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Precipitation studies of Pb in single crystal PbTe

Walter Ludwig Erhard
Lehigh University

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PRECIPITATION STUDIES OF Pb IN
SINGLE CRYSTAL PbTe

by

WALTER LUDWIG ERHARD

A THESIS

Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Master of Science

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

May 9, 1969
(date)

Richard M. Tauber
Professor in Charge

G. P. Casard
Head of the Department

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ABSTRACT

A study of the kinetics of precipitation of excess Pb in PbTe was made by the use of Hall measurements. The objective was to find how excess Pb precipitated. Earlier work done by Scanlon¹³ with Te-rich PbTe indicated that precipitation was occurring at dislocations due to the solute interaction with the stress field of the dislocation. The results of this study indicate that this is not the case in Pb rich PbTe. In addition, the uncovering of a mistake in Scanlon's calculations invalidates his claim that precipitation is occurring at dislocations in Te-rich PbTe.

The results from this kinetic study of precipitation show that the data at a given temperature fall on two straight lines, when the data are plotted on a $-\log \ln [1-f(t)]$ vs $\log t$ graph. This indicates that the kinetics can be described by an equation of the form

$$f(t) = 1 - \exp[(-t/\tau)^n]$$

where $f(t)$ is the fraction precipitated at a given time, and n is equal to the slope of the line on a $-\log \ln [1-f(t)]$ vs $\log t$ graph. Since at each temperature there are two values of n , two stages of precipitation are present. The first stage of precipitation had values of $n = 1.3, .78$ and $.60$ at $462^\circ\text{C}, 406^\circ\text{C}$ and 340°C , respectively. The value of n for the second stage was equal to $.2$ for all three temperatures.

The only plausible explanation for a variance in n values for the first stage is that the number of nucleating sites is changing with temperature. Wert¹⁷ working with precipitation in α iron found that the value of n at 50°C could be significantly increased if aging at 50°C was preceded by a short period of aging at room temperature. The explanation given for the increase in n was that aging at room temperature introduced more nuclei, than could have formed at 50°C in the same period of time. When the specimen was brought up to 50°C, the nuclei didn't dissolve and strongly influenced the aging behavior at 50°C.

The results of this investigation show an increase of n with temperature, indicating that as the temperature of precipitation was increased the number of nuclei also increased. This is contrary to what classical nucleation theory predicts. However, Abrams²⁰ found that nucleation in PbSe, a compound very similar to PbTe did not behave as theory predicts.

Since the number of vacancies increases with temperature, vacancies are postulated as the nucleating site for precipitation. Dislocations are ruled out as a major site of precipitation since the observed kinetics was two orders of magnitude faster than predicted by stress-induced precipitation theory. In addition, the observed value of

n of 1,3 at 462°C, is evidence of the formation of spheroidal particles. Spheroidal precipitate particles are closely linked with precipitation at vacancies.

The explanation given for the observed second stage precipitation process is that due to surface energy effects the velocity of solute atoms crossing the matrix-precipitate interface is decreased.

The precipitation theories used to develop these conclusions and the methods used in obtaining the data are discussed in the main text.

I. INTRODUCTION

A) STATEMENT OF THE PROBLEM

As of the present IV-VI semiconductor compounds such as PbS, PbSe, and PbTe have been used as thermoelectric devices and infrared detectors. However, with the ever increasing need for new semiconductor devices, it is quite likely that the applicability of this group of materials will increase. One interesting property of this group of materials, is the retrograde solubility of their respective components.⁽¹⁾ This property makes it possible to control the carrier concentration with precision. For practical reasons, studies were made on PbTe to determine if the desired carrier concentration could be attained more rapidly by an internal precipitation process, rather than by a vapor diffusion process. For scientific reasons, the kinetics of the precipitation were studied to determine the mechanism of precipitation and to give a clue as to how excess atoms are incorporated into the crystal lattice.

PbTe is thermodynamically stable over a narrow range near its stoichiometric composition.⁽¹⁾ This deviation from the stoichiometric proportions is due to defects such as vacancies or interstitials. In semiconductors, such as PbTe, the amount of such defects change the electron or hole concentration. Thus the concentration of defects can be accurately determined by carrier concentration measurements. One way of determining the carrier concentration

is by making Hall effect measurements, Brebrick and Allgaier, (2) by measuring Hall voltages, were able to establish the composition limits of PbTe from 400°C to its melting point at 925°C. It was found that at temperatures of around 800°C the crystal could incorporate an excess of Te of about .013 at % and an excess of about .006 at % Pb. Such narrow composition limits could not have been established by conventional chemical means. Below 800°C, the excess amount of Pb and Te decreases with decreasing temperature. At a temperature of 400°C they found the solubility of Te in PbTe is reduced to .00257 at % and that of excess Pb to .00027 at %. Above 800°C the amounts of excess atoms decrease until an invariant melting point is reached at 925°C. The foregoing facts are schematically shown by the phase diagram of PbTe shown in Figure 1.

Brebrick and Allgaier, were able to obtain the maximum amount of excess atoms at a desired temperature by a vapor diffusion process. By equilibrating a crystal in contact through the vapor phase with a Pb rich ingot that is partially solid and partially liquid at the desired temperature, equilibrium conditions according to the Gibbs Phase Rule are satisfied when the composition of the crystal has the maximum concentration of Pb for that particular temperature. As can be seen from Figure 1, the

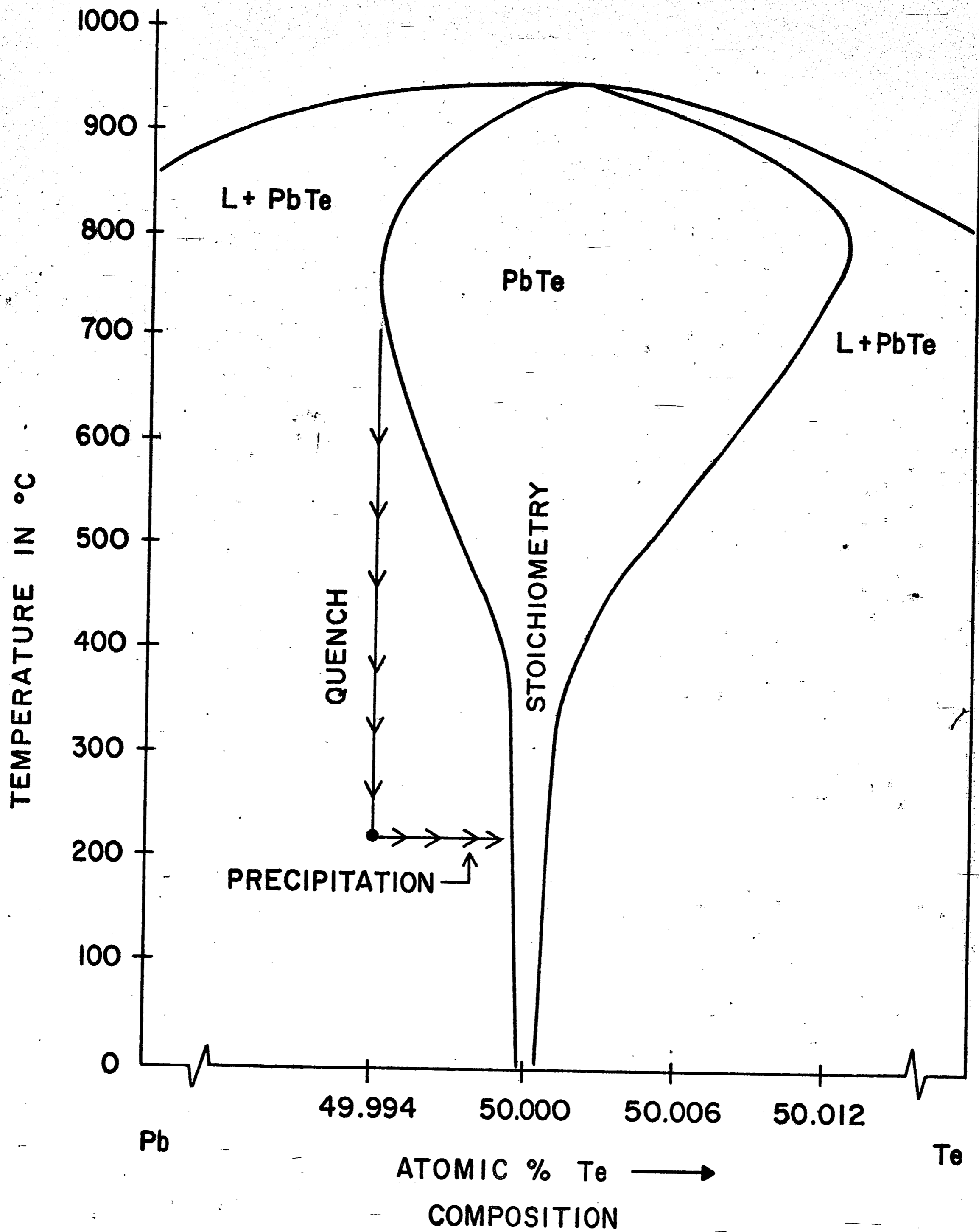


FIGURE 1. Schematic of PbTe phase diagram near the stoichiometric composition.

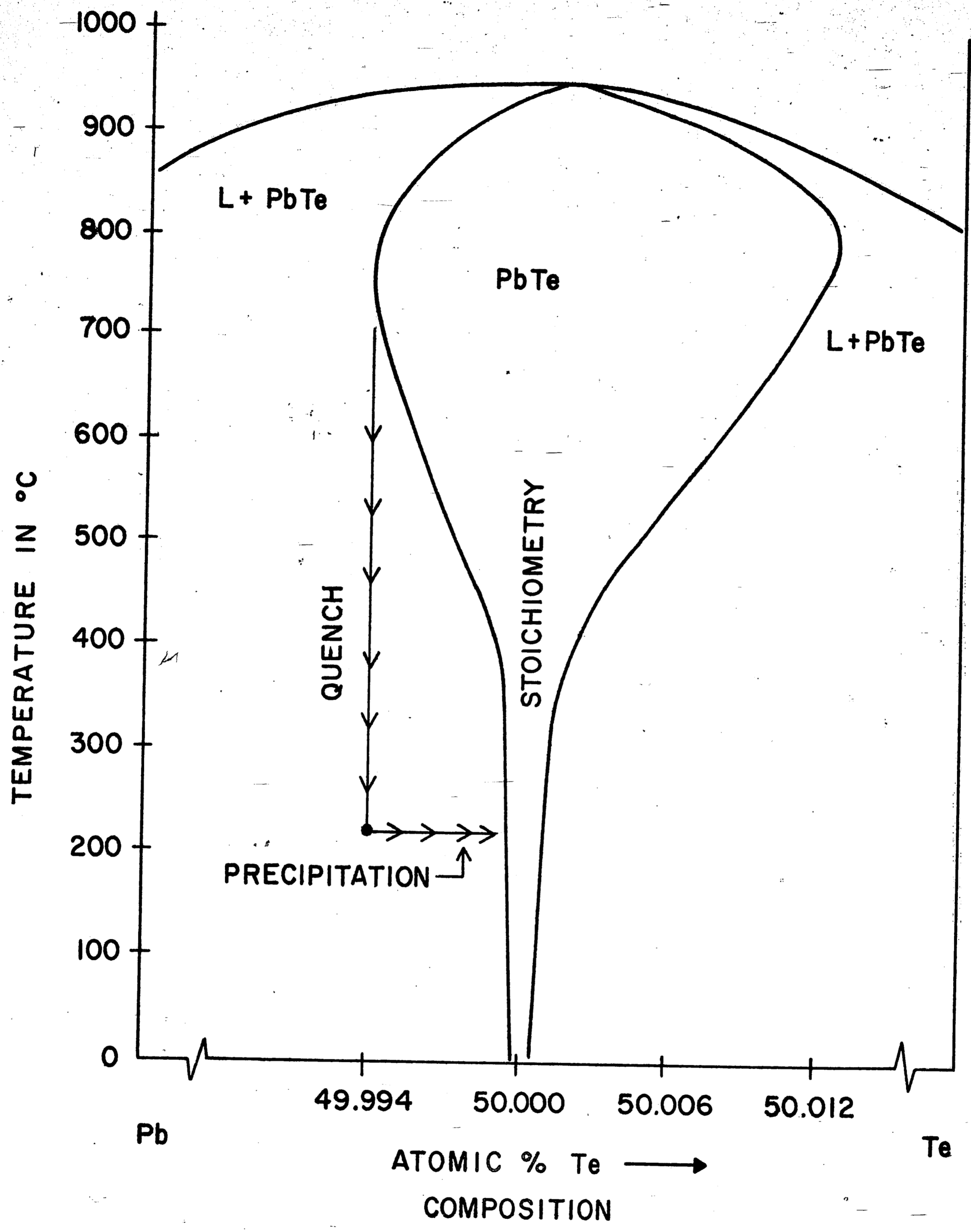


FIGURE 1. Schematic of PbTe phase diagram near the stoichiometric composition.

