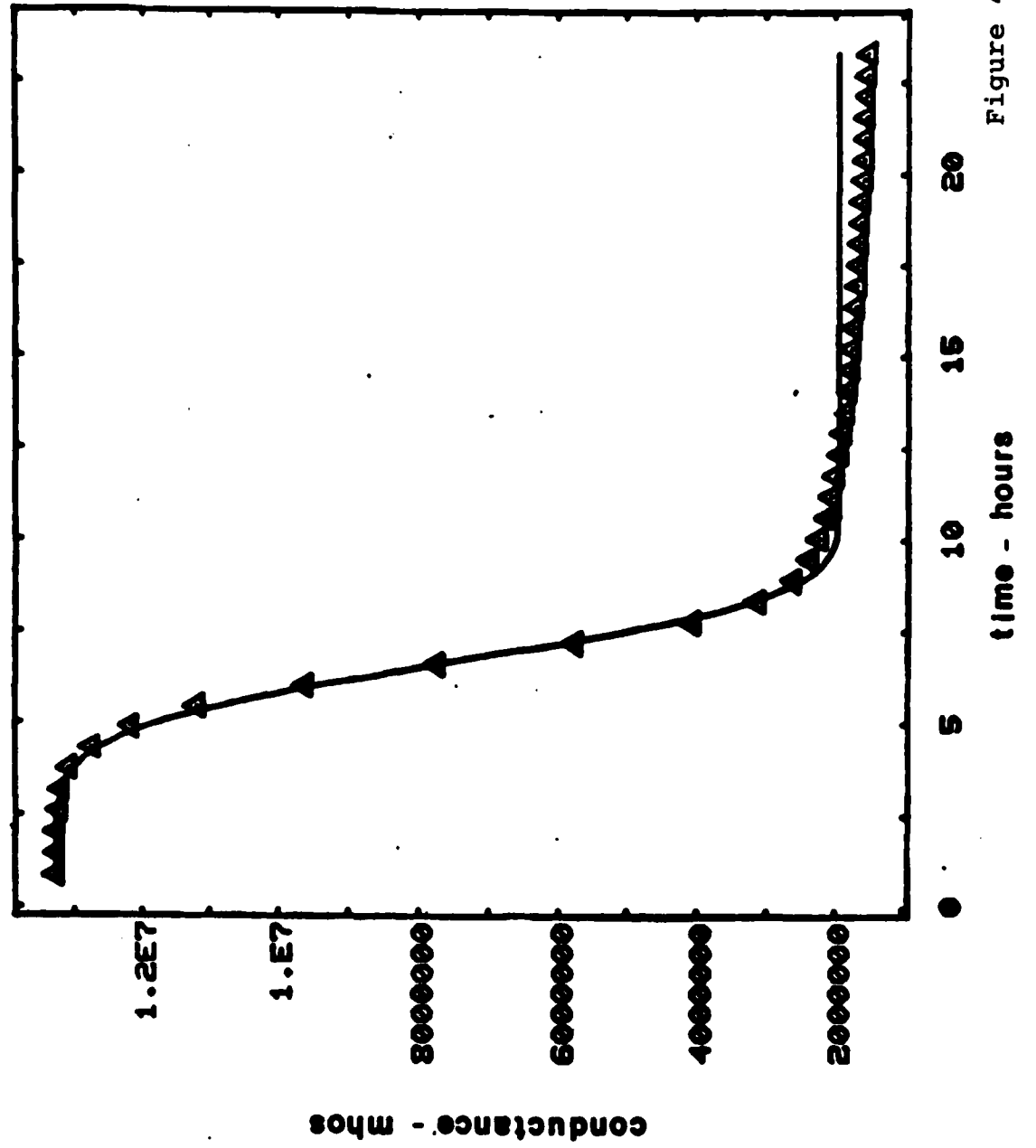


Figure 4-2

4.3 Discussion

A casual look at the results presented herein reveals much. First, the very occurrence of the phase transition below roughly 3000 bars was not expected. This observation and the strong belief that PbF_2 is metastable below 600K tend to make the behavior of PbF_2 somewhat more orthodox. The existence of materials in two different states at the same time is not unusual, for instance carbon. However, the thought of a material for which no state is in any way favored over a range of pressures and temperatures is very unsettling. The data collected here suggest the possibility that the orthorhombic phase of PbF_2 is thermodynamically favored below 600K. If not the above, then it is certain that the range of pressures in which the orthorhombic phase of PbF_2 is favored has been extended by this work. However, the data taken in this work have been restricted to transformations that occur in a relatively short time frame. The acid test for the stability of the cubic phase would be to wait for the transformation to occur at room temperature and pressure, but an experiment of this kind would likely take a prohibitive amount of time. A more reasonable approach (and the one taken in this work) is to associate the rate of the transformation with the pressure at which it occurs. In this way a relation

may be found that directly links the rate of the transformation to the pressure at which it occurs. From a relation of this type it would be a simple matter to extrapolate to the point at which the rate would go to zero if, indeed, that ever occurs at temperatures below 500k. In this work to date not enough data has been collected to determine this relationship. Future work may provide the necessary data.

