

PRESSURE INDUCED SOLID-SOLID TRANSITIONS
IN LOW ENERGY GAP SEMI-CONDUCTORS

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ABSTRACT

PRESSURE INDUCED SOLID-SOLID TRANSITIONS,
IN LOW ENERGY GAP SEMI-CONDUCTORS

by

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A study of pressure induced solid-solid polymorphic transformations in mercury chalcogenides is presented.

Polymorphic transitions for the HgSe-HgTe system were monitored by electrical resistance techniques, since the transitions are accompanied by a hysteresis effect and are characterized by a change in the resistivity of about five orders in magnitude. A linear dependence upon the transition pressures was discernible as the amount of selenium decreased in the alloys.

By measuring the rates of transition during the up-stroke and down-stroke cycles, the mechanism governing the velocity of the reaction was of the first-order type and was characterized by activation volumes.

The experimental results indicate that a mono-nucleonic reaction initiated these transformations. The motion of an interface, corresponding to Bridgman's "surface of separation", was detected during the up-stroke and down-stroke transitions. An investigation of Bridgman's "zone of indifference" established, by means of an "inflection" point, the equilibrium pressure for HgSe at 9.02 ± 0.04 kbar.

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INTRODUCTION

High pressure research has contributed to the determination of some fundamental properties of semi-conductors, such as their band structure, their conductivity, and their susceptibility.

The purpose of the present investigation was to examine the nature of the solid-solid polymorphic transformations exhibited by mercury chalcogenides under hydrostatic pressures. These transformations are accompanied by a small change in volume (8 - 9%), since the crystal structure is modified from the cubic-zincblend low pressure polymorph to the hexagonal cinnabar high pressure polymorph. This crystal structure change is also accompanied by a modification of the electronic structure of the solid, which is characterized by a resistivity increase of about five orders in magnitude. This large change in resistivity is such that the transformation can be studied with greater sensitivity by electrical measurement techniques than by volumetric measurement techniques. The characteristic hysteresis effect experienced by the two crystals--mercury selenide (HgSe) and mercury telluride (HgTe)--and detected by resistivity measurements by Blair and Smith (1) and Kafalas, et al (2) was also observed for the alloys. The up-stroke and down-stroke transition pressures were sufficiently reproducible for all the series of compounds so that the effect of the concentration of selenium (Se) in the alloys on the transition pressures was discernible.

The nature of the polymorphic phase transition was further investigated in view of establishing the existence of a "moving interface" which accompanies both the up-stroke and the down-stroke transitions. Soon after the initiation of the high pressure phase, such a barrier develops because of the inherent nucleation. While this interface traverses the solid, the high pressure phase grows, whereas the low pressure phase diminishes during the up-stroke transition. A similar behaviour was observed after the initiation of the low pressure phase in the case of the down-stroke transition.

In order to better understand the mechanism governing these polymorphic transitions, volumes of activation were measured for the HgSe - HgTe system, and the effect of the concentration of selenium (Se) in the alloys was also observed.

By following the solid-solid rate of transition, the possibility of the existence of a zero or very small rate of transition within the hysteresis curve was investigated. This range of pressure at which the rate of reaction should be almost zero, was defined by Bridgman (3) as a "zone of indifference".

Chapter I of this paper deals with the theoretical interpretation of the nature of solid-solid pressure induced phase transformations. Chapter II describes the experimental techniques employed to obtain our results. Chapter III interprets our experimental results. A final part contains a conclusion and presents some recommendations.

CHAPTER I

THEORETICAL INTERPRETATION

P. W. Bridgman (4) reported that he was able to measure the velocity of polymorphic changes in solids. His research provided the basis for a better understanding of the nature of these transitions, and has helped in the determining of the mechanisms governing the solid-solid transformation--be it kinetic, thermodynamic, or both. Lacam, et al (5) (6) have demonstrated that the kinetic phenomenon can be observed by taking resistivity measurements in order to follow the rate of transition.

Bridgman (4) measured the rate of the phase transition by observing the rate at which the pressure changed at a constant working volume of the high pressure instrument. By means of transition velocity or rate of reaction measurements he was able to detect, in many cases, a pressure region within which this rate of transition became zero, even when both phases were in contact in the crystal. He called this pressure region the "zone of indifference" (ZOI). Since his results were arrived at by volumetric means, he was only able to determine the range, or band of pressure where the rate of reaction would basically stop, and where both phases--the high pressure and the low pressure-- would be in equilibrium. The center of this band was the equilibrium pressure. Figure 1 illustrates typically how Bridgman observed rates of

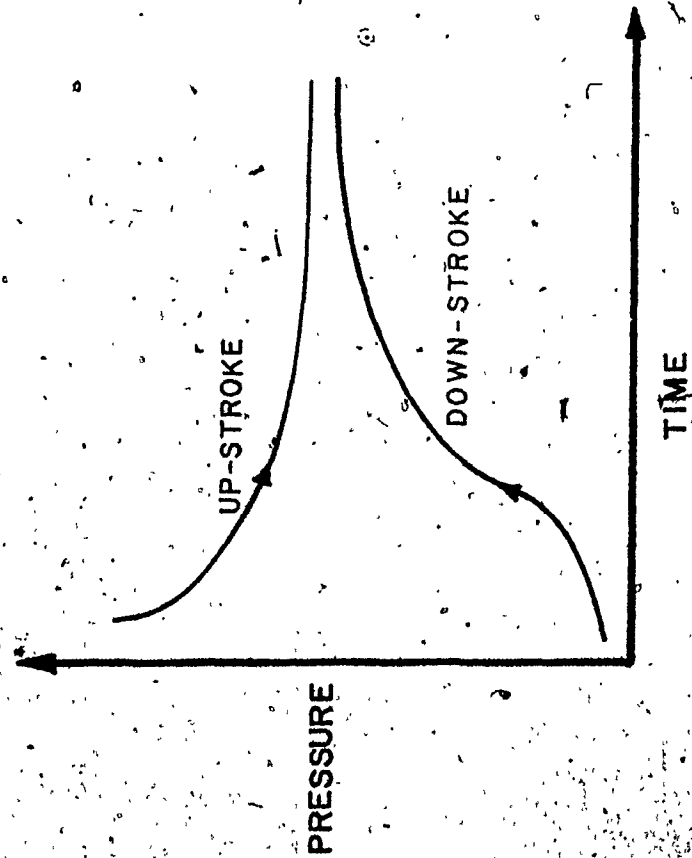


Fig. 1.--The rate pressure rises or falls toward the equilibrium pressure during a polymorphic transition.

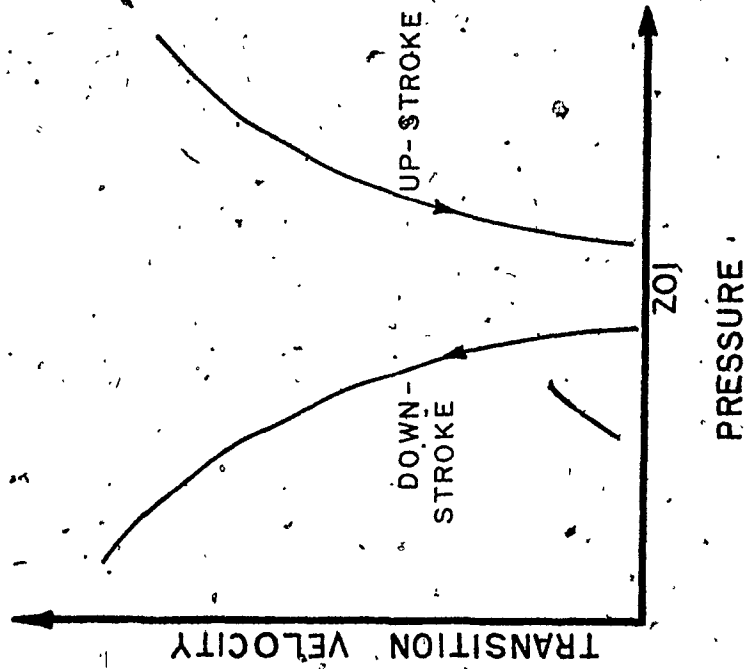


Fig. 2.--Slope of Figure 1 expressing the transition velocity (change of volume per minute) as a function of pressure.

reaction during polymorphic transitions. Figure 2 illustrates how, by differentiating the curves in Figure 1, he was able to determine his ZOIs.

Bridgman defined the "velocity" of a transition as the resulting increase in speed of the transition caused by a change of pressure away from the equilibrium pressure. He then stated that he took the slope of the reaction velocity curve versus pressure (Fig. 2) as a measure of the speed of transition (4, p. 62). Therefore his interpretation of the "speed" of the transition is essentially the acceleration of the transition. By obtaining acceleration of reaction curves for both the up-stroke and the down-stroke transitions, the location of the ZOI could also be defined.

Furthermore, Bridgman speculated that, as the formation of the higher or lower phase begins, there exists a "surface of separation" which completely traverses the crystal as the reaction progresses. He deduced this phenomenon while measuring the transition velocity in silver nitrate. He attributed the hook in the velocity curve (4, p. 60) to the formation of the nuclei of the new phase. He stated that, immediately after the formation of the nuclei, the rate of growth of the new phase was slower than it was after the "surface of separation" or interface had been fully developed. He went on to measure the rate at which this "surface of separation" moved away from the equilibrium pressure.

Bridgman's (3) (4) interpretation of the ZOI is shown in Figure 3 in which the potential energy of the lattice is plotted against a lattice parameter (i.e. reaction co-ordinate) to indicate

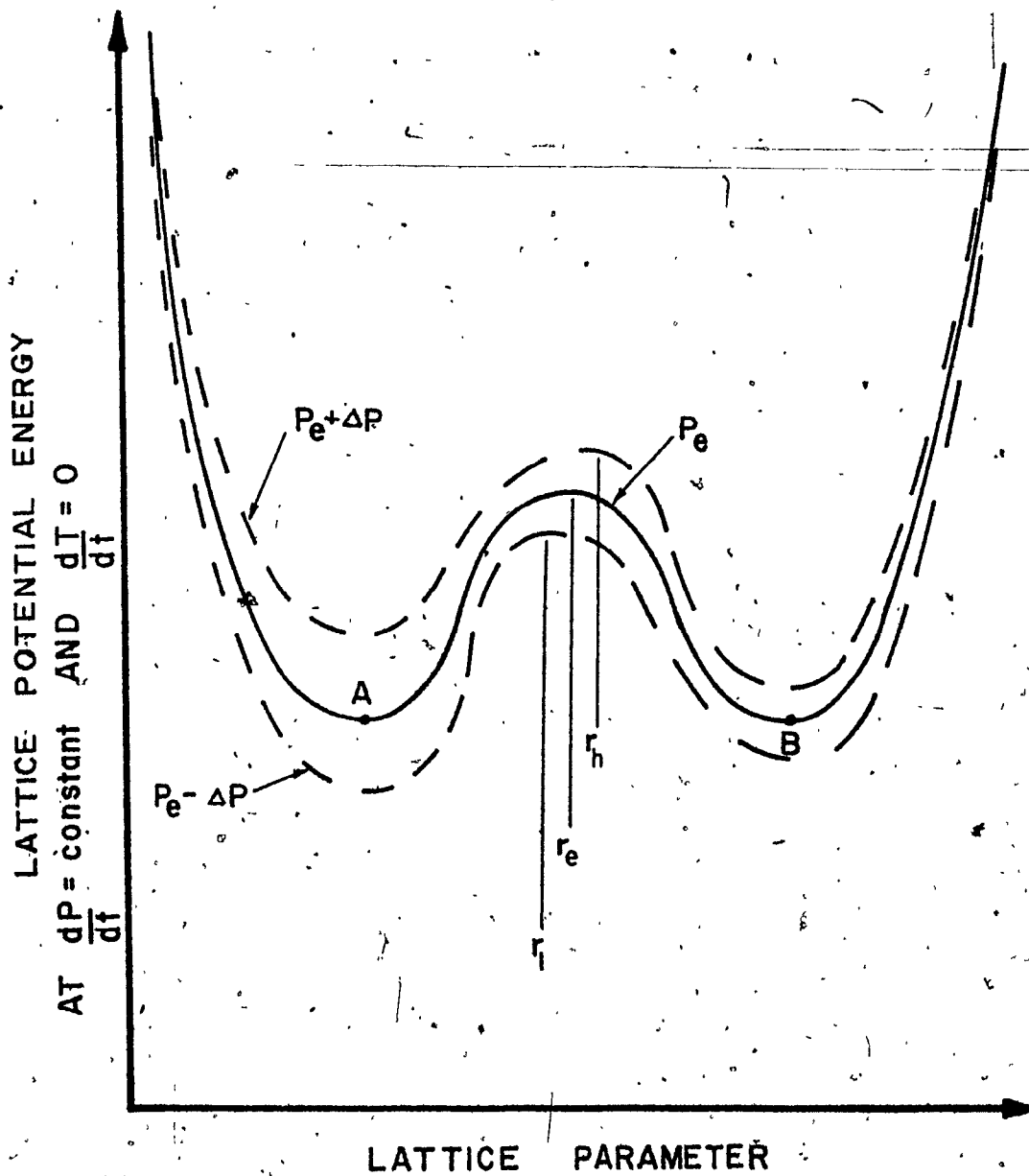


Fig. 3.--Bridgman's interpretation of the existence of a Zone of Indifference.

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the existence of both polymorphs. Since the crystal has two possible stability arrangements, there will be two minima, and the lowest one will correspond to the absolute stable form.