temperature at which the maximum amount of Pb is incorporated into the crystal is 800°C. A crystal equilibrated at 800°C and quenched to point B, would no longer have the equilibrium concentration of defects. In order for the crystal to adjust to the new equilibrium conditions, the excess lead must precipitate.

In addition to being able to quantitatively determine solubility limits by electronic measurements, it is also possible to measure quantitatively the amount of precipitation that takes place over a given time period. By measuring the carrier concentration at various time intervals between point B and C in Figure 1, the amount of excess Pb in solution is directly found. A one to one relationship is assumed to exist between the electron concentration and the amount of excess Pb in solution, (2). Since those atoms which leave solution are precipitating, one can measure the kinetics of precipitation by measuring the decrease of excess Pb in solution. The information one obtains on the precipitation process by a study of the kinetics of the process, is discussed in the next section.

B) REVIEW OF PRECIPITATION THEORIES

To achieve equilibrium conditions, precipitation will occur by the process which is most energetically favorable. Dislocations and grain boundaries are sites where the precipitation process is sometimes initiated because of the disregistry of atoms in such a region. Thus the strain energy caused by the solute atom in solution and the strain energy associated with the dislocation, can be relieved by the atom migrating to the dislocation. That precipitates do in fact nucleate at dislocations and grain boundaries has been confirmed by numerous investigators, Dash⁽³⁾ has shown that precipitation of Cu in Si occurs at dislocations by using infrared techniques. Various phenomena, such as yielding and strain aging have been explained by the locking of dislocations by impurity atmospheres,⁽⁴⁾ However, in certain systems it has been found that precipitation occurs at imperfections other than dislocations or grain boundaries. For instance in germanium, vacant germanium lattice sites act as nucleation centers for lithium precipitates.⁽⁵⁾ Tyler and Dash⁽⁶⁾ in studying precipitation of lithium in germanium found that above 575°C, the kinetic of precipitation were independent of dislocation density. However, they found that at temperatures of 400°C, samples that were deformed and consequently had a higher dislocation density, showed more rapid precipitation. In samples with

low dislocation densities, evidence existed that precipitates existed both at dislocations and at random sites in the matrix.

To understand the nucleation and the growth of precipitates more fully, methods other than visual observation have been employed. One of the most powerful techniques is following the kinetics of the precipitating constituents. The interpretation of such kinetic data rest on various theories.

One of the earliest theories of precipitation kinetics was put forth by Cottrell and Bilby, when they explained strain aging. This theory which considers the kinetics of precipitation on dislocations, has been called the Drift Approximation because they consider the flux of solute atoms to the dislocation to be due only to the strain field of the dislocation interacting with the strain field of the solute atom. This is obviously an oversimplification, since when the solute atom precipitates, the region around the precipitate becomes depleted of this solute constituent and the established concentration gradient will result in a flux of atoms due to diffusion processes.

Thus, a more adequate theory must account for the flux of solute atoms to a dislocation by considering diffusion and drift. The Ham Analysis⁽⁷⁾ of precipitation in a stress field of a dislocation does this, but at the

same time makes many simplifying assumptions. The analysis centers around the concept of "effective capture radius", denoted by R . This is the radius of a cylinder which for certain problems has essentially the same probability of capturing diffusing atoms as the dislocation with its associated stress field. The physical justification for replacing the dislocation and its associated stress field by a cylinder which has the boundary condition of zero concentration of solute at R and has zero value of potential for all values of r , is as follows. The dislocation due to its interaction with the solute depletes a region around it of solute. When all the solute initially in the region $r = R$, where R is the capture radius, has precipitated, the movement of solute in regions outside of R is due only to the existing concentration gradient. Thus, R is approximately equal to the range over which the interaction of the solute atom with the dislocation is appreciable. Ham shows that the equation describing the amount of precipitation with respect to time using these boundary values gives the same result as numerically integrating the diffusion equation.

Ham uses the concept of effective capture radius to simplify the calculation of precipitation when there is an array of dislocations. This problem has been previously considered by Harper⁽⁸⁾ who in analogy to the work of Johnson and Mehl,⁽⁹⁾ proposed that the decrease in pre-

precipitation rate is proportional to the fraction already precipitated. The precipitated fraction W , or excess solute should then satisfy the equation

$$W = 1 - \exp \left[-3 \left(\frac{\pi}{2} \right)^{1/3} L \left(\frac{ADt}{kT} \right)^{2/3} \right] \quad (1-1)$$

where:

W is the precipitated fraction

A is a constant dependent on the size of the atoms and the elastic properties of the solvent

D is the solute diffusion coefficient

t is the time

T is the absolute temperature

k is the Boltzmann constant

L is the dislocation density

In this expression, the exponent is obtained by considering solute current to an isolated dislocation as derived in the Drift Approximation. Ham criticizes this procedure from two standpoints. One is that the expression for solute current to an isolated dislocation from the Drift Approximation is wrong. Secondly, Ham contends that the assumption of a decrease in precipitation rate being proportional to the fraction precipitated is wrong. All that he shows is that the curve obtained for W from equation (1-1) does not yield the same curve as obtained in the Ham analysis for a regular array of dislocations, even when the solute current

used considers both drift and diffusion.

In Ham's treatment of the competitive situation, a regular array of dislocations is replaced by an array of cylinders. In place of each dislocation, there is now a cylinder whose radius, r_s , is defined by $L = (\pi r_s^2)^{-1}$, where L is the number of dislocation lines intersecting a square centimeter.

Since each cylinder is identical, the precipitation rate equation for the entire array can be solved by mathematically considering only one cylinder by using an eigenfunction expansion Ham derives the following rate equation.

$$W = 1 - \exp\left(-\frac{t}{T}\right) \quad (1-2)$$

$$\text{where } t = \frac{1}{\lambda_0^2 D} \quad (1-3)$$

In the above expression D is the solute diffusivity at the temperature of precipitation and λ_0 is given by

$$\lambda_0^2 = \frac{2}{r_s^2} \left[\ln \left(\frac{r_2^{3/5}}{R} \right) \right]^{-1} \quad (1-4)$$

Using equation (1-2) Ham derives a curve relating $D\tau/r_s^2$ to r_s/R . $D\tau/r_s^2$ is called the reduced time and it is a parameter without units. Since τ is the time it takes for the fraction $(1 - \frac{1}{e})$ to precipitate, τ can be found experimentally. By determining τ and r_s experimentally and using his derived curve, a value of r_s/R can be determined.

Although Ham's theory appears to be more sound than that of Harper's, there are no experimental data that

support the Ham theory. This is not the case for the Harper theory. Data taken by Pitsch and Lucke⁽¹⁰⁾ on the precipitation of carbon and nitrogen in cold-worked alpha iron fit the $[1 - \exp(-\alpha t^{2/3})]$ form of Harper very well. Thomas and Leak⁽¹¹⁾ also found that the kinetics of carbon precipitation on dislocations follow the Harper equations.

This agreement is considered quite fortuitous.

Ham's criticisms of Harper's theory, as previously stated, are theoretically justifiable. In particular Harper's neglect of considering the contribution of concentration gradients to the flux of solute to the precipitate particle, makes his theory untenable. Because of these reasons, Bullough and Newman⁽¹²⁾ attempt to explain these experimental results in light of the Ham theory. They modify the Ham theory by introducing a parameter, α , to represent any rate limiting process occurring at the matrix-precipitate interface. When $\alpha \rightarrow \infty$ they have the same boundary conditions as in the Ham analysis. A value of α equal to zero corresponds to the situation where an "impurity atmosphere" is created around the dislocation without any precipitation occurring. By using a value of α between .03 and .1 they give a theoretically derived result that coincides with the data Thomas and Leak obtained. Their argument that a rate limiting process, other than diffusion, is occurring is supported by the fact that a plot of precipitated

fraction vs, reduced time does not bring the curves from different temperature into coincidence. They maintain that for the process to be diffusion limited this coincidence is necessary.

As of the present, no experimental work justifies Ham's stress-assisted precipitation theory. Scanlon,⁽¹³⁾ studying PbTe, made an attempt to correlate his data of precipitation of Te with the Ham theory. Monitoring the precipitation by thermoelectric power measurements he obtained a graph of fraction precipitated vs reduced time. As shown in the paper his experimentally determined points lie scattered around the curve derived by Ham. However, Scanlon made a mistake in calculating the diffusion coefficient at the temperature of precipitation. Using the diffusion data of Boltaks and Mokhovs,⁽¹⁴⁾ Scanlon calculates a diffusion coefficient at 204°C of 3×10^{-12} cm²/sec. This writer using the same data calculates a coefficient equal to 3.2×10^{-14} cm²/sec, at 204°C, which compares reasonably well to the value of 4.7×10^{-14} cm²/sec found by extrapolating Boltaks and Mokhovs curve to 204°C. Applying this correction to Scanlon's data results in a 10^2 decrease in the value for the reduced time. Whereas, Scanlon previously obtained a value of $r_2/R = 8$, by referring to Ham's derived curve relating $D\tau/r_2^2$ to r_s/R , his value of r_s/R changes to 1 when one corrects for the mistake. With a dislocation density of $10^5/\text{cm}^2$, as reported by Scanlon, the r_s value is 1.78×10^5 Å. Accordingly, the R value has the same

magnitude, This result is not compatible with modern dislocation theory. The range over which a dislocation exerts a stress, as represented by R in Ham's theory is considered to be of the order of 20 to 100 Å. Since Scanlon didn't directly observe if precipitation occurred at dislocations one can't assess if this discrepancy is due to Ham's theoretical model. It is more reasonable to assume that precipitation wasn't occurring at dislocations. If such were the case one would find it unlikely that the precipitation data of Scanlon would fit Ham's model.