Figures 3-2 and 3-3 also indicate another observation of significance. Two separate processes appear to be occurring in the transition of PbF_2 . In addition to this, the addition of anion excess materials such as HoF_3 tend to reduce or eliminate the first phase of this transition. This suggests that the first stage of the phase transition is associated with the generation of interstitials within the lattice. It is possible that as the pressure on the sample increases ions may be ejected from the lattice as a mechanism to relieve stress generated by the pressure. This process may continue until a point is reached where the population of interstitials has increased enough to make the restructuring of interstitials into the more stable orthorhombic structure more likely. This restructuring is the nucleation of the crystal, and through this

mechanism the crystal is able to find a new mechanism for the relief of stress. The reason the generation of new defects does not increase the conductance is that the lattice structure becomes distorted in order to best relieve to applied stress. This deformation of the lattice hinders the movement of both interstitials and vacancies causing a net decrease in conductance. The reordering of the crystal structure into the orthorhombic phase relieves much of this stress and allows the conductance to again increase.

In a material that already has a large number of interstitials the first stress relieving mechanism is thwarted and the interstitials are already present to make nucleation more likely. A future experiment would vacancy dope a sample of PbF_2 in order to see if it would enhance or suppress the first part of the transition.

4.4. Summary

This work on capacitive pressure transducers and pressure fixed points has produced four major results.

First, the cubic-orthorhombic phase transition of lead fluoride occurs at pressures far below the previously reported values. The data also suggest the possibility that cubic lead fluoride is entirely metastable below 600K.

Second, it was found that the phase transition of lead fluoride can be considered a two-stage process. The first stage of this process is linked to the generation of interstitials within the lattice, since it can be suppressed by the utilization of +3 valence materials as dopants.

Third, the phase transition of lead fluoride can be modeled mathematically by the use of the Avrami equations.

Fourth, the use of divalent dopants allows the possibility that a capacitive transducer with a zero temperature coefficient can indeed be constructed.

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Appendix--The Complex Impedance Bridge

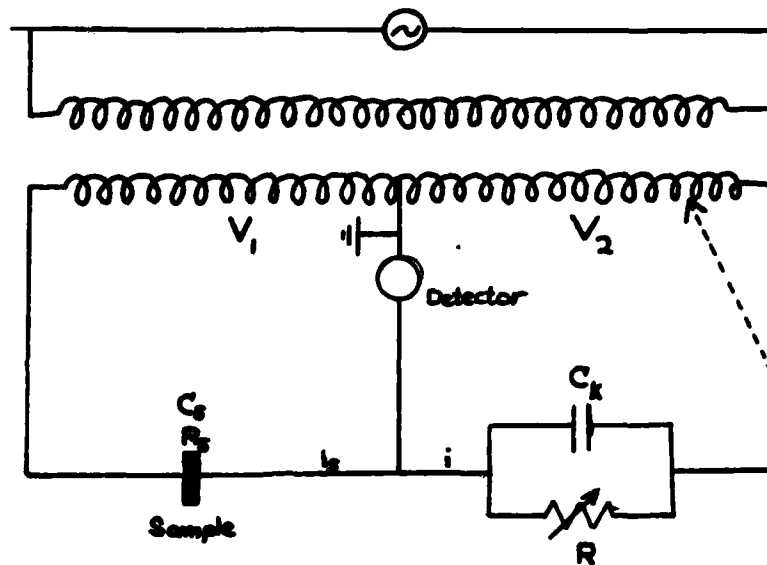


Figure A-1 Schematic of a complex impedance bridge. (G.C.Kolodziejczak in Radiation Induced Dielectric Relaxation in Rare Earth Doped Calcium Fluoride. Report to the Trident Scholar Committee. Annapolis, Md.: U.S. Naval Academy, 1978.)

The data in this work was all taken using a complex impedance bridge. There is an aesthetic simplicity in its design

The known constants are V_1 and C_k . The known values of V_2 and R are then varied so that the current flowing through the detector is zero. At that point the current i_s is exactly equal to i . When this occurs the following conditions are met.

$$V_1 = i_s R_s$$

$$V_2 = iR$$

also, since,

$$V_1 = i_s / (\omega C_s)$$

$$V_2 = i / (\omega C_k)$$

the following can be obtained,

$$V_2/V_1 = C_k/C_s$$

giving the following equations that yield the conductance and the capacitance.

$$C_s = V_1 C_k / V_2$$

and

$$G = 1/R_s = R V_1 / V_2$$

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The audio frequency electrical properties of lead fluoride have been studied in order to investigate its possible use in the construction of a capacitive pressure transducer. Previously, the construction of this device has been precluded by lack of materials with both a high pressure coefficient of capacitance and a low coefficient of temperature. Lead Fluoride has been doped with strontium fluoride in an attempt to create a material desirable for such a device. It was found that a material of the desired properties could (OVER)		

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be approached by increasing the concentration of strontium dopant. However the crystals with dopants at the desired concentrations could not be grown easily and effort in this area was curtailed in order to pursue the definition of fixed points for lead fluoride at various dopant concentrations.

The pursuit of data on fixed points led to the discovery that PbF_2 will transform from the cubic to the orthorhombic phase at pressures significantly below those previously reported. The trend of the data suggests the possibility that the cubic phase of PbF_2 may be entirely metastable below 600K. Also evidence was found indicating that the phase transformation of PbF_2 is a two stage process, and that the introduction of anion excess materials as dopants may suppress the first stage of the transition allowing the second stage to proceed immediately.

PbF_2 is a rather good superionic conductor. And, as a result, the increased understanding of its behavior provided by this work may lead to an application as a solid state electrolyte.

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