Points A and B in Figure 3 correspond to the existence of a low pressure and a high pressure phase respectively of the crystal lattice at the equilibrium pressure P_e . In this state, the potential energy of both lattice structures are equal, since both phases are in equilibrium with each other and are separated by an energy barrier whose magnitude and nature will be discussed later on. Let the center of the barrier be denoted by r_e being the equilibrium reaction co-ordinate in Figure 3. Then, by applying a change of pressure ΔP at a $\frac{dP}{dt} = \text{constant}$ and at a $\frac{dT}{dt} = 0$ ($T = \text{temp}$), the potential energy of the system will change to the extent that, if the center of the energy barrier is displaced by a magnitude greater than r_h when the internal energy of the system at A will be sufficient to pass over the barrier, the reaction will go to completion. That is, the minimum of the potential energy at A will be above the one of B, and the reaction will continue at the expense of the low pressure phase until the high pressure phase is the only one existing within the crystal structure.

Similarly, by applying a change of pressure $-\Delta P$ at a $\frac{dP}{dt} = \text{constant}$ and at a $\frac{dT}{dt} = 0$, the potential energy of the system will change and cause the center of the energy barrier to be displaced toward r_1 . Beyond the limit r_1 the reaction will go to completion,

and the high pressure minimum at B will now be above the one of A. Therefore, there is a range of pressure $2\Delta P$ where the potential energy of the crystal will not be altered sufficiently, and where the lattice parameter will lie between r_l and r_h : that is, the rate of reaction could be considered as being zero. In this region where the rate of reaction would be zero lies the ZOI. One can also say that there exists a Δr for the crystal structure, where the change in internal energy is below the activation energy necessary to cross the barrier. This Δr is dependent upon ΔP .

Theoretical calculations of equilibrium pressures for ionic crystals have proven to be of some significance in this respect. Jacobs (7) calculated equilibrium pressures empirically for polymorphic transitions in metallic halides by using the relation

$$P_e \approx \frac{E_2(r) - E_1(r)}{V_1 - V_2} \quad (I,1)$$

where: the subscripts 1 and 2 refer to the lower and higher phases; $E(r)$ refers to the lattice energies which are thermodynamic potential expressions (with nearest-neighbours distance dependence); V_1 and V_2 are the volumes of the respective phases.

Now, let us consider that the behaviour of polymorphic transitions can be characterized by Figure 4, where the crystal lattice energy is plotted against a lattice parameter (reaction co-ordinate) which is pressure dependent. When the system is relaxed, the crystal's energy is located at E_I corresponding to I. As pressure is increased, the crystal lattice--which is stable at I-- acquires

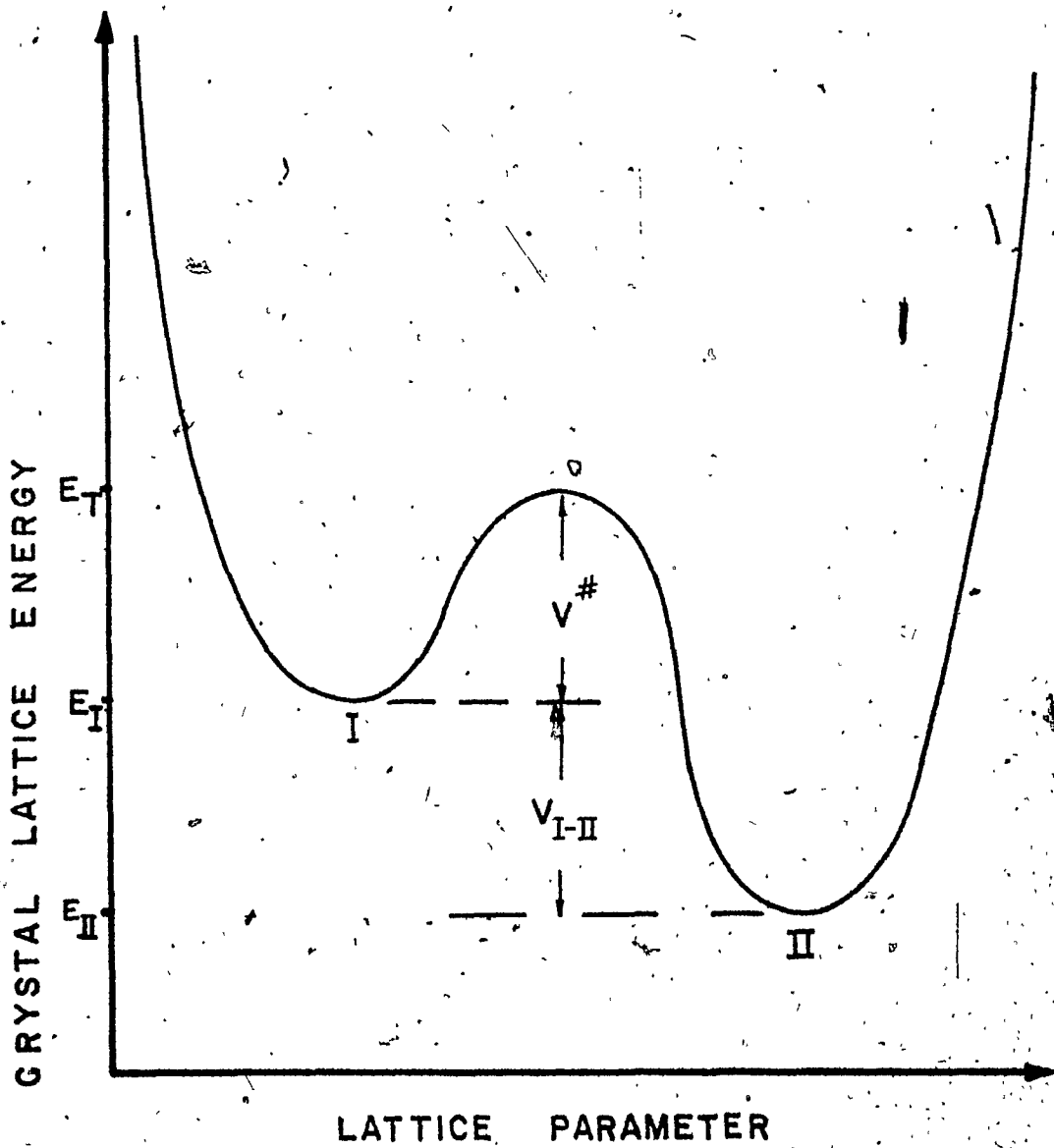


Fig. 4.--The behaviour of a polymorphic transition with respect to its crystal lattice energy as a function of a lattice parameter.

internal energy in the form of $dPdV$. Further increase in pressure brings about an increase in internal energy and, as long as the excess crystal lattice energy is less than the height of the barrier (E_T) separating both stable forms of the crystal, the reaction does not proceed, and no transition occurs. However, at a "transition" pressure, the crystal lattice energy is sufficient to create a reordering of its crystal structure which is characterized by the atoms at I crossing the barrier and moving toward the valley at II. This sudden reordering of the crystal structure cannot be interpreted as an instantaneous reaction since the strain transfer in the solid is sluggish: that is, only those atoms with sufficient internal energy cross over the barrier if pressure is maintained constant at the initial transition pressure. This energy barrier which must be crossed in order that the stable high pressure crystal lattice exist, is analogous to the "activation energy" in the case of temperature variation, and "activation volume" in the case of pressure variation as a driving force for the transformation.

The nature of the polymorphic transition is illustrated more clearly in Figure 5 where crystal volumes for the low pressure state (V_I), transition state (V_T), and high pressure state (V_{II}) are plotted against pressure. If K is a reaction velocity constant defined by Evans and Polani (8) as existing between the initial and transition states; and if α and α' are factors such that $(\alpha - \alpha')f$ expresses the change of energy exhibited by the system in passing from the initial to the transition state, and if f is a variable parameter of the system, then the relation

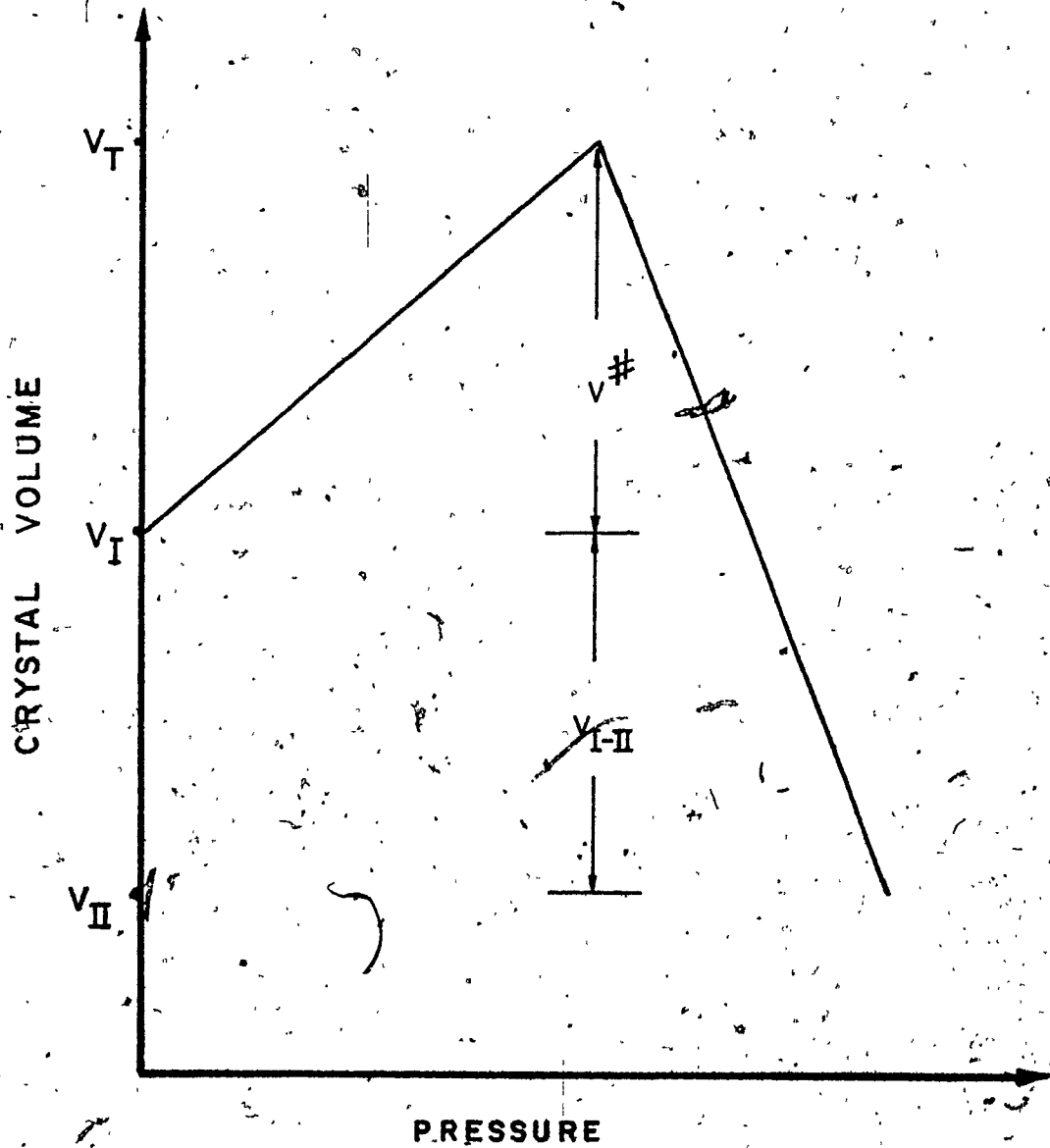


Fig. 5.--The behaviour of a polymorphic transition with respect to its crystal volume as a function of pressure.

$$\frac{d \log_e K}{df} = \frac{\alpha - \alpha'}{R_0 T} \quad (I,2)$$

expresses the nature of the transition. If $f=T$ (temperature), then $(\alpha - \alpha') = E^*/T$ (activation energy over temperature), and (I,2) corresponds to Arrhenius' equation $K = K_0 \exp(E^*/R_0 T)$.

In our consideration $f = P$, (hydrostatic pressure) and $\alpha - \alpha' = \Delta V$ (the volume change accompanying the formation of the transition state). Therefore, in our case,

$$\frac{d \log_e K}{dP} = \frac{V_I - V_T}{R_0 T} = \frac{\Delta V}{R_0 T} \quad (I,3)$$

or

$$K = K_0 \exp(P \Delta V / R_0 T).$$

Now, defining $\Delta V = V^\ddagger$ as the activation volume, we can write

$$V^\ddagger = R_0 T \frac{d \log_e K}{dP} \quad (I,4)$$

where K can be the rate of change of the reaction, or, in this case, the rate of change of resistance $(\Delta R / \Delta t)$. The equation for the activation volume at 21°C is

$$V^\ddagger = R_0 T \left. \frac{d \ln(\Delta R / \Delta t)}{dP} \right|_{\frac{dT}{dt} = 0} = 24,444 \left. \frac{d \ln(\Delta R / \Delta t)}{dP} \right|_{\frac{dT}{dt} = 0} \quad (I,5)$$

where R_0 is the gas constant and P is expressed in bars.

Bridgman (4) noted that the reaction proceeded at a much greater rate during the down-stroke transition than during the up-stroke transition. This can be explained by the fact that, as the internal energy of the lattice is decreased in order for the crystal to assume its stable high pressure phase, the volume is decreased from V_I to V_{II} . However, prior to the up-stroke transition, the crystal lattice energy must be increased and, as a result, the system must go through the activation state having the volume of $V^\#$. This increase in volume is not governed by a thermodynamic mechanism but by a truly kinetic one. Therefore, the amount of energy required to change V_I to V_{II} during the up-stroke transition is related to $V^\#$. At the stable phase V_{II} , and before the stable V_I phase can begin to grow during the down-stroke cycle, the change of volume required is greater than $V^\#$ by at least $V_I - V_{II}$ (volume change accompanying the transition). Once this energy (required to change volume by $V_I - V_{II} + V^\#$) is supplied to the crystal lattice, the down-stroke reaction rate will dominate.