Another model constructed by Ham⁽¹⁵⁾ that has found much greater applicability for work in precipitation, is his theory of diffusion limited precipitation. To some extent, he is able to get away from some of the problems that lead to the idealized model for precipitation at dislocations. In his solution for a spherical precipitate his model could be made to approach physical reality more closely. To deal with precipitation at dislocations, Ham worked with two dimensions. One could ignore the third dimension if dislocations are assumed parallel, which is precisely what Ham does. However, the assumption of parallel dislocations throughout the crystal is questionable. Such an assumption need not be made in dealing with spherical particles, since each dimension is symmetric to the other dimensions. In addition, he no

longer has to contend with the problem of the dislocation and its interaction with a solute atom. However, Ham oversimplifies the problem by not dealing at all with the problem of nucleation. He assumes small spherical particles are already present and considers only the problem of the growth of these particles under diffusion limited conditions.

This problem had previously been treated by Zener and Wert.^(16,17) By assuming that the decrease in the rate of precipitation is proportional to the amount already precipitated. Wert obtains the following equation to describe the kinetics of precipitation

$$f(t) = 1 - \exp\left(-\frac{t}{T}\right)^n$$

This equation has the same form as the one developed by Ham in his analysis of diffusion-limited precipitation. In both theories, the exponent n is related to the particle shape, but according to the Ham theory will be influenced by pre-precipitation. However, the theories differ in ascribing what value of n belongs to a certain particle shape. Wert ascribes a value of n of 1 to cylinders, or precipitates at dislocations, n of $3/2$ to spherical particles, $5/2$ to disks, and 2 to rods. Ham's more rigorous mathematical analysis yields a value of 1 and $3/2$ for cylindrical and spherical particles, respectively. However, the analysis yields n values of $3/2$ for disks

and rods. The last two values are in disagreement with the values Wert obtained.

Experimental evidence supports Ham's position. Hardy⁽¹⁸⁾ and Lankes and Wasserman,⁽¹⁷⁾ both of whom working on aluminum-copper alloys found values of $n = 1.5$ for precipitate particles found to be disks by Guinier using electron microscopy. Ham's derivation also shows that when the initial volume of the precipitate is approximately 1/10 the final volume, n takes on a value between 1 and 1.5. This reconciles the value of $n = 1.15$ found by Pitsch and Lueke studying carbide precipitation.¹⁰ A value of 1.15 could not previously be explained. However, it should not be thought that the Ham diffusion-limited theory is complete. Wert's⁽¹⁷⁾ experiments with nitride precipitation in α iron showed that the kinetic of precipitation, and consequently the n values, were drastically effected when precipitation at a higher temperature was preceded by a very short precipitation period at a lower temperature. Wert concluded that more nuclei had a chance to form at a lower temperature than would have formed at the more elevated temperature during the same period of time. The presence of a greater number of nuclei, than would normally be present at the elevated temperature caused an increase in the precipitation rate.

Provided that a process can be shown to be diffusion-limited, Ham's theory in general should be very useful

in correlating n values with the shape of the precipitation particle. In addition, the Ham analysis of diffusion-limited precipitation allows one to calculate the particle size and distribution from an experimentally determined value of τ . Use of this expression was made by Abrams²⁰ in studying the precipitation of Pb and Se in PbSe.

In addition to showing that the process is diffusion-limited, two other criteria must be met to apply the Ham theory. One is that the density of solute be very low and the other is that the ratio of solute density in solution to that in the precipitate phase ρ_0/ρ_c be less than 10^{-2} . Both are satisfied when excess Pb precipitates in PbTe.

For this reason, coupled with the fact that kinetics of precipitation could be accurately determined by Hall coefficient measurements, it was felt that a kinetic study would provide knowledge of the precipitation processes of Pb in PbTe.

II. EXPERIMENTAL PROCEDURES

A) PREPARATION OF SINGLE CRYSTAL SAMPLES OF PbTe

The preparation of single crystals proved to be the most time consuming aspect of the project, mainly due to the fact that there was no existing equipment to grow the crystals by the Bridgman-Stockbarger technique. It was decided that this technique was best for the following reasons:

1. It was used with previous success in growing PbTe crystals.²¹
2. Fumes of Te which are very hazardous can be contained.
3. Construction of apparatus is easier than for other methods,
4. Less expensive,

Basically, the Bridgman-Stockbarger technique consists of lowering an evacuated vacor capsule containing the material to be made monocrystalline, through a sharp temperature gradient at the melting point of the material. To accomplish this a vertically upright furnace with a sharp temperature gradient had to be constructed, a mechanism for lowering a capsule slowly through this gradient had to be developed and a capsule containing Pb had to be encapsulated in vacuum with Te.

To obtain a sharp gradient, a grooved core, obtained from Norton Refractories, was wound for its entire length

with Nichrome wire with an additional second winding that started from the top of the core and terminated in the middle. Thus a capsule starting at the top of the furnace would be molten and pass through a freezing interface somewhere in the mid-section of the furnace.

To successfully grow a single crystal it is necessary that growth proceed slowly. Since in this particular technique, the furnace remains stationary, it was necessary to build an apparatus that would lower the capsule containing the charge into the furnace at a very slow rate. As reported in the literature,²² a rate of two inches a day was required. This was accomplished by reducing the revolutions transmitted from a motor to a worm gear by a factor 57,000 to 1. This reduction was made by the use of two gear boxes. The worm gear moved a table on which a pulley was attached. This pulley transmitted the motion of the table to a capsule via a stainless steel cord. The rate of descent of the capsule could be controlled by a variac connected to the motor.

Another, important condition that has to be met to grow crystals by the Bridgman-Stockbarger technique is to nucleate a seed crystal in the capsule. This condition can be met by having a fine point at the end of the capsule. To isolate the tip from the stainless frame that held the capsule, a neck was produced in the middle of the capsule. Such isolation was desirable due to the fact that the

stainless steel frame could cause thermal disturbances around the tip.

Before placing a stoichiometric charge of Pb and Te into the quartz capsule, it was cleaned with hydrofluoric and nitric acids. It was then rinsed numerous times with de-ionized water. To prevent the sides of the capsule from constraining the crystal growth, the inside of the capsule was coated with Aquadag. After inserting the charge and necking down the quartz above it, the system was attached to a vacuum pump. After two days, the capsule was removed from the pump by sealing off the necked portion. A period of four days was used to grow the crystal.

The crystal obtained on the first attempt was cut at Western Electric in Allentown using a diamond blade. Since the test samples were cut to small dimensions, additional attempts were made at growing single crystals. Thermal grooving occurring during the vapor diffusion process indicated these attempts failed to produce single crystals. Consequently all the data was taken from the crystal grown on the first run.

The as grown crystal for the most part was p-type. Since in this investigation, n-type or Pb rich PbTe was being investigated, the carrier concentration had to be adjusted by a vapor diffusion process. As previously discussed in the introduction, this required equilibrating

a test sample with a Pb rich ingot at a temperature of 800°C. By maintaining the system at this temperature for the required time and then rapidly quenching it, a maximum concentration of carriers was insured.

The initial procedure adopted for the vapor diffusion was that Brebrick.⁽²⁾ A Vycor capsule 3 to 4 inches in length with a 15 mm diameter was cleaned and coated with Aquadag. To prevent the crystal and the ingot from coming into contact, they were separated by a dike made by pushing one side of the tube in. The capsule after being evacuated, was placed horizontally in a furnace. After a heat treatment of 48 hours, the capsule was removed and rapidly quenched. In all cases, the dimensions of crystals after the diffusion process, were seriously altered. The apparent explanation for this is that vapor from the crystal condensed at cooler parts of the crystal. In an effort to minimize this effect, the capsules were shortened and placed in a lavite fixture. Lavite being an excellent insulator minimized the effect of the inherent thermal fluctuations in a furnace. In addition, capsules were placed vertically into the furnace, since it was found that thermal gradients were less in the vertical direction. Using this procedure, the dimensions of the test samples were not appreciably altered. However, without an Aquadag coating present, the test samples either had their dimensions drastically changed or disappeared completely.

To restore samples to their previous rectangular geometry, they were carefully polished on French emery grade 4/0. The final width and height of test samples varied from 65 mil to 60 mil. The length was in the range of 370 mil to 400 mil,

B) PRECIPITATION OF PbTe SAMPLES

Originally, it was desired to perform measurements "in situ". In other words, measurements were to be made at the temperature at which the sample was precipitating. However, the experimental difficulty in performing this proved to be insurmountable. At the temperature of interest, PbTe oxidized. Hence, it was necessary to enclose the system in a vacuum. But the fixture and leads used in making the measurements, could not be made compact enough to prevent the presence of a thermal gradient in the enclosure. Thus the problem of loss of material due to vapor transport, was recurring. The dilemma was resolved, by making room temperature Hall coefficients measurements. The sample was allowed to precipitate at the temperature of interest, for a certain period of time, and then quenched. After measuring the amount of precipitation that occurred, by Hall measurements the sample was again re-heated to allow for precipitation. This procedure was performed at temperatures of 340°C, 406°C, and 462°C.

C) MEASUREMENT OF HALL COEFFICIENT

As has been stated, Hall coefficient measurements provided an accurate means for determining the amount of precipitation occurring over a given time span at a given temperature. The measurements utilize a phenomena known as the Hall effect. The Hall effect arises when a transverse magnetic field acts upon an electric current to produce an electric field in a mutually perpendicular direction. By carefully measuring all the parameters involved, one can calculate the Hall coefficient. This coefficient is related to these parameters by the following expression

$$R_H = \frac{V_H t}{IB} \times 10^8 \quad (2-1)$$

where:

R_H = Hall coefficient in $\text{cm}^3/\text{coulomb}$

V_H = Hall voltage in volts

t = specimen thickness in centimeters

B = magnetic field in Gauss

I = specimen current in amperes

At room temperature PbTe with excess Pb is extrinsic. R_H is thus related to the electronic concentration by the following relation

$$n = \frac{1}{R_H e} \quad (2-2)$$

where:

n = electron concentration in carriers/cm³

e = electron charge, 1.6×10^{-19} coulomb

Measurements were made by using a plexiglass fixture, shown on the next page. This fixture made at Western Electric in Allentown was carefully machined to insure alignment of contacts. The screws were plated with gold so that ohmic contact resistance was minimized.

A water-cooled Varian V3700 6" electromagnet and power supply provided the magnetic field. The maximum attainable field on this unit is 40,000 gauss. The field used for all measurements in this project was 7,000 gauss. By using a gaussmeter, it was found that a gradient of about 4000 gauss per half inch existed in certain regions between the pole pieces. Thus the fixture was always placed in the same position. The field strength at this position as measured by a gaussmeter was the same as that set on the Fieldail controlled power supply. A potentiometric circuit was used to make the various electrical measurements. The salient features of this circuit are:

1. Current through the specimen could be reversed.
2. The current could be accurately measured by using a .01000 ohm standard resistor.
3. All voltages could be read with extreme accuracy by the potentiometer being hooked to a Honeywell Model 3972 Microvolt Null Detector. A schematic of the

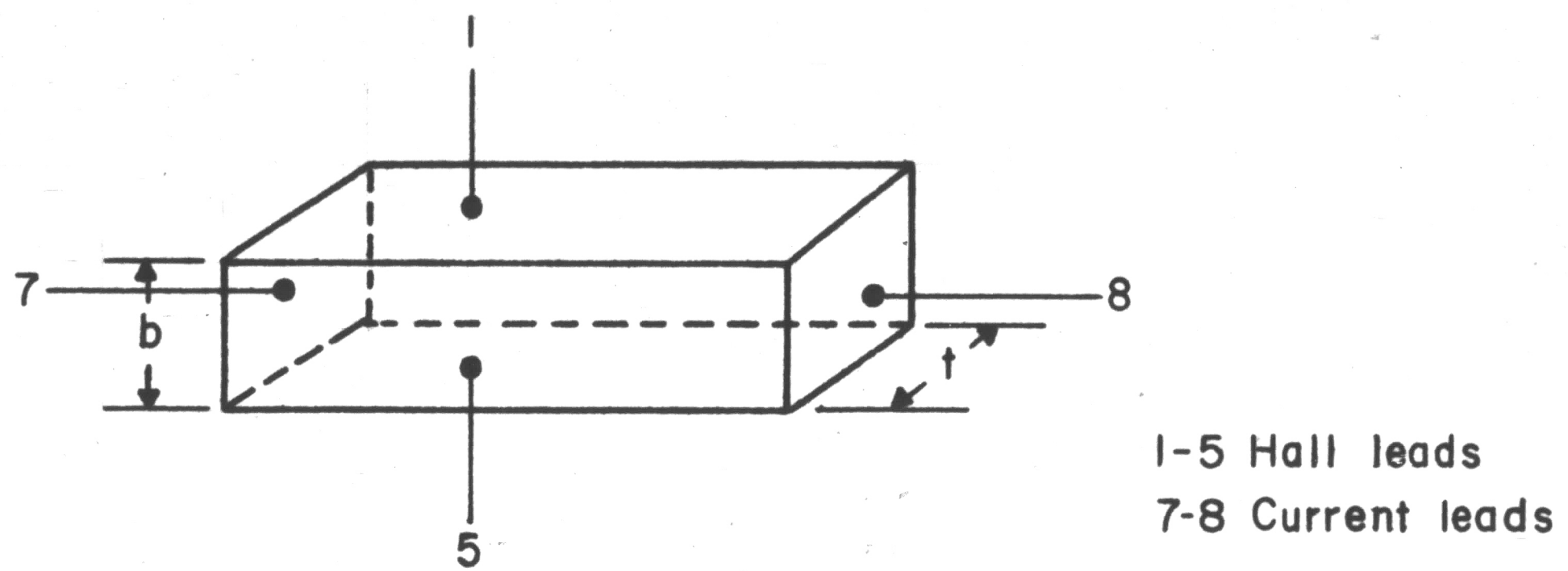


FIGURE 2. Schematic representation of test sample.



FIGURE 3. Fixture used for room temperature Hall effect with test sample.

circuit is shown in Figure 4,

In measurements of the Hall voltage, certain associated effects give rise to potentials. The largest of these effects is the IR drop due to the misalignment of the contacts. Of a smaller magnitude, usually on the order of 20 to 30 mv, are the voltages caused by galvanic and thermomagnetic effects. These effects, similar to the Hall effect, are present whenever a magnetic field is perpendicular to an electric or thermal current. To accurately determine the Hall voltage, the following procedure was used referring to Figure 4. The voltage between leads 1 and 5 was measured with current having a + directionality and the magnetic field having a + polarity. Another voltage reading was taken without current flowing through the specimen. This voltage caused by thermomagnetic effects was subtracted from the original voltage reading. The direction of the current and the polarity of the field were then changed. In an analogous procedure voltage readings were made with and without current. The voltage reading made without any current flow was again subtracted from the larger voltage. To obtain the Hall voltage, the adjusted voltage values were then averaged to eliminate the IR drop. From the Hall voltage, and the measured current, magnetic field strength and sample dimensions, the Hall coefficient was calculated.

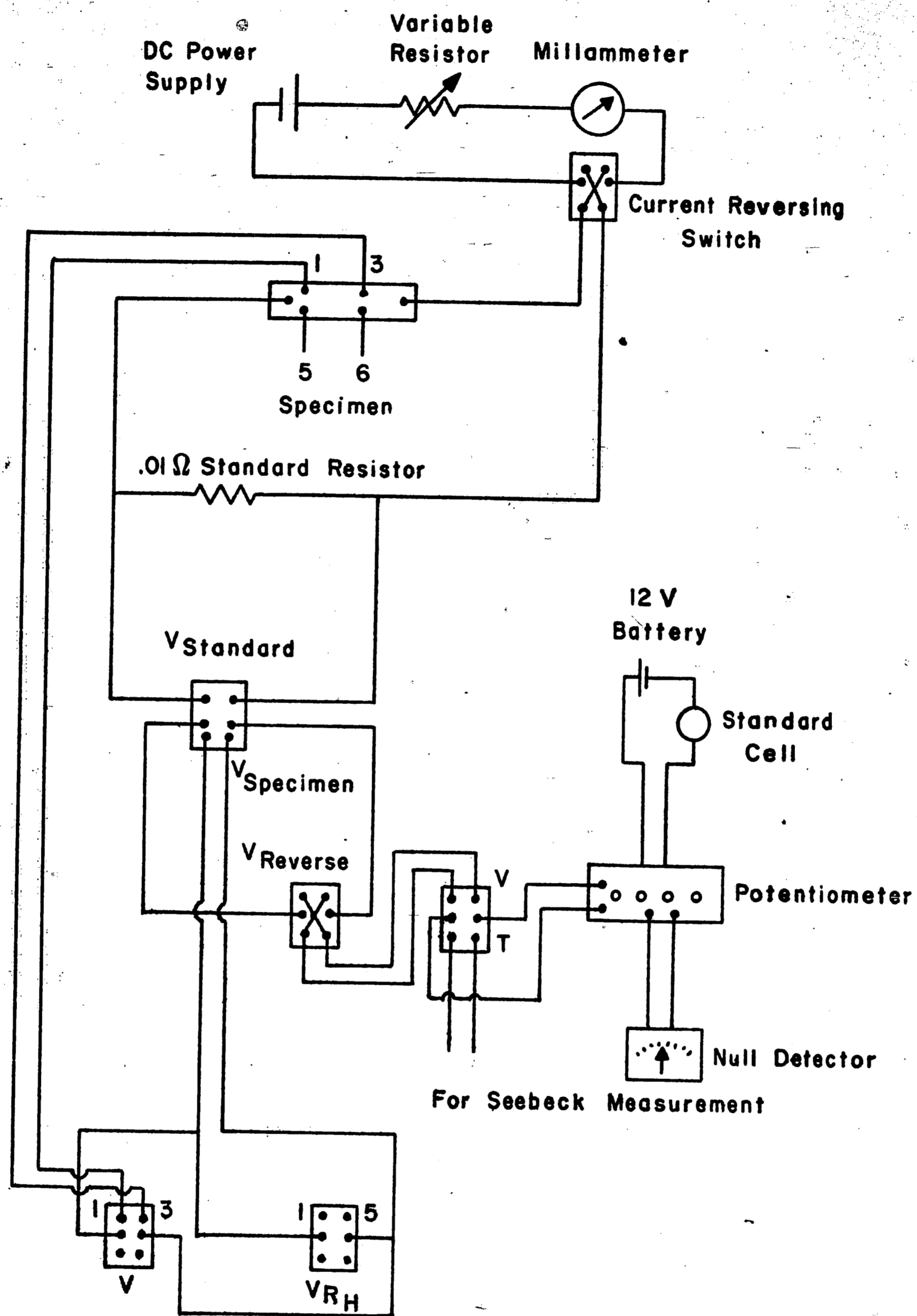


FIGURE 4. Electrical test circuit which could be used for both Hall effect and Seebeck measurements.

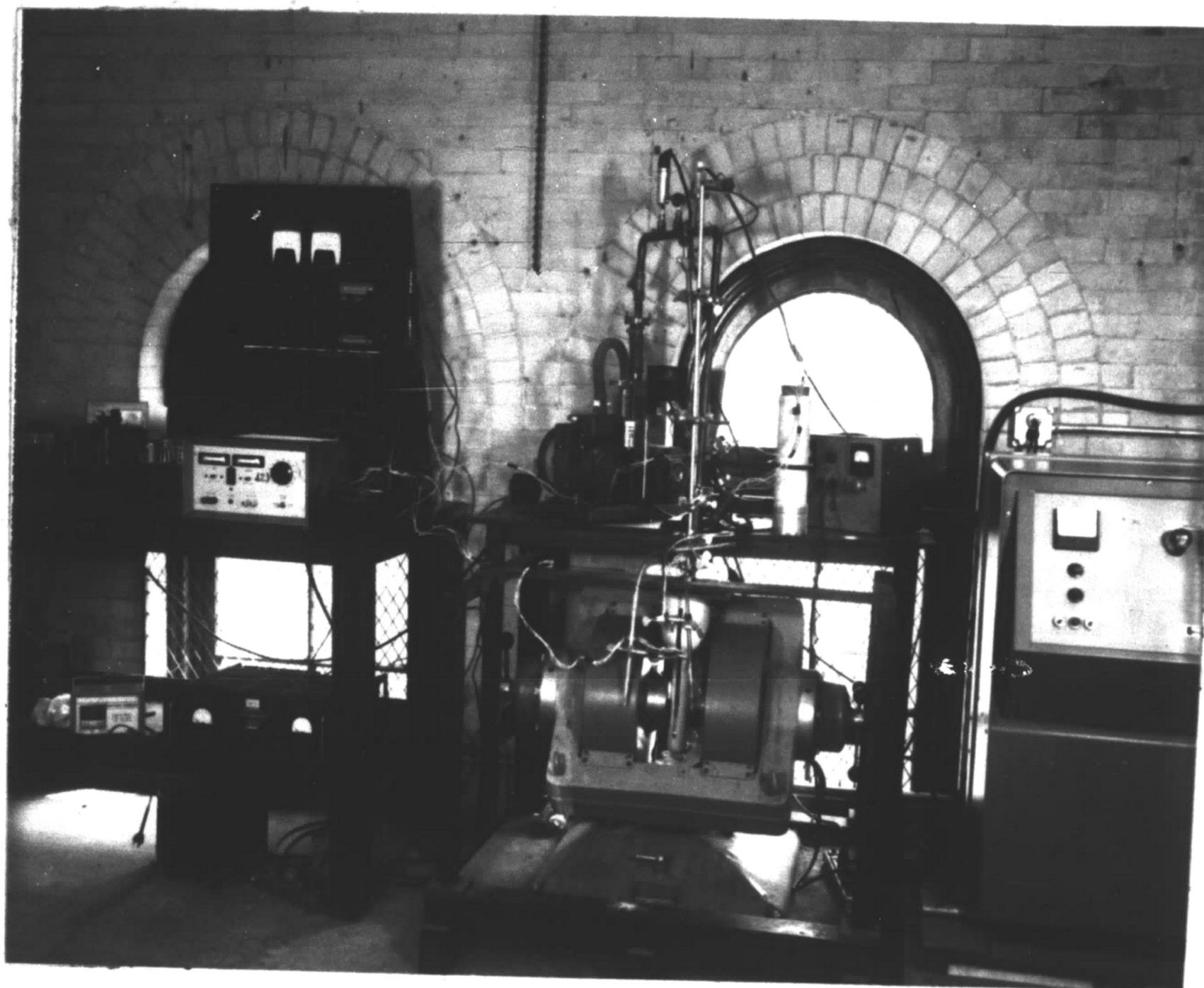


FIGURE 5. Apparatus used for making Hall effect measurements.

D) MEASUREMENT OF PbTe DISLOCATION DENSITY

As was stated in the introduction, dislocations often act as nucleation centers. In order to find out if dislocations are acting as centers for nucleation, it is necessary to know the dislocation density. The dislocation density, or the number of dislocations intersecting a unit area, is a variable needed for calculating the reduced time, a parameter Ham uses in his theory of stress assisted precipitation on dislocations.