Now, let us use Figure 5 in order to explain the possible existence of a zone of indifference. If the reaction has undergone 50% of its course (that is, both phases are present in the crystal at the same time), a state of equilibrium will prevail as 50% of the crystal structure exists at V_I and the other 50% exists at V_{II} . This state of polymorphic equilibrium would occur only at a certain pressure range, the center of which is the equilibrium pressure P_e . This P_e would be the pressure at which there exists a probability

of finding: a) 50% of the atoms stable, with a lattice energy corresponding to V_{II} and having crossed the barrier; b) the remaining 50% of the atoms having a lattice energy sufficient enough to potentially cross the said barrier. The same interpretation would apply in the case of the down-stroke transition.

Now, let us apply this interpretation to the hysteresis curve as illustrated in Figure 6 in order to try and locate the ZOI. Here we show the variation of resistance with pressure characterizing the transition. The up-stroke and down-stroke initiation pressures are P_u and P_d respectively. We should locate the ZOI within the hysteresis curve since by definition both phases have to be present at the same time. We have arbitrarily located the position of the ZOI in Figure 6. Lagan and Peyronneau (9) have shown that the center of a hysteresis curve is not necessarily the ZOI.

When both phases are present in the crystal, and when there is insufficient internal energy for either of the phases to cross over the barrier (corresponding to the activation state), the rate of transition should be characterized by a zero or very small rate of change. This would mean that during either the up-stroke or down-stroke transition the rate of transition (as a function of the applied pressure) should go through an inflection point--that is, the derivative of the rate of transition (i.e. acceleration) at a constant rate of change of pressure should be zero.

The existence of the ZOI within the hysteresis curve would be anticipated either near the up-stroke transition curve or near

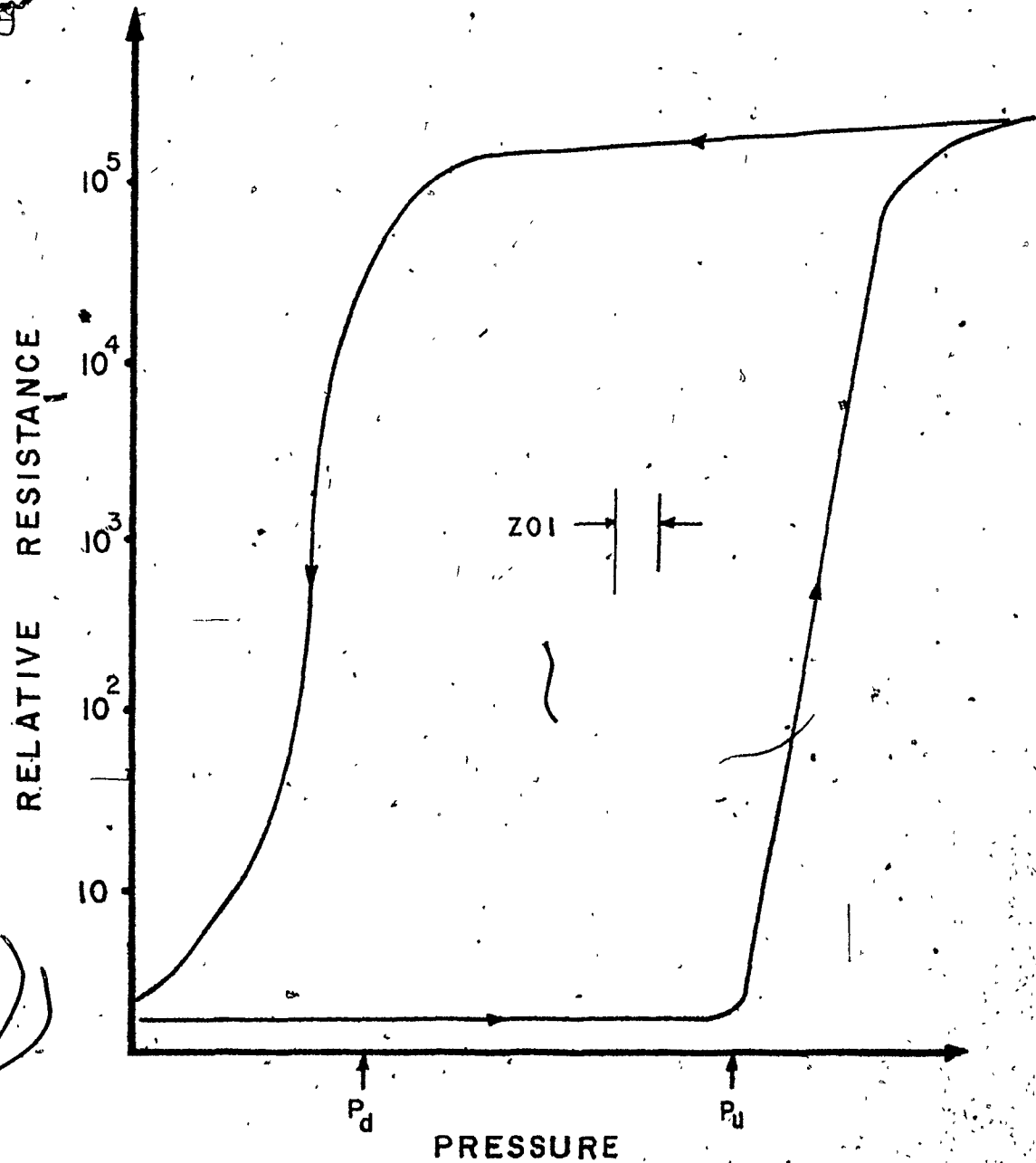


Fig. 6.--Characteristic hysteresis effect from resistance measurements and the possible location of the ZOI.

the down-stroke transition curve. Vanfleet and Zeto (10) (11) (12) have demonstrated that for the bismuth I - II transition the ZOI lies a few hundred bars away from the up-stroke initiation pressure. If, then, the ZOI were quite near the up-stroke transition pressure curve, and if the reaction were allowed to go to 50% completion, upon decreasing the pressure at a constant rate, there can arise two possibilities. Either the rate of reaction will slowly decrease at a constant rate (negative slope), or there will be no reaction (zero slope) until the lower transition branch of the hysteresis curve is reached. In the latter case one can judge that the ZOI exists in the interior of the hysteresis curve, and, only by repeating the process during the down-stroke transition and by observing a similar behaviour, can one locate the ZOI.

Ideally, a zero rate of reaction would be observed when a constant rate of decrease of pressure is applied to the crystal soon after the initiation of the up-stroke transition until it reaches I again (A, Fig. 7). Then, if the pressure were increased until the up-stroke transition were initiated for a second time, and if the reaction were allowed to proceed to completion at the high pressure phase (II, Fig. 7), a zero rate of reaction during the down-stroke transition could be investigated. Now, if the down-stroke transition were initiated, and a constant rate of increase of pressure were applied (B, Fig. 7), then the region at which both these zero rates overlap (C, Fig. 7) would define the ZOI.

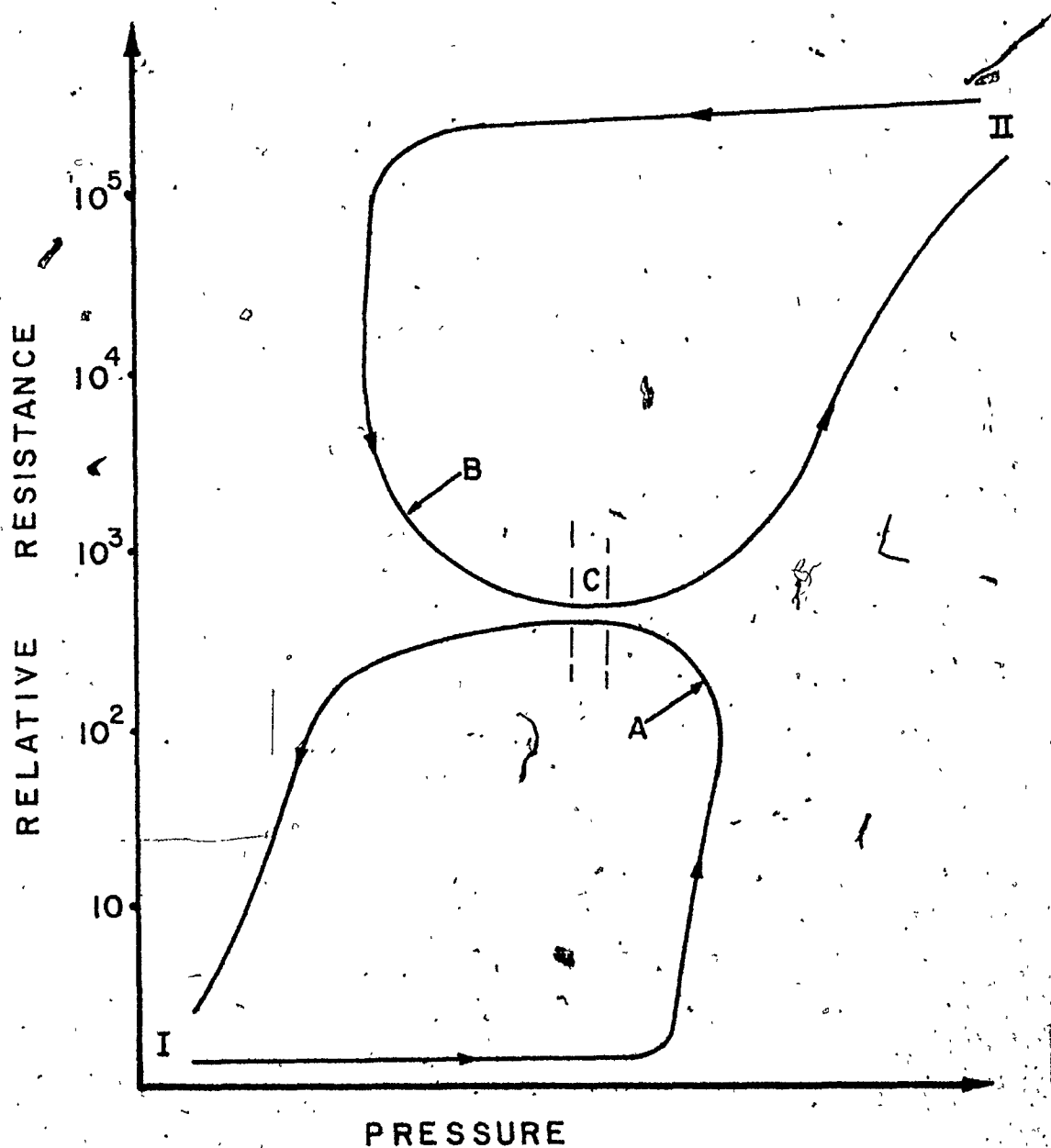


Fig. 7.--Overlapping of zero transition rates defining the Zone of Indifference.

Since the rates of reaction are different for the up-stroke and down-stroke transitions, the ZOI is expected to lie asymmetrically within the hysteresis curve.

CHAPTER II

EXPERIMENTAL PROCEDURE

Material Used

Polymorphic transitions of $\text{HgSe}_x\text{Te}_{1-x}$, with a variation of $0 \leq x \leq 1$ by $x = 0.2$, induced by hydrostatic pressures were investigated. The crystals and alloys were prepared by the modified Bridgman technique, using direct synthesis from their elements under controlled pressure of the volatile components in a sealed silica tube to prevent dissociation, and to insure stoichiometry. Semiconductor grade materials, that is, 99.9999% pure, were used for the synthesis of all the crystals. These compounds having large fragments of single crystals were prepared by Dr. B. A. Lombos in the Microelectronics Laboratory at Sir George Williams University, Montreal. These crystals were characterized by Hall effect measurements, the results of which will be reported in the near future. The physical properties of HgSe , HgTe , and some alloys have already been reported (13) (14) (15) (16) (17) (18) (19) (20).

Pressure and Resistance Measurement Apparatus

A piston-cylinder type apparatus capable of generating pressures up to 28 kilobars¹ was employed. The physical arrangement of the

¹One kilobar (kbar) = 1000 bars = 1.0×10^9 dynes/cm² = 986.92 atm. = 1.0197×10^3 kgf/cm².

components which generated high pressure and which allowed measurements to be made within the high pressure chamber are labeled in Figure 8. Samples were mounted on a holder (A) which was fixed to the obturator (B). All electrical measurements within the pressure chamber were provided by 5 twin-lead thermocoax cables (C). One cable was used by the pressure sensor and the remaining four were used to measure resistance variations of the samples. Pressure was supplied by a 300-ton hydraulic pump and, due to the area differential, high pressure was created in the volume (D) between the top of the piston (E) and the obturator as the pushrod (F) moved the piston higher in the chamber.

An equivolume mixture of n-pentane and iso-pentane served as the pressure transmitting medium. This liquid environment was confirmed as truly hydrostatic by Barnett and Bosco (21) up to 60 kbar, under certain conditions. The pressure was measured by the resistance variation of a manganin coil which had been calibrated with Birch's (22) transition point of KBr ($18,430 \text{ kgf/cm}^2$). The variation of the resistance of the manganin coil was monitored by using the coil as one of the arms in a Wheatstone bridge configuration. A Keithley microvoltammeter was used to monitor the balanced condition of the bridge circuit. Any unbalancing of the bridge was due solely to the variation of the resistance of the manganin coil itself, since low temperature coefficient resistors were used for the other arms of the bridge. Any variation of the coil resistance was within the linear operating range of the bridge circuit.