The method used was to etch a freshly cleaved surface of PbTe. It has been established that a one-to-one correspondence exists between etch pits and dislocations.²³ The dislocation etch solution used is that of Coates,²⁴ It is prepared from 10 volumes of aqueous KOH (saturated at 20°C), 1 volume of 30% H₂O₂ solution, and 10 volumes of ethylene glycol. It was found that the prescribed time of five minutes was insufficient to properly etch dislocation pits. A ten minute etch gave better results.

All dislocation density measurements were made on crystals that had not been vapor diffused, since as grown crystals could be readily cleaved. It was felt that performing similar measurements on vapor diffused samples would be unnecessary, since Abrams²⁰ established in his work in PbSe that the vapor diffusion process does not alter the dislocation density.

III. PRESENTATION OF RESULTS

This chapter of the dissertation presents the results of the electronic and dislocation etch measurements. The kinetic data is portrayed in two ways. The reasoning for this is made more evident in the discussion.

A. KINETIC MEASUREMENT RESULTS

1. Fraction Precipitated Versus Log Time

The most straightforward way of presenting kinetic data is to plot the fraction precipitated versus log time. The fraction precipitated is defined by equation (3.1).

$$f(t) = \frac{C_0 - C_t}{C_0 - C_\infty}$$

where:

$f(t)$ is the fraction precipitated

C_0 is the carrier concentration at $t=0$ (i.e., after diffusion to maximum saturation),

C_t is the carrier concentration at time t ,

C_∞ is the carrier concentration at equilibrium (i.e. $t = \infty$ effectively).

As an example, the fraction precipitated at 406°C after 1.5 hours is found to be

$$f(t) = \frac{1.64 - 1.01}{1.55} = 0.245$$

where:

$$C_t = 1.64 \times 10^{18} \text{ carriers/cm}^3$$

$$C_o = 5.01 \times 10^{18} \text{ carriers/cm}^3$$

$$C_\infty = 1.55 \times 10^{18} \text{ carriers/cm}^3$$

The fraction precipitated is plotted versus log time for Pb saturated PbTe at temperatures of 462°C, 406°C, and 340°C in Figure 6,

2. Log Ln [1-f(t)] Versus Log Time

According to existing theories on precipitation in solids the kinetics of precipitation should have a behavior described by the formula

$$f(t) = 1 - \exp [(-t/\tau)^n]$$

The shape of the precipitate particle is related to n and according to Ham⁽¹⁵⁾ the size and density of the precipitate particle is related to τ . Transposing the numeral 1 and taking the natural logarithm of both sides the equation appears as:

$$\ln [1-f(t)] = -(t/\tau)^n \quad (3.2)$$

Thus, if the process occurs by a single mechanism, the data when plotted on an ln log graph should give a straight line whose slope equals n . As can be seen in Figure 7, the data falls on two straight lines at a given temperature. After 50% has precipitated there is a dramatic decrease in slope, indicating that a different precipitation becomes predominant.

At 462°C, the n value changes from 1.3 to 0.185, at 406°C, the change is from 0.781 to 0.206 and at 340°C n changes from 0.606 to 0.182. The kinetics beyond the 50% point, will be referred to as second stage precipitation in the discussion.

B. DISLOCATION ETCH COUNT

The dislocation density was obtained by examining many randomly selected samples at various magnifications and counting the number of isolated dislocations. The counting was restricted by randomly selecting a 5 X 5 centimeter square and counting the number of etch pits inside the square. To obtain the dislocation density, this number was multiplied by the magnification and then divided by 25. As an example, Figure 9 shows etch pits at a magnification of 800.

$$\text{No. of Dislocations/cm}^2 = \frac{43 \times 8 \times 10^2}{25} = 1.35 \times 10^3$$

As can be seen in Figures 8-10, when the time of etching was increased from five minutes to ten minutes, the pyramidal nature of the pits became more evident.

Sampling taken from many cleavage planes indicated that on the average about 1.4×10^3 dislocations/cm² existed. This is a much lower count than would be expected from a crystal grown by the Bridgeman-Stockburger technique.

However, the author feels the dislocation density was accurately determined to within an order of magnitude, since increasing the etching time did not increase the number of dislocation etch pits.

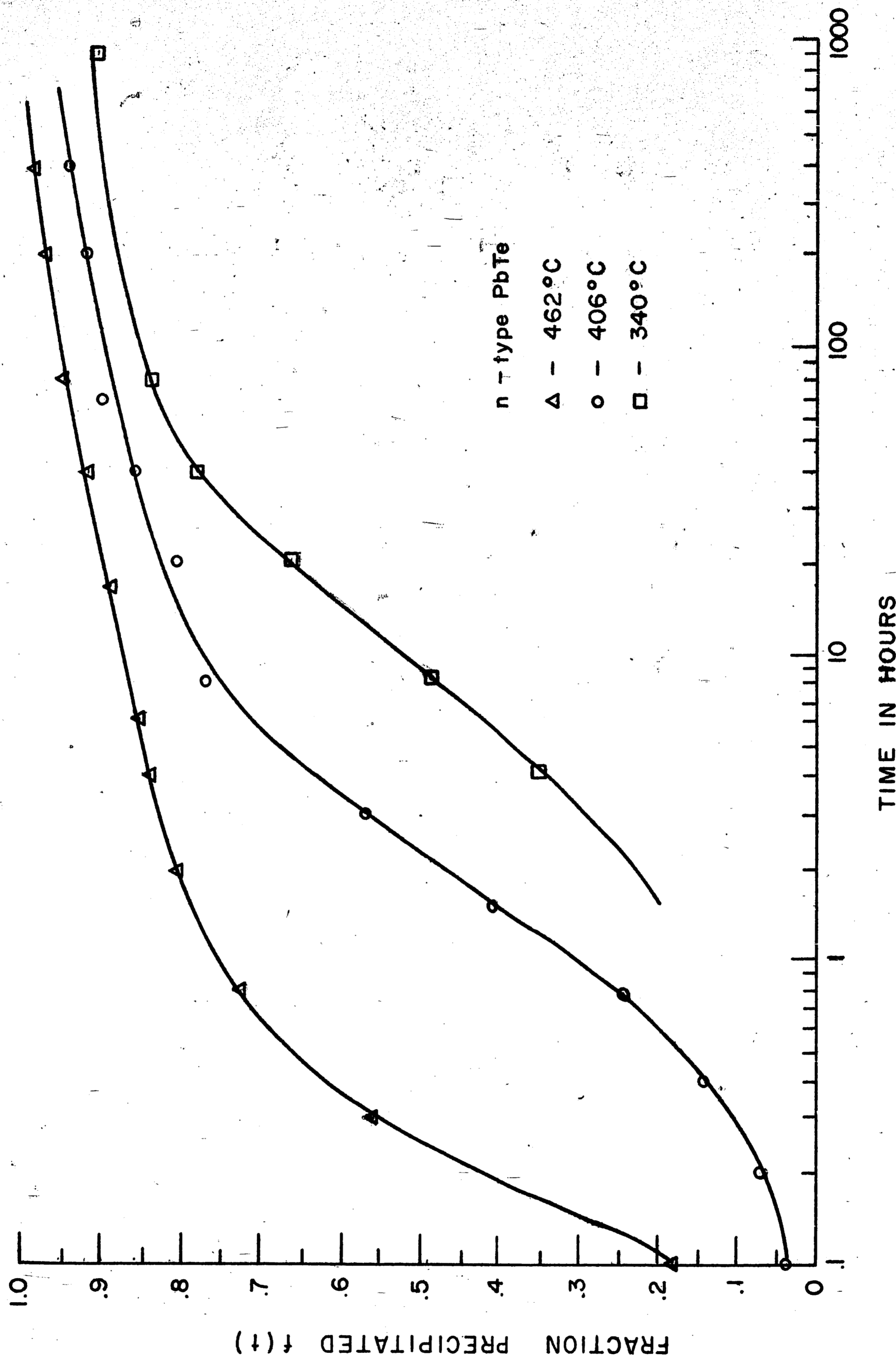


FIGURE 6. Fraction precipitated versus \log_{10} time for n-type PbTe

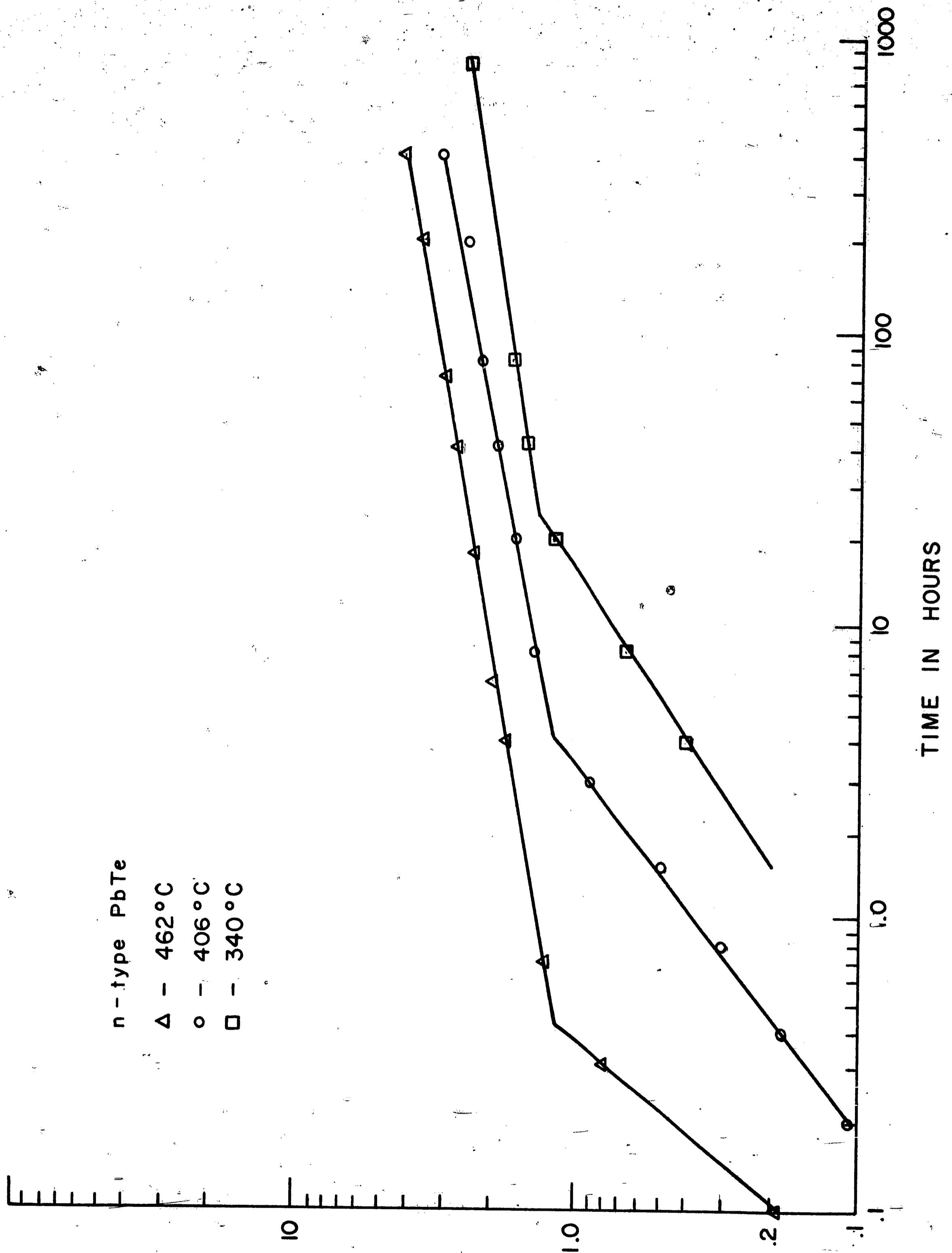


FIGURE 7. $\text{Log Ln } [1-f(t)]$ versus log time for n-type PbTe.