The relation between pressure and the change of resistance of

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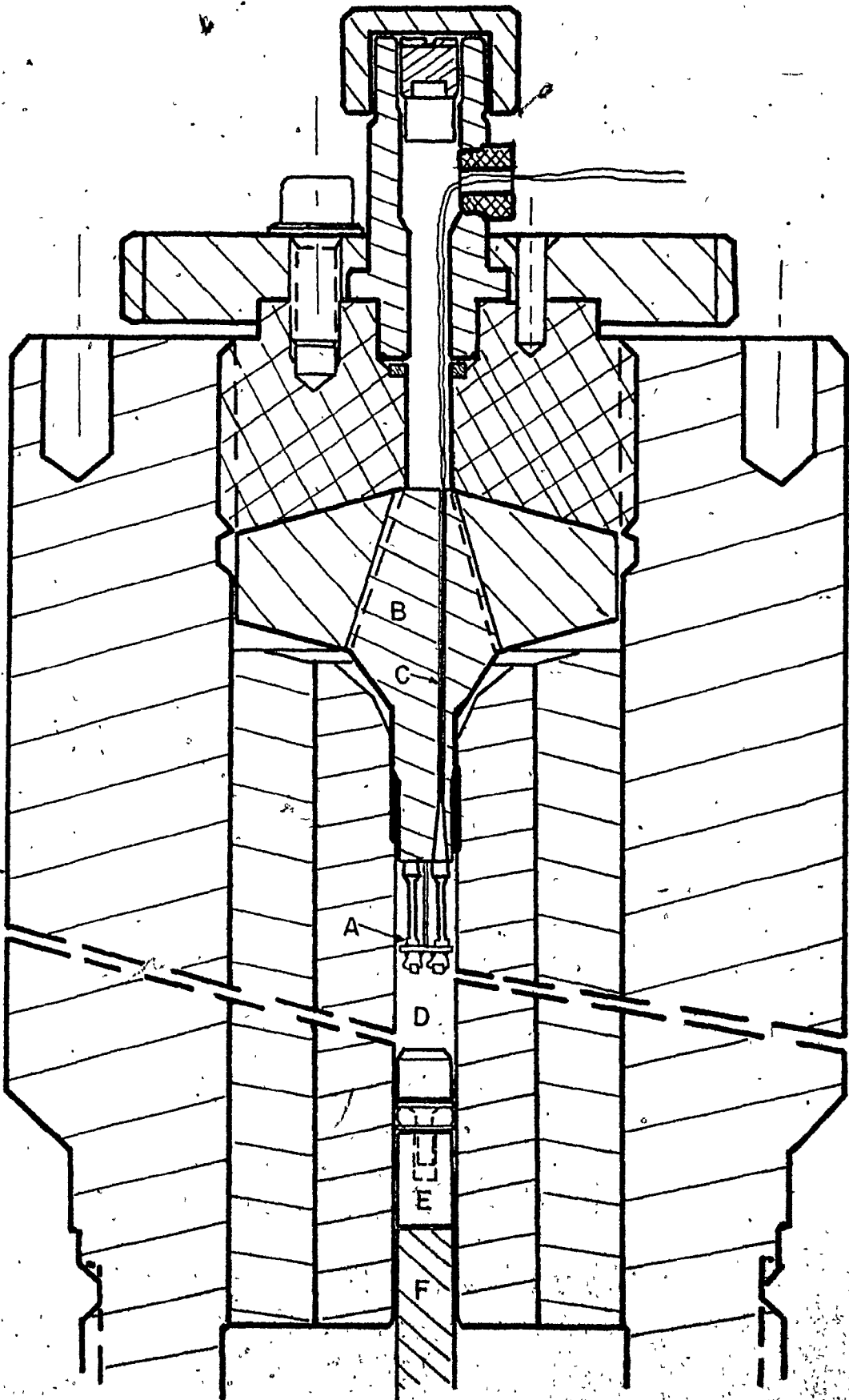


Fig. 8.--High-pressure chamber assembly

the coil used was

$$P = 420 \frac{\Delta R}{R_{atm}} \quad (II, 1)$$

where P is in kbar, where R_{atm} is the resistance of the coil at atmospheric pressure, and where ΔR is the respective change in resistance of the coil.

For a change of resistance of 0.2Ω the deflection corresponded to $600\mu V$ which indicated a pressure difference of approximately 654 bars. Appendix A shows the calculation of the resolution of the bridge circuit.

Sample volumes were maintained at approximately 10 mm^3 which, when compared to the usable volume of the pressure chamber, are approximately 10^{-4} times smaller than the volume of the chamber. Therefore, the effect of the volume variations of the samples on the pressure sensor could be neglected.

In order to measure the resistance variations of the samples, constant current sources of 0.1 mA, 1.0 mA, and 10 mA were available. Thus, by passing a constant current through the sample, one can easily monitor the variations of resistance of the sample due to pressure.

Since the resistivity of the sample was of the order of 10^{-3} to 10^{-4} ohm-cm, and since the resistance change of the sample was of the order of 10^4 , the heating effect to the specimen by the current was negligible.

Contacts to the sample were ohmic and made by indium solder

using 0.004" diameter silver plated copper wire after the sample had been lapped and properly cleaned with trichloroethylene, acetone, and methanol to remove any surface contamination.

The physical arrangements of the contacts applied to the specimens are shown in Figure 9.

All measurements were recorded continuously as voltages, and were displayed on a four channel strip chart recorder (chart speed = 1cm/min). One channel displayed the unbalancing of the bridge which was the output of a microvoltammeter. The sensitivity of the pressure measurement was generally 8.160 bars, but this was increased by a factor of 10 and a difference of 1.0 bar was then easily detected. The other channels recorded changes of the voltage drops across the samples. Voltage variations of 10 μ V were measured at the greatest sensitivity range.

Figure 10 shows schematically the physical setup that was used to monitor pressure and resistance variations of the samples.

Experimental Techniques

Since the transition pressures for the alloys of HgSe and HgTe had not yet been reported, both volumetric and resistivity measurements were performed, in part simultaneously with Lacam, et al (23), and independently by us in order to observe the trends in the values of the up-stroke and down-stroke transition pressures.

Repeated experiments were performed using the contact arrangements in Figure 9a1) and 9a11) for different constant currents. It was found that the transition pressures were not dependent upon the magnitude of the current flowing through the sample. However, the transition pressures for identical samples exhibited a spread of

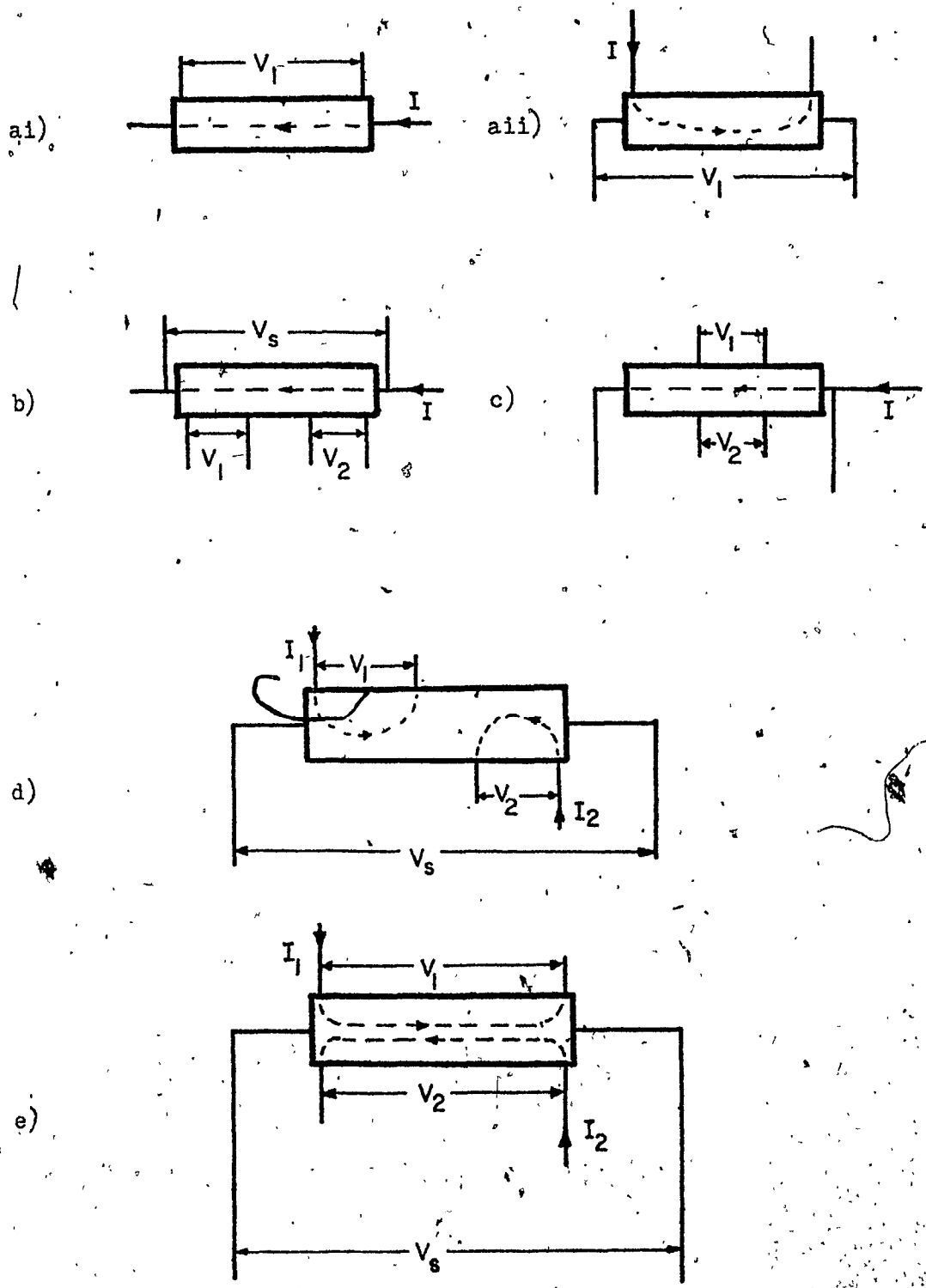


Fig. 9.--Contact arrangements applied to samples

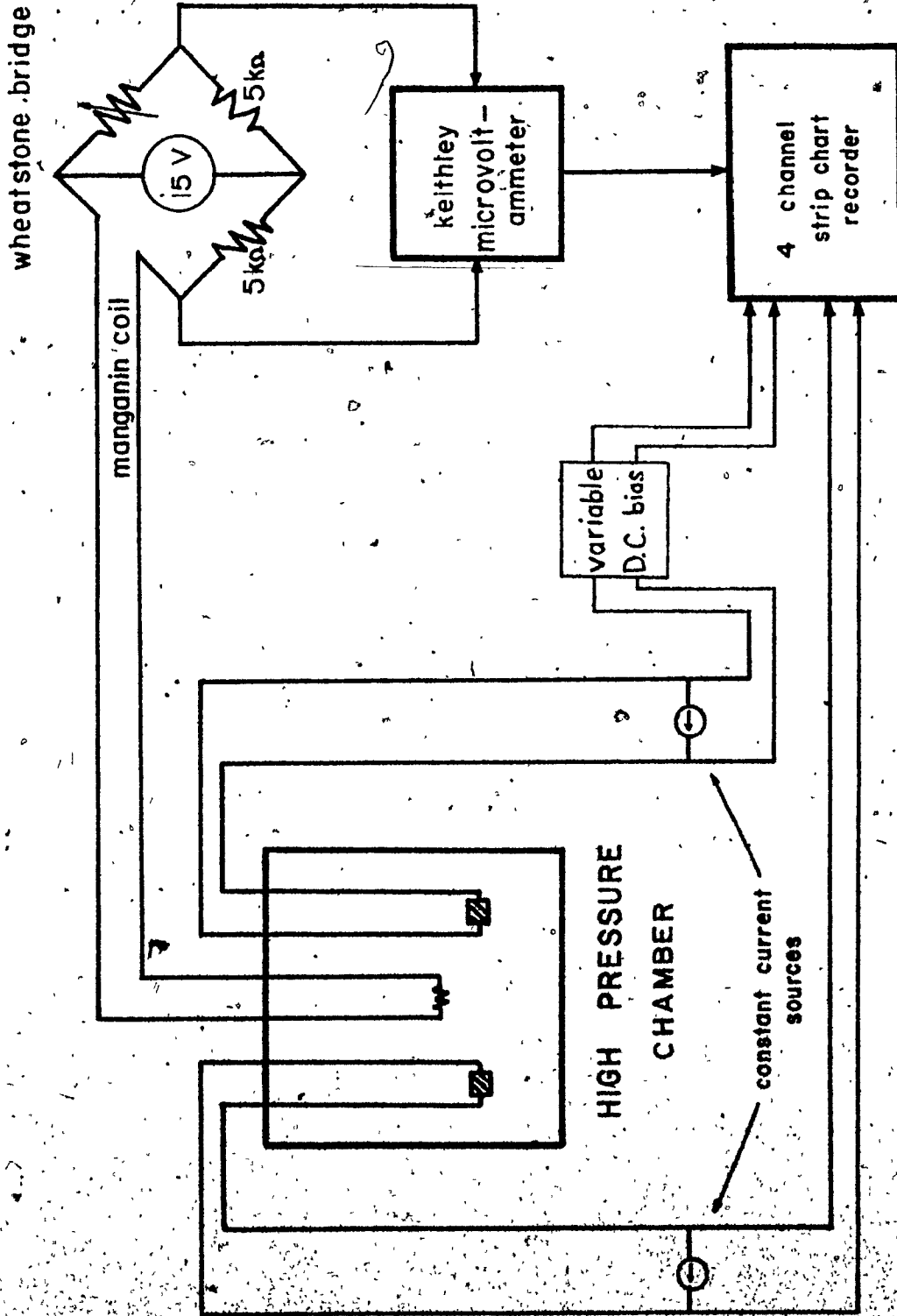


Fig. 10. Setup for monitoring pressure and resistance variations of the samples.

less than 500 bars for the up-stroke pressure and approximately 1 kbar for the down-stroke. These deviations are attributed to the different rates at which pressure was applied to the sample just prior to the transition. If the rate of change of pressure were greater than 100 bars per minute, the transition pressure would occur at an earlier pressure than if the rate were one tenth that value.