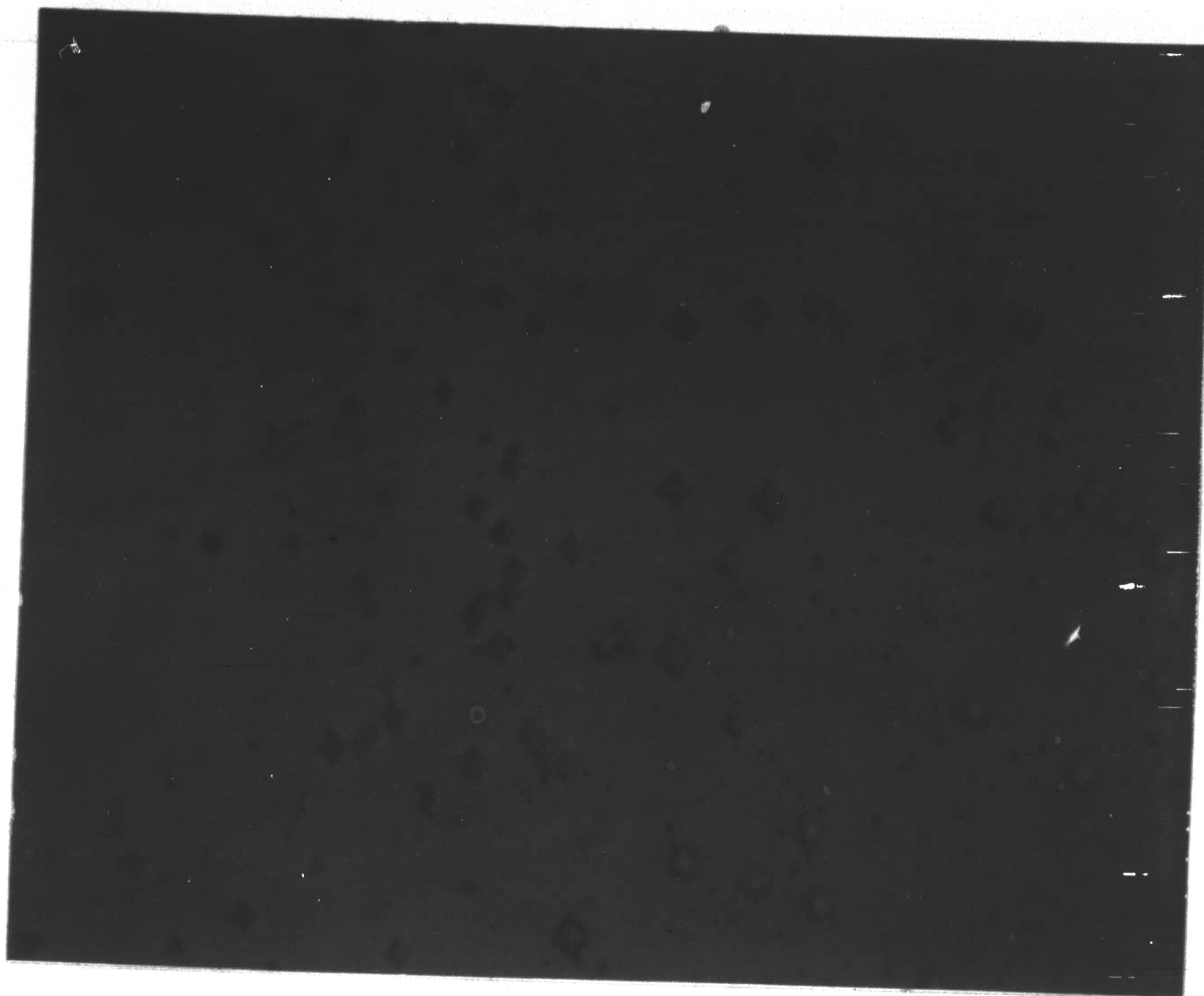


FIGURE 8. Dislocation etch pits in as-grown PbTe at magnification of 1200X, and etched for five minutes.

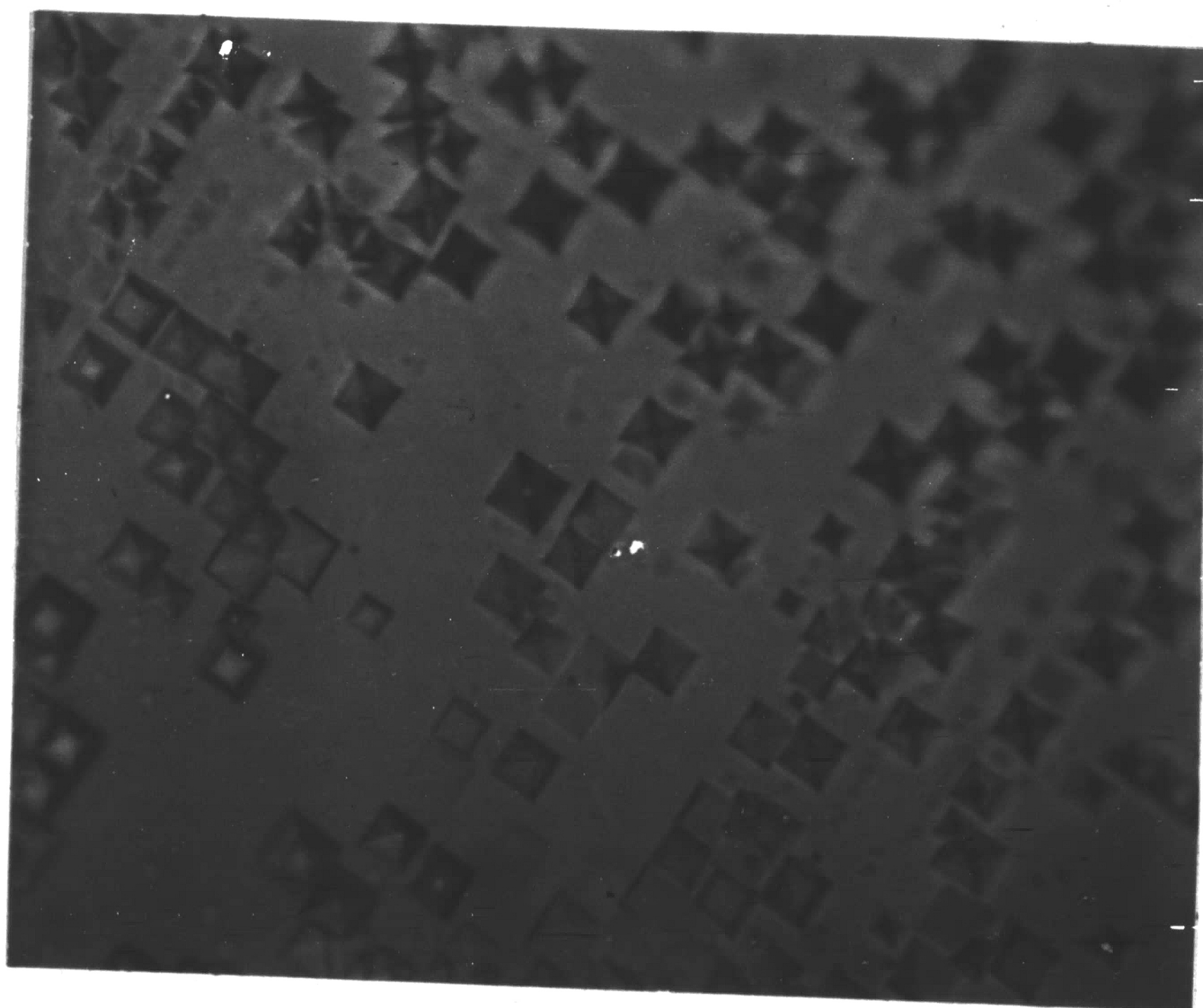


FIGURE 9. Dislocation etch pits in as-grown PbTe at magnification of 800X and etched for ten minutes.



FIGURE 10. Dislocation etch pits in as grown PbTe at magnification of 1200X and etched for ten minutes. Note the pyramidal nature of the pits.

IV. DISCUSSION OF RESULTS

In this particular study, it is important to establish whether the precipitation process is diffusion limited. As outlined in the introduction, if diffusion is shown to be the rate limiting step, then the kinetic data can be very useful in determining the shape of the precipitate particle and whether or not a pre-precipitation phenomenon is taking place. To show that a process is diffusion limited, the experimentally determined activation energy has to have a value equal to the diffusion activation energy of the diffusing constituent. To obtain a value for the activation energy a procedure, developed by Wert¹⁶ is followed. The reasoning that led to this procedure will now be discussed. Wert obtained kinetic data on the precipitation of C and N in iron by measuring the internal friction peak associated with the stress-induced interstitial diffusion of the solute atoms. A curve of the amount of precipitate as a function of the tempering time can be obtained since only atoms of C or N which remain in solid solution contribute to the internal friction. The height of the internal friction being directly proportional to the amount of C or N remaining in solid solution. By using an apparatus developed by Ke²⁵ to measure the internal friction peak, Wert was able to plot a set of curves similar to those shown in Figure 6 of this paper. The similarity between

the curves obtained by Wert and those being presented in this paper, is the dependence of the rate of precipitation on temperature. Wert felt that this dependence manifested itself in two forms. Temperature could change the rate of precipitation by changing the rate of diffusion or by changing the number of nucleating sites. Thus

$$\tau = L^2/D \quad (4-1)$$

where:

τ is the time it takes for a constant fraction of solute to precipitate. This constant fraction is taken as $(1 - \frac{1}{e})$ which equals 0.63.

L is proportional to the mean distance of diffusion and hence related to the mean distance between the particle of precipitate.

D is the diffusion coefficient

Since:

$D = D_0 e^{-\Delta H/RT}$, one may write

$$\tau = \frac{L^2}{D_0} e^{-\Delta H/RT} \quad (4-2)$$

In Wert's paper, ΔH is the heat of activation associated with the interstitial diffusion of the solute atoms. If the rate of precipitation is defined as being inversely proportional to τ , equation (4-1) may be rewritten as

$$FR(T) = \frac{D_0}{L^2} e^{-\Delta H/RT} \quad (4-3)$$

Thus the value for H may be obtained by plotting the reciprocal of the experimentally determined value of τ on the ln scale vs. the reciprocal of temperature. These points will yield a straight line, the slope being equal to the activation energy of diffusion provided that L is not temperature dependent. If L is temperature dependent, it would mean that the number of nucleation sites changed with temperature, since L is the distance between particles. Any determination of an activation energy when L is not a constant would give an erroneous result.

Although the curves in Figure 3-1 are helpful in obtaining a value of τ , which is needed for calculating the activation energy, these curves can be misleading. The curves plotted in Figure 7 give a far more comprehensive view of kinetic data. For one, if the data fall on a straight line Figure 7, one is assured that the equation 1-5 is obeyed.

$$f(t) = 1 - \exp [(-t/\tau)^n]$$

Secondly, if the slope of the curves plotted in a log ln (1-f(t)) vs. log t graph are not equal, one will not obtain a true value for the activation energy.

This has been shown by Barford,²⁶ in his study of the kinetics of NbC precipitation in austenite. The system Barford worked with circumvented the possibility of more than one carbide forming, since niobium is a stable carbide-forming element. Barford's data when plotted on

a $-\log \ln [1-f(t)]$ vs $\log t$ curve showed one straight line for the entire precipitation process at a given temperature. As shown in Figure 2 a and 2 b in his paper, the slope of the lines vary slightly. By finding the activation energy at different constant fractions of precipitation, Barford showed that the value obtained for the activation energy depended on what fraction of precipitation was chosen. Had all the curves on a $-\log \ln [1-f(t)]$ vs. $\log t$ plot been parallel, only one value of activation need have been calculated. Thus, if one is to calculate a value for the activation energy, by use of Figure 6, it is first necessary that the slopes in Figure 7 are equal.

As shown in Figure 7 the slopes of the curves for the first part of the precipitation process vary considerably with the temperature at which precipitation occurs. At a temperature of 462°C, the slope for the first stage is 1.3 whereas for a temperature of 340°C it is 0.68. Thus, an activation energy cannot be calculated, from the τ values obtainable in Figure 6. Although an activation energy cannot be calculated over this range in temperature, it should not be assumed that a different precipitation process is operative at each of the three temperatures used in this investigation. As was pointed out previously, an accurate determination of the activation energy depends

on the number of nucleating sites remaining constant with temperature.

The effect of the number of nucleating sites on the kinetics is most dramatically shown by an experiment performed by Wert. In this experiment, the kinetics of precipitation of N in α iron at 50°C were monitored by internal friction peak measurements. After measurements were taken for the complete precipitation process, the specimen was reheated to re-dissolve all the precipitates. The specimen was then quenched and the same experiment was again performed with one exception. The aging of the specimen at 50°C, was preceded by a precipitation period of 100 minutes at 27°C. During this length of time, approximately six per cent of the nitrogen precipitated. The specimen was then heated up to 50°C, and the kinetics of precipitation again monitored by internal friction peak measurements. As can be seen in Figure 5 of Wert's paper, there is a dramatic increase in the rate of precipitation when aging at 50°C is preceded by a short aging period at 27°C. The only explanation for this behavior is that more nuclei are present when a specimen is aged at 27°C. When the specimen is then aged at 50°C, these nuclei don't dissolve, and strongly influence the aging behavior at the more elevated temperatures. Thus if the number of nuclei is dependent on temperature, the slopes of the curves on a $-\log \ln [1-f(t)]$ vs. $\log t$ plot are

influenced in the following manner. If the number of nuclei increase with decreasing temperature, the slopes on $-\log \ln [1-f(t)]$ vs. $\log t$ plot should increase as the aging temperature is lowered, provided that the process over the temperature range is singularly activated. Graphs as shown in the Wert paper illustrate this point. The value for the activation energy as calculated from these graphs is 14,000 cal/mole. This is considerably lower than the value of 20,000 cal/mole for nitrogen precipitation in α iron. However, as has been discussed any determination of an activation energy from curves where n varies with temperature would be erroneous. In an effort to see if the slopes could be made parallel by keeping the number of nucleation sites constant with temperature, Wert ran the same tests again but each specimen underwent a short aging period at 27°C. In this instance, the activation energy as calculated from these curves gave a value that matched the activation energy of nitrogen in α iron. These experiments prove that nucleation does in fact influence the slope of the lines in a $\log \ln [1-f(t)]$ vs. $\log t$ plot. Wert's determination of the true activation energy when the number of nucleating sites remain constant, clearly shows this. As a consequence, the author feels that the variance of n with temperature as found in the system PbTe for the first stage of precipitation or the Pb-rich side, is probably due to nucleation and not be-

cause the process has a different activation energy at each temperature.

If indeed nucleation is influencing the value of n , one expects the slope to increase as the number of nucleating sites increase. In the results shown in this paper, the number of nucleating sites would be increasing with increasing temperature, since the maximum slope is observed at the highest temperature. This is contrary to what Wert observed and is also contrary to classical nucleation theory which states that as the temperature of aging is increased the number of nucleating sites decreases. However, there have been reported instances where the number of nucleating sites increase with increasing temperature. Dehlinger and Knapp²⁷ have observed this behavior in aluminum-silver alloy for the first decomposition product, Ag rich clusters. Abrams²⁰ working with PbSe, a system of close chemical nature to PbTe, found similar precipitation behavior. As was done in the present work, Abrams followed the precipitation of Pb in PbSe by use of Hall effect measurements. When Abrams data were plotted on a $\log \ln [1-f(t)]$ vs $\log t$ plot, the values of n were 1.35, 1.02, and 1.00 for precipitation temperature of 390°C, 303°C, and 242°C, respectively. Qualitatively, this behavior is the same as in PbTe, however, the decrease in slope with temperature is not as severe. Using the diffusion-limited theory of Ham, Abrams calculates the number of nucleating sites at each

temperature. To justify the use of the theory, it is of necessity that the process can be shown to be diffusion limited. As has been discussed earlier, one does this by showing that the activation energy of the process is equal to the activation energy of the diffusing species. Abrams finds an activation energy of .84 ev. for the process which compares quite favorably to the activation energy of .83 ev. for the diffusion of Pb in PbSe single crystals as reported by Seltzer and Wagner,²⁸ Abrams then uses the following formulas of Ham to find the particle size and number.

$$\tau = \frac{1}{\lambda_0^2 D} \quad (4-4)$$

where:

$$\lambda_0^2 = \frac{3r_0}{r_s} \left(1 + \frac{9}{5} \frac{r_0}{r_s} \right) \text{ for spherical particles}$$

with $\frac{r_s}{r_0} \gg 1$

Using a trial and error method, Abrams finds the value of r_0 that gives a calculated value of τ which corresponds to the experimental value of τ that is associated with a certain aging temperature. By knowing the size of each particle, the number of atoms associated with each particle can be calculated. Since the number of atoms/cm³ that have precipitated are known from Hall measurements, one can calculate the number of precipitate particles/cm³ by

dividing the total number of precipitated atoms/cm³ by the number of Pb atoms in a precipitated particle. Using equation (4-4), Abrams calculated the number of precipitate particles/cm³ to be 2.39×10^{13} , 4.7×10^{12} , 4.50×10^{12} for temperatures of 390°C, 303°C, and 242°C, respectively. Since at time τ , precipitation is in the second stage for the lower two temperatures, Abrams extrapolates on a log ln [1-f(t)] vs. log t the first stage behavior to time τ . He then recalculates the number of precipitate particles/cm² for the lower two temperatures. In this instance, there is not an increase in the number of nuclei with an increase in temperature, as was true for the nonextrapolated case. For the extrapolated case, the number of precipitate particles/cm³ are 2.39×10^{13} , and 2.81×10^{13} , for 390°C, 303°C, and 242°C, respectively. It is the latter values that Abrams accepted, as valid. This is justifiable since the second stage kinetics are so much different from the first stage that its inclusion in the calculation will affect the outcome of the calculations.

One is now faced with explaining why the Ham equation gives a result that cannot be explained by the results of the Wert paper. According to Wert as the n value increased the number of nucleating sites increased. Yet, according to the calculations performed by Abrams using an equation from the Ham analysis, even though the n value increased with temperature of aging, the number of nucleating sites

at both 390°C and 303°C was lower than at 242°C. In the author's opinion, it could be for either of two reasons. One is that Abrams' determination of the activation of the activation energy was not entirely accurate. Both the variance of n values with temperature and the calculation of the number of nucleating sites showed that the number of sites changed with temperature. As has been previously discussed, the prime prerequisite for an accurate determination of the activation energy is that the number of sites remain constant. Thus, it is possible that the true activation energy for the process is not close enough to .84 ev, the activation energy of Pb diffusing in PbSe, to conclude that the process is diffusion-limited. If this were true, then any conclusions drawn from Ham's diffusion-limited theory would be erroneous. However, since the n values of Abrams do not vary that considerably, 1.00 at 242°C to 1.35 at 390°C, it is more reasonable to assume that the process is diffusion-limited; than to assume it is not. With such an assumption the only other explanation for the discrepancy between Wert's experimental results and the results of Abrams' work explained in light of the Ham analysis, is that the Ham formulation has shortcomings. Such a stand is not unreasonable, when one considers that the effect of the number of nucleating sites has on the value of n is not considered in the Ham theory.

Since nucleation has a strong influence on the observed kinetics, it is of interest to consider, where it occurs. Gross imperfections, such as grain boundaries and voids can be excluded, since from all indications the material was a single crystal. Although an X-ray determination was not made, every specimen that was used had parallel cleavage planes along an edge. Furthermore, there was no indication of thermal grooving on the specimen used. In the polycrystalline crystals that were grown, thermal grooving occurred on nearly every test specimen. Other sites where nucleation would be energetically favorable could be dislocations and vacancies. That nucleation is occurring solely at dislocations is very doubtful. For one, the experimental value for τ does not correspond to the values of τ predicted by the theories dealing with precipitation at dislocations. As explained in the introduction, the value of τ does not correspond to the values of τ predicted by the theories dealing with precipitation at dislocations. As explained in the introduction, the value of τ can be related to r_s/R by a derived curve from the Ham analysis. Using the value of τ , the reduced time, was calculated to be 0.073. The reduced time is related to τ and r_s by the following expression

$$T = \frac{D\tau}{r_s^2}$$

By using Ham's derived curve, this value of T corresponds to a value of 1 for r_s/R . Since r_s is equal to $1.4 \times 10^5 \text{ \AA}$, a value of such magnitude for R , the effective capture radius, would be totally incompatible with dislocation theory. A different formulation by Morin and Reiss⁴ in their experiments, also rules out the possibility of precipitation occurring solely at dislocations in the present investigation. This formula, is identical to equation (4-1), which was used by Wert under diffusion-limited conditions. It would appear that using the same formula for a situation where motion is due only to diffusion and also for a situation where motion is due to diffusion and the drift associated with a stress field is inconsistent. However, Ham showed in his analysis that motion due to drift is only influential in the very early stages of precipitation. Using equation (4-1), a value of τ equal to 8.85×10^5 is calculated. This value is two orders of magnitude greater than the experimental value found of τ . In order that the experimental value of τ correspond to that calculated by equation (4-1), the experimental value for the dislocation density would have to have been four orders of magnitude greater than what was found. The n value of 1.3 for the first stage of precipitation at a temperature of 462°C , is additional evidence for precipitate not being solely at dislocations. All existing theories or kinetics attach a value of $n = 1$ or less for precipitation at dislocations.

With the exclusion of dislocations as acting as the sole site for nucleation, it is quite likely that precipitation is predominantly occurring at vacancies. There have been numerous reported instances of precipitation at vacancies. Morin and Reiss⁴ give considerable evidence that the nucleation centers for lithium in germanium are vacant germanium lattice sites. Abrams²⁷ contends that vacant Pb sites act as nucleating sites to explain the lack of a second stage precipitation phenomena in Se rich PbSe. It has been shown by H. Gobrecht and A. Richter²⁹ that Pb rich PbSe is most likely accommodated by Pb vacancies. If vacancies acted as nucleating sites, many more sites would be available for nucleation in Se rich PbSe. Thus, with the precipitating atoms being distributed at a greater number of sites, the precipitate particles don't reach the necessary size for the onset of second stage precipitation. That Pb vacancies also act as the predominant nucleating sites in PbTe is supported by the experimental evidence of this investigation. These results indicate that the number of nucleating sites are increasing with temperature. If the nucleating sites were dislocations, the number of sites would not change with temperature. However, according to thermodynamics the number of vacancies increase with the temperature of aging. This relation is true according to the law of mass action, even if excess Pb were to occupy interstitial sites.