In order to measure the rates of phase transition, it was necessary to arrive at the transition pressures at a small $\frac{dP}{dt}$ so as to ensure that the reaction did not proceed to completion at an uncontrollable rate without changing the pressure. That is, once there was the slightest sign indicating that the reaction had been initiated, the pressure was maintained constant, and the reaction was allowed to proceed until a plateau was arrived at. This plateau signified that the difference between the external pressure applied to the system and the pressure within the crystal itself was almost nil--i.e. a state of quasi-equilibrium existed. At this point the reaction would proceed until completion without any further pressure change. This behaviour was expected.

By subjecting the system to controlled rates of change of pressure, followed by zero rates of change of pressure, the rates of phase transition of the sample were easily measured. This technique corresponded basically to applying step inputs to the system, and to recording the sample response. These plateaus were applied while the transitions were progressing both on the up-stroke and on the down-stroke. This technique further provided the means of calculating

the "activation volumes" using the relation derived from Evans and Polani (8).

Once we were able to obtain sufficient information about the transition pressures of each alloy, and regarding its activation volumes, our attention was directed towards the task of determining the existence of Bridgman's "surface of separation".

Since $\text{HgSe}_{.4}\text{Te}_{.6}$ lay near the middle of the alloy system, it was chosen as the starting point of this investigation. Modified four-point probe techniques (24) were employed, as shown in Figure 9b, 9c, 9d, and 9e, to detect the existence of the motion of an interface which would traverse the sample.

The contact arrangements shown in Figure 9ai) and 9aii) were initially employed to determine the transition pressures and to measure the rates of transition.

By making potentiometric measurements (V_1 and V_2) at the surface as shown in Figure 9b and 9c, it was confirmed that the rates of transition were the same as predicted.

However, when equal constant currents were applied to opposite surfaces of the crystal (as in Figure 9d), and when the potential difference (V_s) at the ends of the crystal was measured, the rate of transition appeared to show on one surface a definitely greater rate of change than on the other. This occurred just following the initiation of the up-stroke and prior to the completion of the down-stroke transition. Finally, with the contact arrangement shown in Figure 9e, where equal currents flowing in opposite directions were applied to opposite surfaces of the sample, an acceleration in the rate of reaction on only one surface of the sample was observed after the

initiation of the up-stroke transition pressure. A deceleration in the rate of reaction was also observed on only one surface of the sample prior to the completion of the down-stroke transition.

In order to determine the "zone of indifference" the contact arrangement of Figure 9e was retained. However, HgSe was used for this investigation because its low transition pressures facilitated the cycling that the pressure instrument had to perform. When constant currents of 2 mA were allowed to flow through the sample in opposite directions (V_1 and V_2), the potential difference between the ends of the sample (V_S) had a magnitude of between 0 and 5 μ V. This small magnitude of potential difference resulted from the misalignment of the contacts on the two opposite surfaces. Ideally this potential difference should be zero. Due to the magnitude of V_S , we were able to detect a variation of 1 m Ω which enabled us to better determine the initiation of the up-stroke transition. Once the transition began, a constant pressure was maintained and the reaction proceeded sluggishly until the pressure was changed. Pressurization rates of between 1-10 bars per minute were applied during the transition. The sample resistance was allowed to increase by a factor of 10^2 to 10^3 at which point the pressure was held constant for 3 hours. Then, pressure was decreased at the same rate until the sample resistance decreased by a factor of approximately 10. Again, pressure was held constant for 3 hours as the down-stroke transition proceeded.

Since the voltage across the sample was approximately 1 volt, an adjustable bias was connected to one of the potentials (V_1 or V_2). This device provided a biasing of 0-5 volts which enabled us to observe

the variations of sample resistance as small as 500 m Ω throughout the operating range of the device. A detailed description of the device is given in Appendix B. With the device installed, the pressure was increased at constant rates as before, and the reaction was allowed to proceed until the pressure was increased to approximately 1 kbar beyond the highest pressure previously reached. Again, a constant pressure was maintained for 3 hours and then the system was brought down to atmospheric pressure in a similar manner as before.

CHAPTER III

INTERPRETATION OF RESULTS

Polymorphic Transitions of $Hg_xSe_xTe_{1-x}$

The first priority of our investigation was to obtain sufficient reproducible information about the transition pressures for the alloys of HgSe - HgTe. As early as 1940 Bridgman (25) reported sharp discontinuities in the compressibilities of HgSe and HgTe. He attributed these discontinuities to a solid-solid transformation and suggested that the crystal structures of these two compounds transformed from the cubic-zincblend low pressure phase to the hexagonal cinnabar high pressure phase. Recently several investigators (1) (2) (5) (6) (26) have reported abrupt discontinuities in electrical resistance for HgSe and HgTe at the transition pressures. The crystal structure of the high pressure phase has also been confirmed by Mariano and Warerois (27) for these two compounds.

The results of our investigation of the transition pressures for the alloys are given in Figure 11. We have already published these results (23) and we found that the transition pressures were independent of the volume (dimensions) of the sample or of the amount of current used.

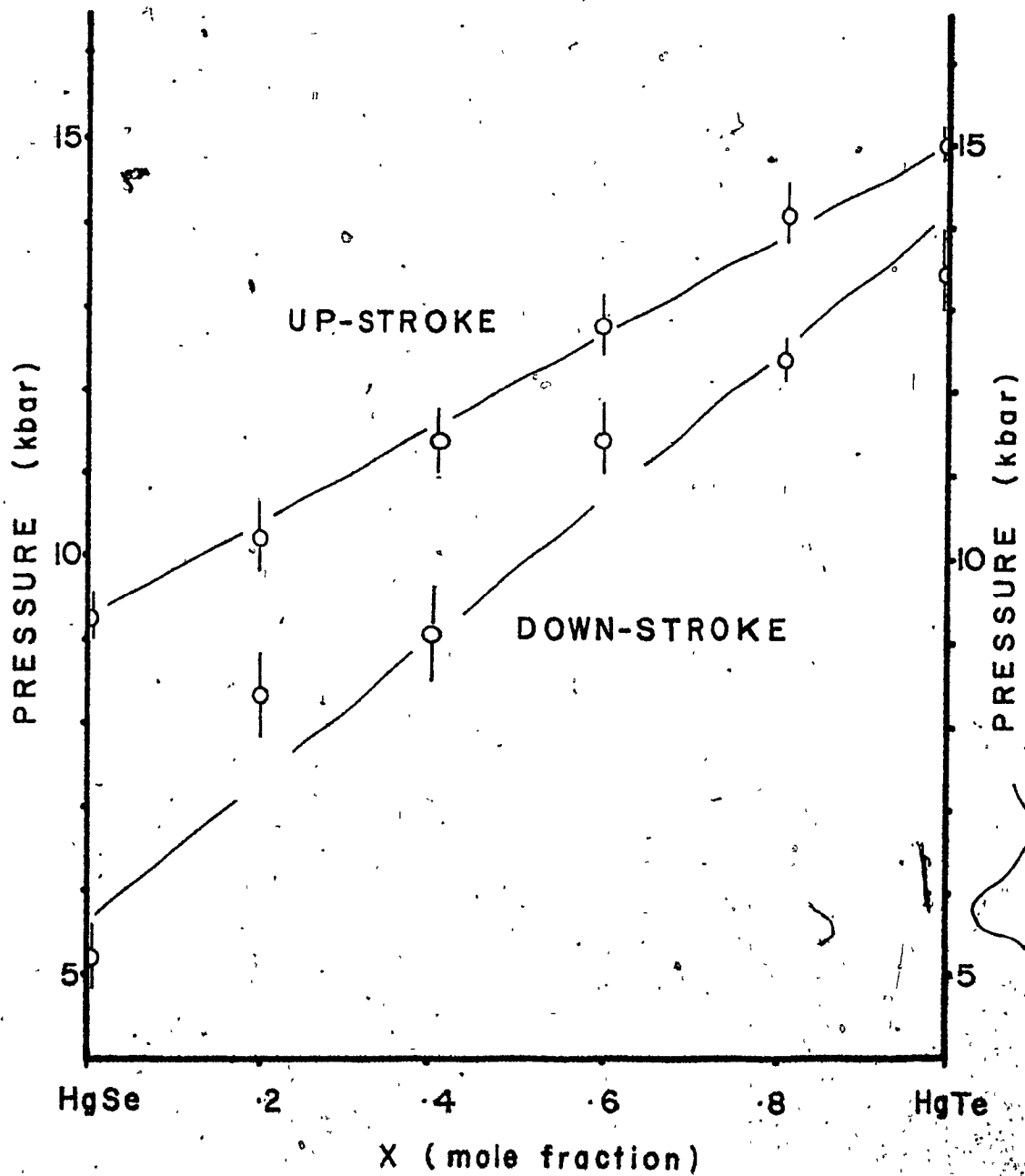


Fig. 11.--Transitions pressures as a function of mole fraction for $\text{HgSe}_x\text{Te}_{1-x}$ from volumetric and resistivity measurements.

However, up-stroke transition pressures exhibited a spread of 500 bars and the down-stroke transition pressures one of 1 kbar. This result can only be attributed to the influence of the pressurization rates which were applied to the sample prior to its transition on the nucleation of the new phase. We found that the greater the rate of application of pressure, the earlier the transition would occur. Since there exists a state of quasi-equilibrium between the pressure exerted by the liquid environment and that experienced by the crystal itself, we can only remark that the spreading decreased as long as consistent pressurization rates were applied to the sample prior to both up-stroke and down-stroke transitions. The progress of the reaction from atmospheric pressure to the up-stroke transition pressure will be discussed later on in reference to the band structure of these alloys.

Another important observation to be made (see Fig. 11) concerns the dependence of the transition pressures on the alloy composition. Clearly, we see that the up-stroke, as well as the down-stroke transition pressure, appears to be a linear function of the alloy composition within our experimental conditions. Also from the results we observed that the width of the hysteresis curve diminished as the amount of tellurium increased in the alloys. And it should be noted that the width of the hysteresis curve for HgSe is approximately twice that of HgTe, (see Fig. 11).

The importance of this last result is twofold: it agrees in principle with theoretical expectations; also, it shows that there is the possibility of theoretically determining transition

pressures for the alloys, and possibly of theoretically determining equilibrium pressures. Regarding the latter, let us recall that both the high pressure and the low pressure crystalline structure parameters have already been measured for the HgSe - HgTe system by Pearson (13). The only requirement then, to determine theoretical transition and equilibrium pressures would be to find out to what degree the dependence of the nearest-neighbours distance has on the transition pressures.

By extracting data from Jacobs' work (7) (see Appendix C) one can see that his theoretical transition pressures were related linearly to the nearest-neighbours distance for the two salt series which he considered. The nature of the solid-solid transformation in his case was from the NaCl crystal structure to the CsCl crystal structure which is comparable to that of the alloys we are presently studying. The most important point is that, since a variation of alloy composition is equivalent to a changing of the nearest-neighbours distance, our experimental results are in complete accord with the theoretical expectations. In Jacobs' work only compounds which exhibited 100% ionic bonding were considered. However, in our case, there exists homopolar bonding, and the difficulty at arriving at theoretical transition pressures lies in the determining of the degree of ionicity exhibited by the alloys. This may require data which is not available to date.

However, we can clearly see that neither the up-stroke or down-stroke transition pressures, nor the center of the hysteresis curve can be used as pressure calibration points. Also, we can

only use the pressure points of these alloys as they are indicative of solid-solid phase transformations in general. Nevertheless we can determine the activation volume $V^{\#}$ for each of the alloys. This is an important physical property necessary in the designing of materials which one wants to have certain characteristics. The activation volumes also provide information concerning the mechanism governing solid-solid transformations.

As outlined in the procedure, the rates of change of resistance of the sample for a zero rate of change of pressure were plotted logarithmically versus pressure. Each data point was obtained by measuring the velocity of the reaction (slope) at the point after which an initial $\frac{dP}{dt} = \text{constant}$ had been applied. Now,

by measuring the slope of this curve, as shown in Figure 12, and by substituting its value into the relation derived from Evans and Polani (8), activation volumes were calculated and are shown in Table 1.

We have plotted the activation volumes as a function of alloy composition in Figure 13 for the up-stroke transition. From Figure 13 we see that, if the trend continues, the activation volume of HgSe is approximately one half that of HgTe. It seems that $V^{\#}$ may be related to the hysteresis curve in that it is a measure of the amount of energy required by the system to change its crystalline structure from one stable low pressure form to another stable form at high pressure. Again, we can state that the activation volumes appear to be a linear function of the alloy composition. By repeating the same procedure for the down-stroke

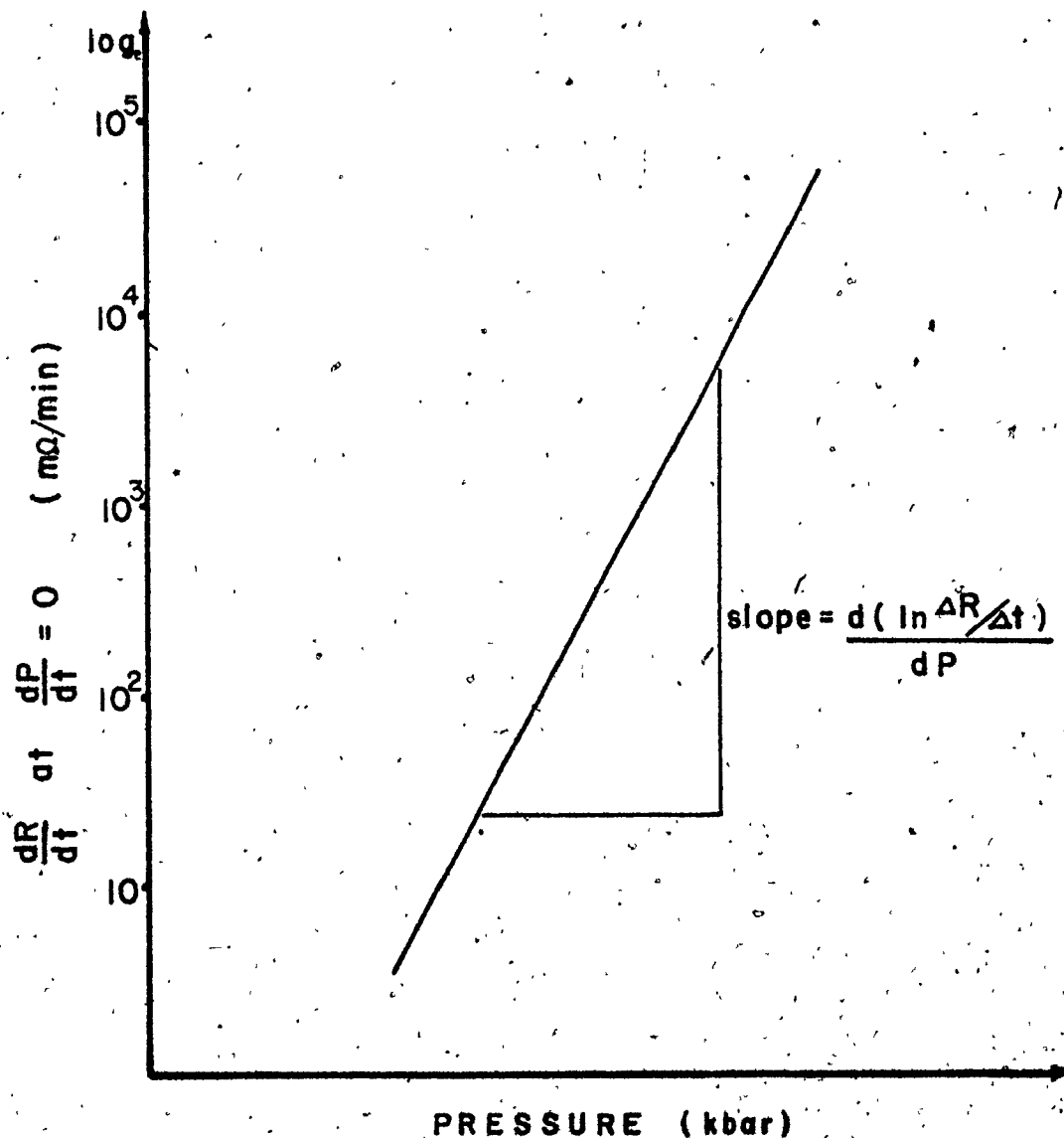


Fig. 12.--Rate of resistance variation during the up-stroke transition following a zero rate of change of pressure plotted logarithmically as a function of pressure.

TABLE 1

MEASURED ACTIVATION VOLUMES FOR THE HgSe-HgTe SYSTEM
(temperature 21°C)

	UP-STROKE	DOWN-STROKE
	$v^{\#}$ (cm ³ /mole)	$v^{\#}$ (cm ³ /mole)
HgSe	-	-
HgSe _{.8} Te _{.2}	72	-
HgSe _{.6} Te _{.4}	74	-
HgSe _{.4} Te _{.6}	86	496
HgSe _{.2} Te _{.8}	103	-
HgTe	126	-

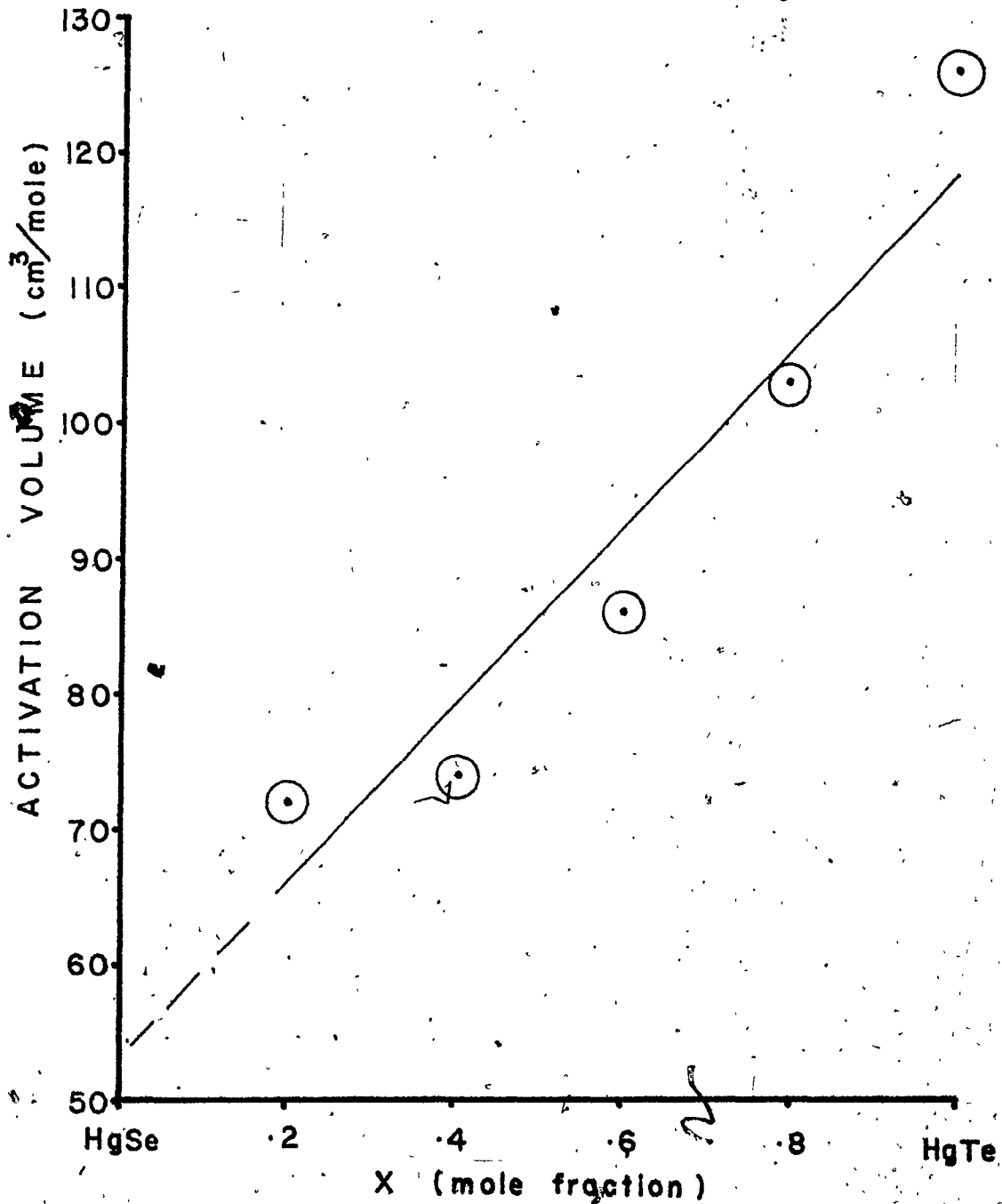


Fig. 13.--Activation volumes as a function of mole fraction for $\text{HgSe}_x\text{Te}_{1-x}$ during the up-stroke transition.

transition, it was possible to measure the down-stroke activation volume for $\text{HgSe}_{.4}\text{Te}_{.6}$. A tentative value we are reporting is $496 \text{ cm}^3/\text{mole}$. Since the reaction is much more rapid than for the up-stroke transition, our value does not seem unreasonable.

As mentioned previously (p. 32), the nature of the reaction prior to the up-stroke transition may provide additional data to interpret the band structure of the $\text{HgSe} - \text{HgTe}$ system. Much controversy developed when T. C. Harman and A. J. Strauss (14) and H. Rodot, H. Rodot, and R. Triboulet (15) presented in the same issue data to justify opposing concepts of the band structure for the $\text{HgSe} - \text{HgTe}$ system. Rodot, Rodot, and Triboulet stated that HgSe and HgTe were both low energy gap semi-conductors, while Harman and Strauss stated that they were both semi-metallic compounds. T. C. Harman (16), applying the theoretical model developed by S. Groves and W. Paul (28) (29), stated that HgSe and HgTe were both semi-metals, and, from the resistivity data, he showed that during their high pressure phase they behaved like semi-conductors. Also, W. Giriat (17) (30), using the same theoretical interpretation as Harman, stated that for the $\text{HgSe} - \text{HgTe}$ system there was a smooth transition from the semi-conducting behaviour of HgTe at one end, to the semi-metallic behaviour of HgSe at the other end. A. Lacam, B. A. Lombos, and B. Vodor (5) (6) confirmed that for HgTe the pressure induced transition was of the semi-metal - semi-conductor type. C. Vérie and G. Martinez (31) also provided the pressure coefficient of the energy gap for HgTe . R. Piotrkowski, et al (32) showed that for a compound with a positive

energy gap (E_g) the pressure coefficient $\frac{d|E_g|}{dP} > 0$ and the compound would be a semi-conductor. Likewise, if the energy gap were negative, $\frac{d|E_g|}{dP} < 0$ and the compound would be a semi-metal.

From the interpretation presented by Piotrkowski, et al we can see that, even though a semi-conductor has a positive energy gap ($E_g > 0$), the pressure dependence of the energy gap may have a positive or negative sign in the case of indirect transitions as in silicon and germanium. Previous experimental results on various III - V and II - VI semi-conductors (33) (34) (35) (36) have confirmed this fact from resistivity versus pressure curves. As regards these above-mentioned results, the slopes of the curves in the pressure region from atmospheric to the initiation of the up-stroke transition have not, to our knowledge, been interpreted in view of characterizing the band structures of II - VI semi-conductors, nor have they even been reported in some cases.

Using the conventional band model for semi-conductors with a direct transition shown in Figure 14, the relation between the dependence of the energy gap and the characteristic resistivity variation with pressure can be explained. For a semi-conductor with a negative pressure dependence on the energy gap ($\frac{dE_g}{dP} < 0$), the pressure region prior to the initiation of the up-stroke transition would be characterized by a negative slope in the resistivity versus pressure curve. This is due to the fact that the energy gap ($E_{\Gamma_6} - E_{\Gamma_8}$) (Γ = symmetry elements of first Brillouin zone for the diamond lattice) would essentially close. For a positive pressure

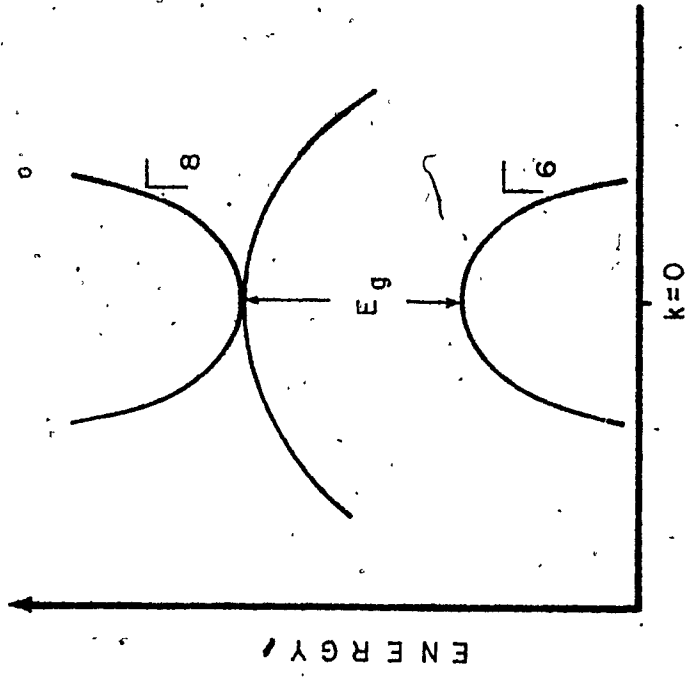


Fig. 14.--Conventional energy band model for a semiconductor at $K = 0$.

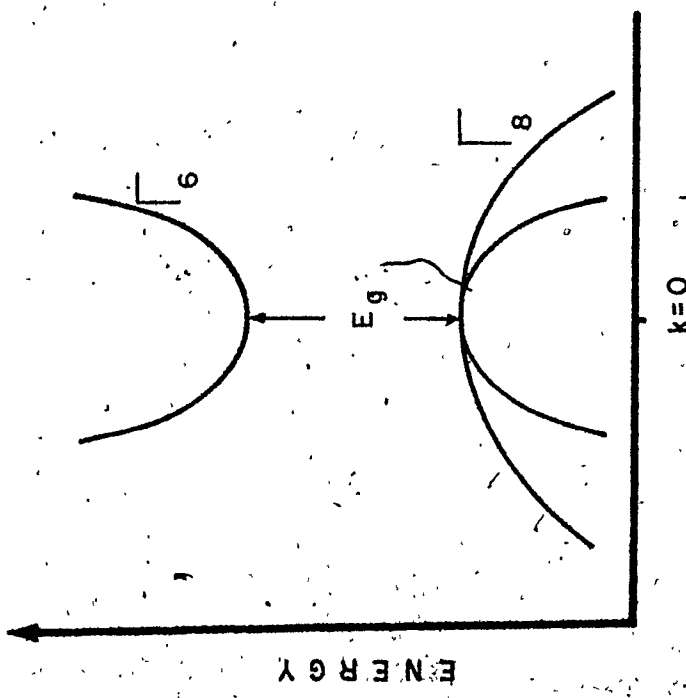


Fig. 15.--New energy band model proposed for HgSe and HgTe by Paul and Groves.

dependence on the energy gap $\left(\frac{dE_g}{dP} > 0\right)$ on the other hand, this same pressure region would then be characterized by a positive slope in the resistivity versus pressure curve since the energy gap, in this case, would open up.