A final consideration, is to discuss the reason for a second stage precipitation process. As was pointed out in Chapter III, there is a dramatic decrease in the n value after 50% of the atoms have precipitated. The same phenomena was observed by Abrams in studying the kinetics of Pb rich PbSe. Butler,³⁰ among others, observed a two-stage precipitation process with carbon precipitating from ferrite. Butler attributed the first stage to be due to the precipitation of ϵ carbide. The loss of carbon from solution in the second stage was attributed to the growth of cementite. In contrast to the precipitation in ferrite, the evidence of this investigation indicates that the second stage kinetics is not due to the formation of a precipitate of different chemical structure. Butler's kinetic data show a plateau existing, where no loss of carbon from solution is occurring. Butler states that during this time, two processes are occurring. Loss of carbon from solution is occurring due to the nucleation of cementite, and simultaneously, unstable ϵ carbide is dissolving. Thus, there is a period where the kinetic measurements show no net loss in carbon from solution. In this investigation, no time delays was observed at any of the temperatures for the onset of the second stage. Stronger evidence supporting the view that the precipitate of the second stage is chemically the same as that of the first stage, is the fact that the final precipitate is Pb. The data showed that

the solubility of Pb in PbTe in equilibrium with the precipitate, was the same as the solubility of Pb in PbTe when PbTe was in equilibrium through the vapor phase with Pb-rich ingots. Had a precipitate different from Pb formed, a solubility relation differing from that found on a PbTe phase diagram would have been observed. That anything but Pb could have precipitated in the first stage is doubtful, since the process was in all likelihood diffusion controlled.

It still remains to consider the cause for a second stage precipitation step. Umlösen, has a $t^{1/3}$ power dependence. The n values obtained in this experiment, are about 0.20. This indicates an exponential $t^{1/5}$ power dependence. The most plausible explanation is the same one given by Bullough and Newman¹¹ to account for $n < 1$ values in stress-assisted precipitation at dislocations. Bullough and Newman, introduce a parameter α which is directly related to the velocity of transfer of solute atoms across the precipitate matrix interface. They propose that V may be large in the early stage of precipitation and gradually decrease due to increased strain present at the precipitate-matrix interface. These strains provide an additional activation barrier which has to be overcome, before precipitation occurs. When transfer across the interface is slower than the arrival of solute to the velocity of the precipitate, the activation barrier at the interface becomes the rate controlling step. Thus, n can assume values from 0 to 1 depending on the height of this additional barrier.

There have been numerous instances where experimental data have been explained using this theory. As already mentioned, Abrams²⁰ used it to explain a second stage precipitation PbSe. Bullough and Newman¹¹ use it to show that the data of Thomas and Leak¹⁰ would conform to the Ham theory when the parameter α is introduced. R. C. Dorward and J. S. Kirkaldy³¹ also used the theory to explain why they obtained $n < 1$ values in their work with Cu precipitation in silicon. As in these experiments, it is most plausible to assume that the slow rate of precipitation in the second stage is due to a rate-limiting process at the precipitate-matrix interface. The cause of this rate-limitation is due probably due to the precipitate reaching critical size beyond which surface-energy effects reduce the velocity of transfer of solute across the interface.

One final consideration of this program was to find if an internal precipitation process would be a more rapid method to obtain desired electron concentrations. It was observed that to obtain the equilibrium concentration at a given temperature, the same time was needed for the internal precipitation process as for vapor diffusion. This is primarily because second stage precipitation occurs at such a slow rate. However, if one were to precipitate and quench at the termination of the first stage, a rapid method for attaining the desired electron concentration is achieved.

V. CONCLUSIONS

- 1) Hall Effect measurements provide an excellent way to monitor precipitation in the compound semiconductors, PbTe.
- 2) An activation energy for the initial stage of precipitation could not be calculated because the number of nucleation sites varied with temperature of precipitation.
- 3) The variance in slope with temperature on a $-\log \ln [1-f(t)]$ vs. $\log t$ plot is considered to be due to nucleation and not because the process is differently activated at each temperature.
- 4) The fact that the slopes of the curves on a $-\log \ln [1-f(t)]$ vs. $\log t$ plot increase with temperature indicates that the number of nucleating sites increases with temperature.
- 5) Vacancies are considered to be the predominant nucleating sites, since the amount of vacancies increase with temperature of aging. In addition, the formation of spheroidal particles as indicated by an n value of 1.3 at the highest temperature of aging supports the view that precipitation is occurring on vacant sites.

- 6) Dislocations are discounted as a primary site for nucleation for the following reasons: the number of nucleating sites would be a constant with respect to temperature if precipitation was occurring at dislocations. The n value of 1.3 found at an aging temperature of 462°C , is too high for precipitation at dislocations. Lastly, the kinetic data showed that precipitation during the first stage was faster than predicted by any of the theories dealing with precipitation at dislocations.
- 7) Precipitation during the first stage is considered to be diffusion-limited.
- 8) The slow rate of precipitation during the second stage is attributed to surface energy effects decreasing the velocity of solute atoms crossing the matrix-precipitate interface.
- 9) Even though precipitation during the second stage is exceedingly slow, precipitation is a more rapid way to obtain desired carrier concentrations.

VI BIBLIOGRAPHY

- 1) W. Albers, C. Haas and H. J. Vink, "Quenching Effects and Determination of the Existence Region of Semiconducting Compounds." Philips Res. Repts. 18, 372 (1963).
- 2) R. F. Brebrick and R. S. Allgaier, "Composition Stability Limits of PbTe II." J. Chem. Phys. 32, 1826 (1960).
- 3) W. C. Dash, "Copper Precipitation on Dislocations in Silicon." J. Appl. Phys. 27, 1193 (1956).
- 4) A. H. Cottrell and B. A. Bilby, "Dislocation Theory of Yielding and Strain Ageing of Iron." Proc. Phys. Soc. (London) A62, 49 (1949).
- 5) F. J. Morin and H. Reiss, "Precipitation of Lithium in Germanium." J. Phys. Chem. Solids 3, 196 (1957).
- 6) W. W. Tyler and W. C. Dash, "Dislocation Arrays in Germanium." J. Appl. Phys. 28, 1221.
- 7) F. S. Ham, "Stress Assisted Precipitation on Dislocations." J. of Appl. Phys. 30, 915 (1959).
- 8) S. Harper, "Precipitation of Carbon and Nitrogen in Cold-Worked Alpha-Iron." Phys. Rev. 83, 709 (1951).
- 9) W. A. Johnson and R. F. Mehl, "Reaction Kinetics in Processes of Nucleation and Growth." Trans. Am. Inst. Mining Engrs. 135, 416 (1939).
- 10) W. Pitsch and K. Lüche, "Zur Ausscheidung von Kohlenstoff aus übersättigter Lösung in α -Eisen Während der Auslagerung." Arch. Eisenhütten 27, 45 (1956).
- 11) W. R. Thomas and G. M. Leak, "The Straining Ageing of Alpha-Iron." J. Iron and Steel Inst. 180, 155 (1955).
- 12) R. Bullough and R. C. Newman, "The Kinetics of Impurity Precipitation on Dislocations Small Drift Theory." Phil. Mag. 6, 403 (1961).
- 13) W. W. Scanlon, "Precipitation of Te and Pb in PbTe Crystals." Phys. Rev. 126, 509 (1962).
- 14) S. I. Boltaks and Iu. N. Mokhov, "Self Diffusion and Diffusion of Impurities in Lead Telluride and Selenide." Soviet Phys. - Tech. Phys. 3, 974 (1958).
- 15) F. S. Ham, "Theory of Diffusion Limited Precipitation." J. Phys. Chem. Solids, 6 335 (1958).

- 16) C. Zener, "Theory of Growth of Spherical Precipitation from Solid Solution." J. of Appl. Phys. 20, 950 (1949).
- 17) C. Q. Wert, "Precipitation from Solid Solutions of C and N in α Iron." J. of Appl. Phys. 20, 943 (1949).
- 18) H. K. Hardy, "The Ageing Characteristics of Binary Aluminum-Copper Alloys." J. Inst. Met. 79, 321 (1951).
- 19) J. C. Llanes and G. Wassermann, "Studies on the Increase and Decrease in Length of an Aluminum Alloy Containing 4% Copper." Z. Metallk. 41, 381 (1950).
- 20) H. Abrams, "Precipitation Studies of Pb and Se in PbSe Single Crystals." Doctoral Dissertation, Lehigh University, (1968).
- 21) W. D. Lawson, "A Method of Growing Single Crystals of Lead Telluride and Lead Selenide." J. of Appl. Phys. 22, 1444.
- 22) E. Miller, K. Komarck and I. Cadoff, "Stoichiometry of Lead Telluride." Trans. of Met. Soc. of AIME. 215, 882 (1959).
- 23) F. L. Vogel, W. G. Pfann, H. E. Corey and E. E. Thomas, "Observations of Dislocations in Lineage Boundaries in Germanium." Phys. Rev. 90, 489 (1953).
- 24) D. G. Coates; as reported by M. Norr, NOLTR 63-156, U.S. Naval Ordnance Lab. (1963).
- 25) T. S. Ke, "Experimental Evidence of the Viscous Behavior of Grain Boundaries in Metals." Phys. Rev. 71, 533 (1947).
- 26) J. Barford, "Kinetics of NbC Precipitation in Austenite." J. Iron and Steel Inst. 204, 134 (1966).
- 27) U. Dehlinger and H. Knapp, "Thermodynamik der Kaltaushaltung." Z. Metallkunde 43, 223 (1952).
- 28) M. S. Seltzer and J. B. Wagner, Jr., "Self Diffusion of Lead 210 in Single Crystals of Lead Selenide." J. of Chem. Phys. 36, 130 (1962).
- 29) H. Gobrecht and A. Rechter, "Density Measurements and Disorder of PbSe." J. Phys. Chem. Solids, 26, 1889 (1965).
- 30) J. F. Butler, "Kinetics of the Two-Stage Precipitation of Carbon from Ferrite." J. Iron and Steel Inst. 204, 127 (1966).
- 31) R. C. Dorward and J. S. Kirkaldy, "The Precipitation Kinetics of Copper in Silicon near Room Temperature." Phil. Mag. 17, 929 (1968).

VITA

Walter L. Erhard was born in New York City on May 17, 1944 to Wendel and Margaret Erhard. He attended Brooklyn Technical High School where he was president of the Honor Society and secretary of the General Organization. He graduated Brooklyn Tech., June of 1962. In the fall of that year he started at Lehigh University. At Lehigh, he majored in Engineering Physics and was a member of Theta χ i fraternity. He was on the class cabinet for all four years of college and participated actively in wrestling and track and field. During the summer of 1965 he worked on an NSF research grant on condensation in shock tubes.

After receiving a B.S. in Engineering Physics in October of 1966, he started on his masters program in Materials Science at Lehigh.

Mr. Erhard started working at IBM in the fall of 1968. He is currently working as a reliability engineer in thin film interconnections and insulators for electronic components.