However, HgSe and HgTe are low (nearly zero) energy gap semiconductors and the band model proposed by Groves and Paul (28) (29), and shown in Figure 15, has been generally adopted for these two compounds. Using this band model the energy gap has a negative sign since, by convention, it is specified by the difference between the Γ_6 and Γ_8 energy levels and Γ_8 is above Γ_6 . Giriat (30) has most recently reported energy gaps of -0.15 eV and -0.08 eV for HgTe and HgSe respectively. This negative energy gap has also been interpreted as being band overlapping. For the new model, Γ_6 has been shown to have a greater pressure coefficient than Γ_8 , and, as a result, the Γ_6 energy level moves faster than the Γ_8 when pressure is applied. Therefore, $|E_g|$ must first decrease, or the amount of band overlapping must decrease as the applied pressure approaches the up-stroke initiation pressure. Therefore, prior to the initiation of the up-stroke transition, as the amount of band overlapping decreases, the resulting resistivity curve as a function of the applied pressure would be characterized by a positive slope.

Early results by J. Blair and A. C. Smith (1) for HgTe and by J. A. Kafalas, et al (2) for HgSe show clearly that, prior to transition (up-stroke), there is a definite positive slope in the resistivity curves of approximately 1% per kilobar increase. The second group stated that this was typical of some semi-metals. We fully realize

that we cannot place too much emphasis on resistivity curves to identify band structures when the amount of band overlapping for the alloys is uncertain.

For the 10 experiments which were performed in our laboratory on each HgSe and HgTe, and along with 15 experiments on the alloys, we did not arrive at the same results as Blair and Smith, and Kafalas, et al regarding the tendencies exhibited by the resistivity curves for HgSe and HgTe in the pressure region prior to the initiation of the up-stroke transition pressure. This may have been due to the fact that:

- a) Our resistivity variations were dependent upon the $\frac{dP}{dt}$ prior to transition.
- b) Fluctuations of the current were in the order of 10 μA for the entire experiment and were neglected.
- c) The sensitivity of our detection was limited, as in many occasions a zero slope was observed.

As a result we can only state that in most cases (90%) we observed a very small positive or a zero slope in the resistivity curves prior to the transition pressures for the HgSe - HgTe system.

Bridgman's Surface of Separation

Bridgman (4) made a number of observations of velocity phenomena during phase transitions. He believed that polymorphic transitions were mono-nucleonic in nature and was able to detect a moving interface--or surface--which separated both stable forms of the solid, and which seemed to traverse the solid lengthwise. This "surface of separation" was deduced by Bridgman from volumetric

measurements. Since phase transformations can be just as faithfully represented by resistance measurements, we made use of them and detected the same phenomena as Bridgman.

With the contact arrangement on the sample shown in Figure 9(e), we measured the resistances on opposite sides of the sample as equal currents flowed in opposite directions. We also measured the potentiometric voltage V_S across the sample.

As concerns the motion of the interface, a small current (μA) flowed through the bulk of the material after equal currents were applied in opposite directions on the sample. In a sense, the sample was polarized with equal sheet currents of opposite polarity at opposite surfaces.

We believed that if the polymorphic transformation were not governed by a mono-nucleonic mechanism, then, at the initiation of the transformation and thereafter, the rates of transition would be identically observed on both surfaces of the sample. However, if the reverse were true, we would expect that, just after the transition pressure had been initiated, the rate of change of resistance on one surface of the sample would experience an acceleration while the opposite surface would show a continuous change of resistance characteristic of all up-stroke transitions. After the acceleration would cease, the velocity or rate of reaction at both surfaces should be identical as long as pressure were maintained constant or increased.

Typical experimental results are shown in Figures 16 and 17 where the resistances at opposing sides of the sample are R_1 and R_2 .

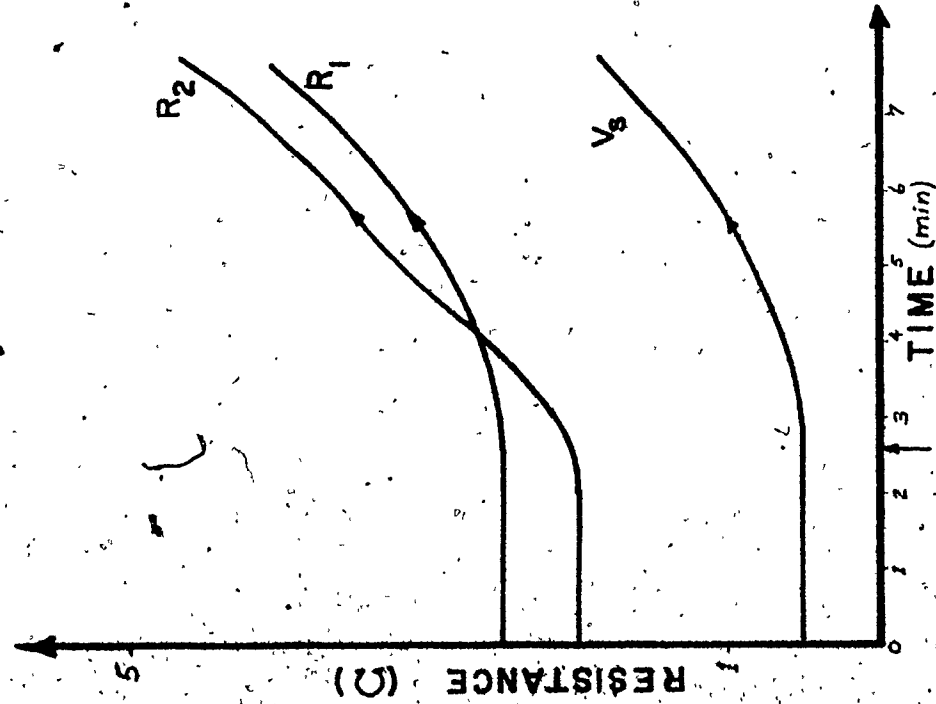


Fig. 16.--Experimental result showing acceleration of resistance at one surface of sample during up-stroke transition (in one case).

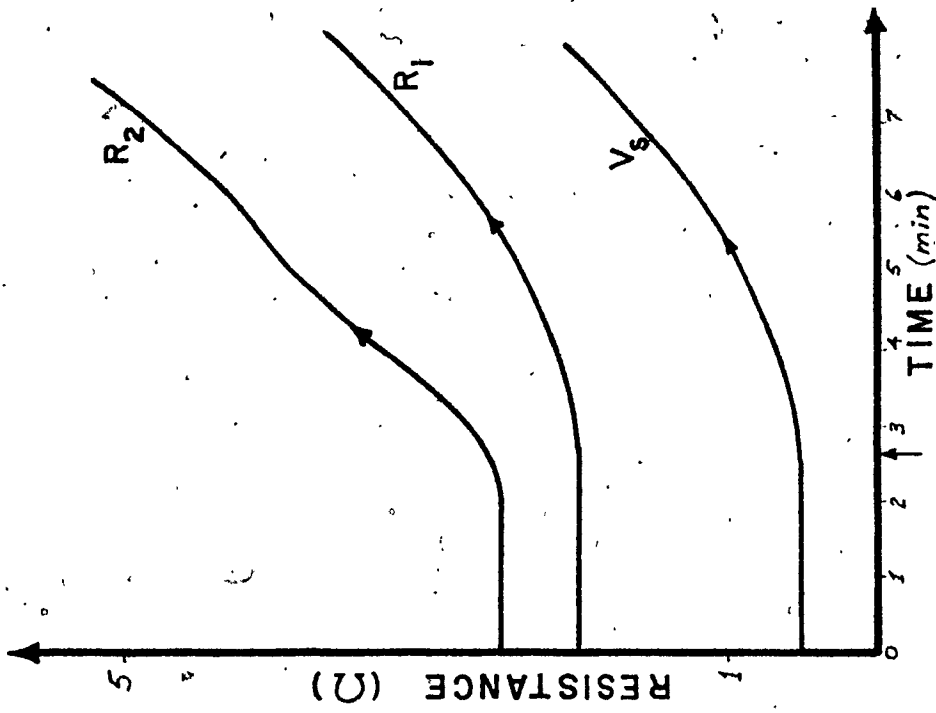


Fig. 17.--Experimental result showing acceleration of resistance at one surface of sample during up-stroke transition (in another case).

and V_S is the potentiometric voltage across the sample. Clearly, we see that just after the initiation of the up-stroke transition, marked by the arrow, the rate of change of resistance on one side, R_2 , has accelerated and then assumed the same rate of change as on the opposing side.

We can, therefore, argue that, at the initiation of the up-stroke transition pressure, the low pressure phase is no longer stable and at a specific point in time a "nucleus" of the high pressure phase is formed at a corner of the sample. As the high pressure nucleus grows and forms an "interface", the rate of reaction at one surface should suddenly accelerate as the interface propagates diagonally through the sample. The duration of this acceleration --or motion of the interface--depends largely on the pressurization rates which were applied to the sample prior to the transition. Experimentally we found that the duration of the acceleration varied from 1 to 5 minutes.

Figure 18 shows schematically what we believed occurred within the bulk of the sample. At point A the high pressure stable polymorph was nucleated and the interface developed which would then proceed diagonally to the end of the sample at surface B. The existence of this interface was pressure dependent.

Upon increasing pressure, the rate of reaction augmented because of the stability of the high pressure phase alone, since sufficient energy was supplied to the system to insure the progress of the high pressure polymorph. The resulting interface can be considered as an energy barrier which activates a regrouping or destruction of the

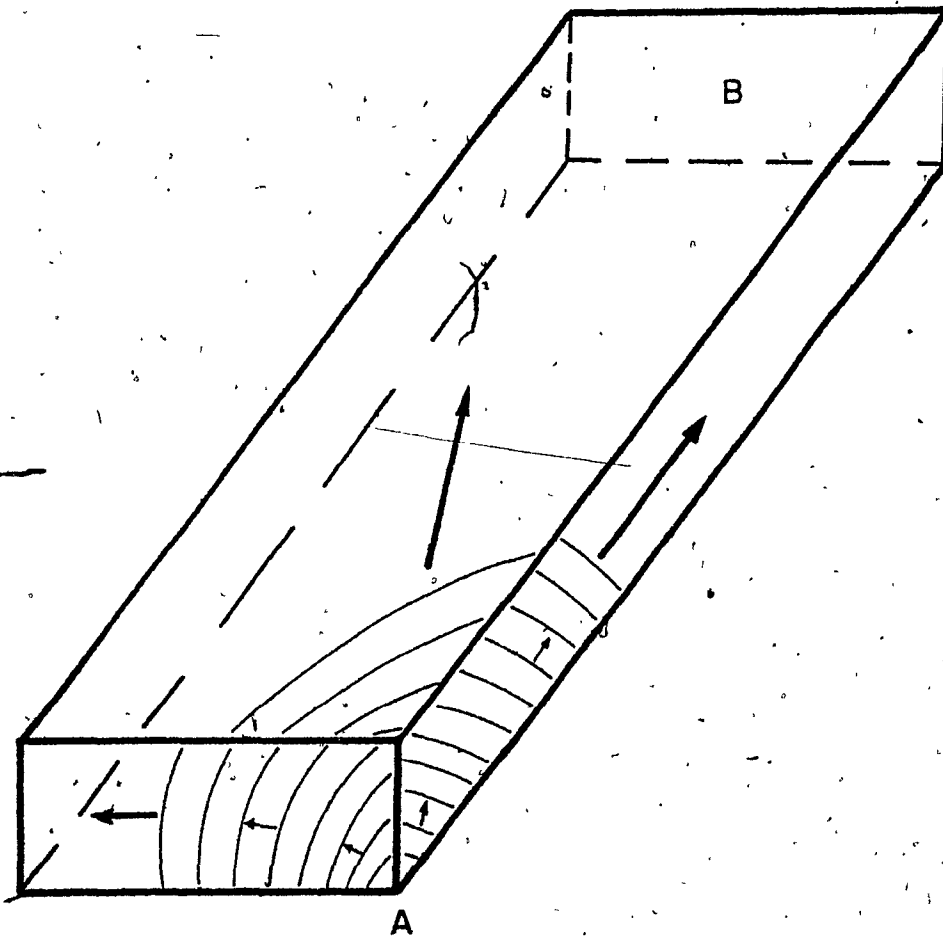


Fig. 18.--Propagation of nucleated high pressure phase interface through bulk of material after up-stroke transition initiated.

bonding within the crystal structure itself. This concept would be analogous to that of "latent heat".

Theoretically we expected that, prior to the completion of the down-stroke transition, the low pressure phase would be nucleated and grow to form an interface which would then propagate diagonally through the sample as was observed during the up-stroke transition. However, we did not expect that this interface would be characterized by an abrupt deceleration in the rate of reaction on the same surface of the sample which first experienced the acceleration during the up-stroke cycle. Typical experimental results are shown in Figures 19 and 20. Just prior to the exhaustion of the high pressure phase (marked by the arrow) a deceleration was observed on the same side of the sample which experienced the acceleration (R_2). Therefore, it is evident that, after the initiation of the down-stroke transition pressure--where the high pressure polymorph is no longer stable--, a "nucleus" of the low pressure phase is also formed at the other corner of the surface (shown in Figure 21 as point A'). This interface again traversed diagonally across the sample at which point the low pressure crystalline structure existed throughout the sample. We must point out that the motion of the interfaces were detected during zero rates of change of pressure. Therefore, we cannot attach much significance to this phenomenon with respect to pressure calibration points. However, our results do support Bridgman's observations and other theories that polymorphic phase transitions are kinetically of the first-order type. A. Lacom, B. A. Lombos, and B. Vodor (5) first suggested this.

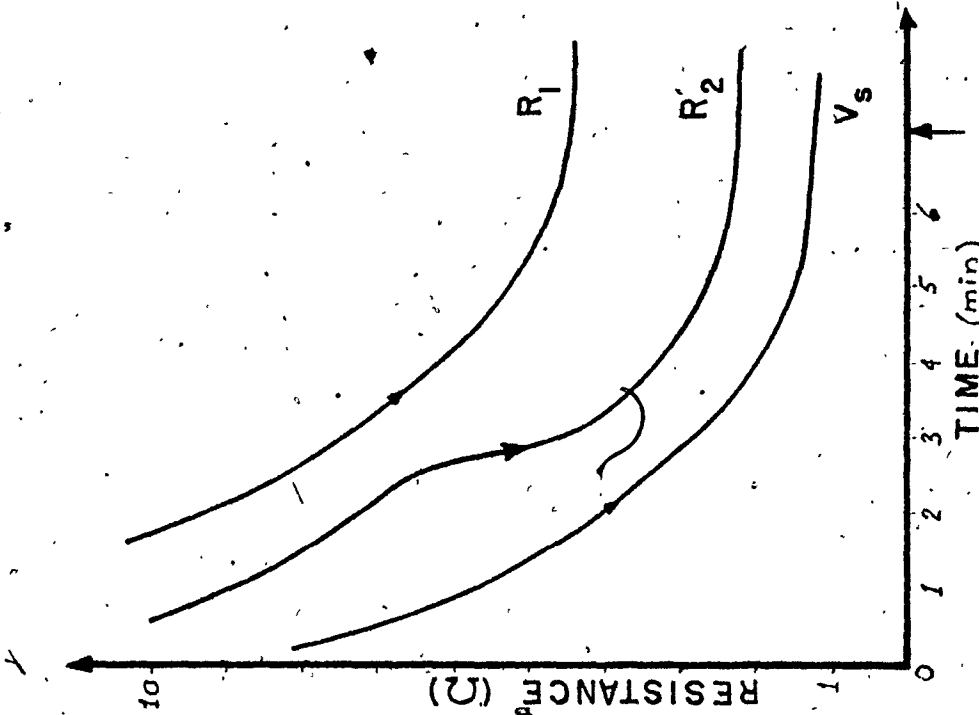


Fig. 20.--Experimental result showing de-
celeration of resistance at one surface of
sample during down-stroke transition (in
another case).

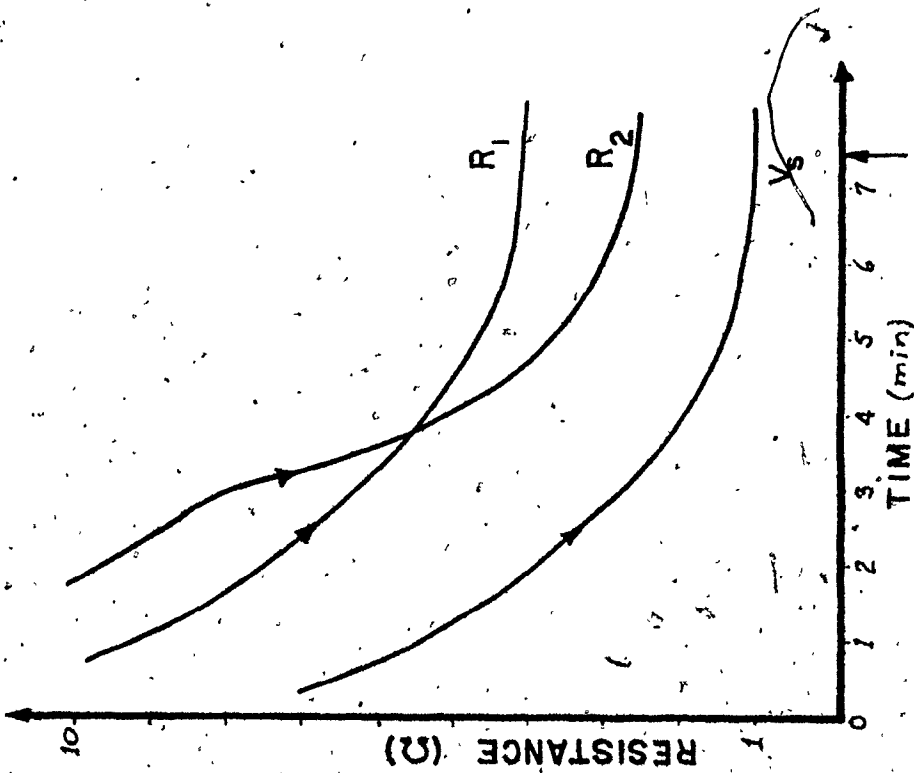


Fig. 19.--Experimental result showing de-
celeration of resistance at one surface of
sample during down-stroke transition (in one
case).

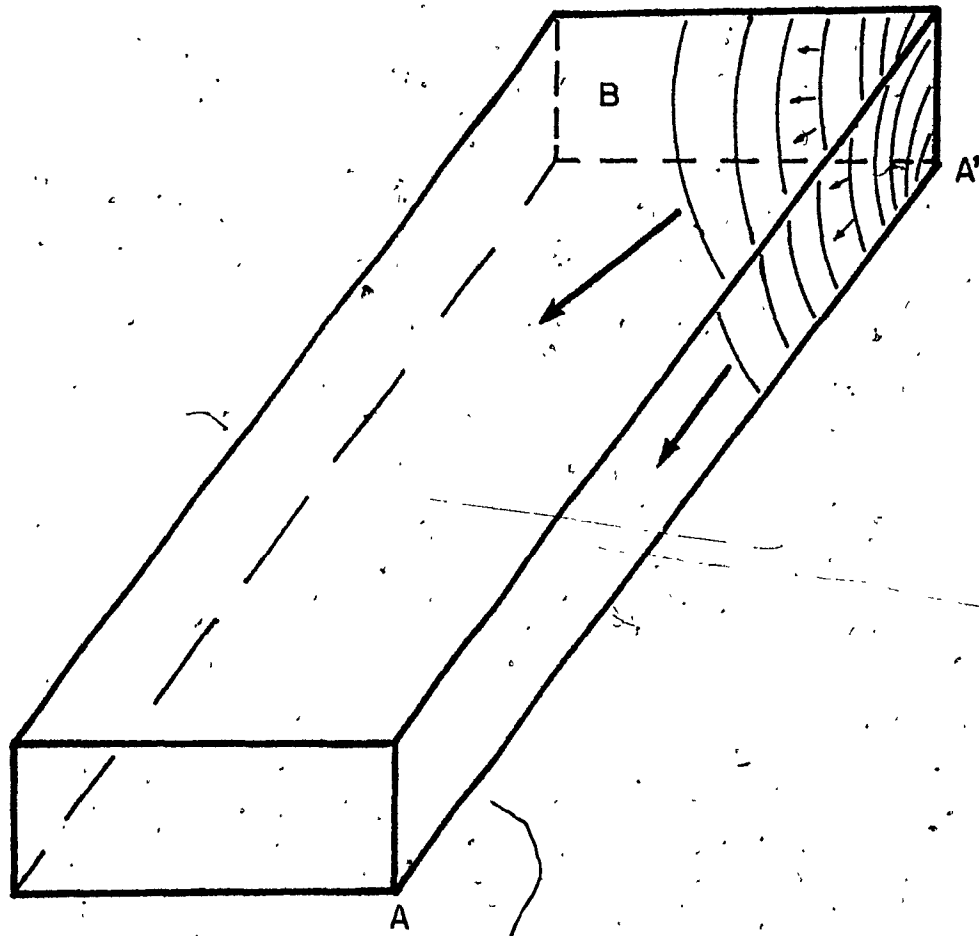


Fig. 21.--Propagation of nucleated low pressure phase interface through bulk of material after down-stroke transition almost completed.

A. Onodera (37) gave a more detailed treatment of the kinetic aspect of this phenomenon for cadmium chalcogenides.

In any case, we reproduced our results in subsequent experiments and confirmed our belief that a moving interface (or barrier) which separates both stable polymorphs during a phase transformation exists. This result in itself is a significant contribution to the study of polymorphic transitions by electrical resistance measurement techniques.

Bridgman's Zone of Indifference

Since the "zone of indifference" has never been reported for the HgSe - HgTe system, we chose to study HgSe due to its low transition pressures and the large width of its hysteresis (~ 4 kbar).

As outlined in the procedure (p.28 of this study), we monitored the transitions continuously as the sample was being cycled twice at controlled pressurization rates. The complete progress of the experiment, which lasted approximately 36 hours, is shown in Figure 22. The up-stroke transition was initiated at P_u at which point the reaction progressed along path A until it commenced path B where pressure was maintained constant for 3 hours. At the end of this first plateau, equal de-pressurization rates were applied to the sample and the reaction proceeded along path C until the start of path D where another pressure plateau was maintained for 3 hours. Again, equal pressurization rates were applied. The reaction proceeded to move upward along path E to the pressure plateau at F--held again for 3 hours. The last stage of the reaction followed path G back down to atmospheric pressure.

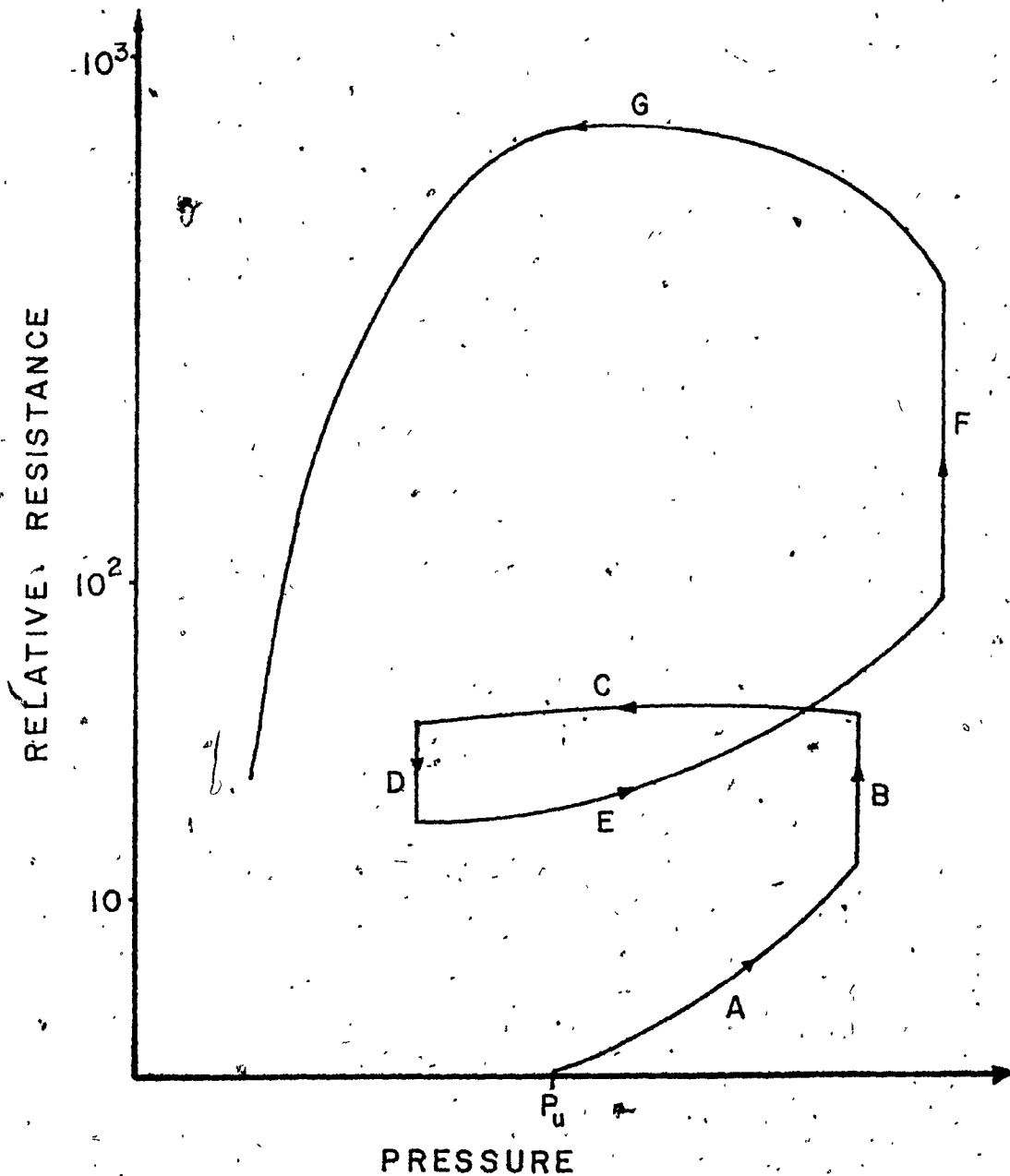


Fig. 22.--Experimental resistance variation as a function of pressure observed on HgSe in order to determine the Zone of Indifference.

With regard to these pressure plateaus at B, D', and F', we observed, after 3 hours, linear increasing or decreasing trends of the reaction during the up-stroke or down-stroke transitions. This linearity confirmed that the progress of the reaction was due solely to the nature of the transition. However, at the end of these plateaus, where pressure was either increased or decreased, a static equilibrium condition existed within the sample. For a pressure range of about 1 kbar wide after the pressure plateaus the reaction essentially stopped, and then progressed again slowly.

From our experimental data we normalized all our pressurization rates to 10 bars per minute, and then calculated the respective rates of change of resistance for each pressure range of the experiment.

resistance versus pressure for the up-stroke and down-stroke transitions respectively. During the first up-stroke transition (A) in Figure 23 we see clearly that at approximately 9.05 kbar a sharp double reversal in slope exists. Also in Figure 24 for the first down-stroke transition (B) an essentially flat region or zero rate of change of resistance occurs. This flat region of the curve also appears in the vicinity of 9.05 kbar. However, the second up-stroke (A') and down-stroke (B') transition rate curves do not appear to indicate any significant happening around this pressure point.

We extracted data points from Figures 23 and 24 in such a way that we were able to measure the respective differences in the normalized rates of change of resistance from one pressure to the next. We plotted the acceleration of the change of resistance (normalized to a

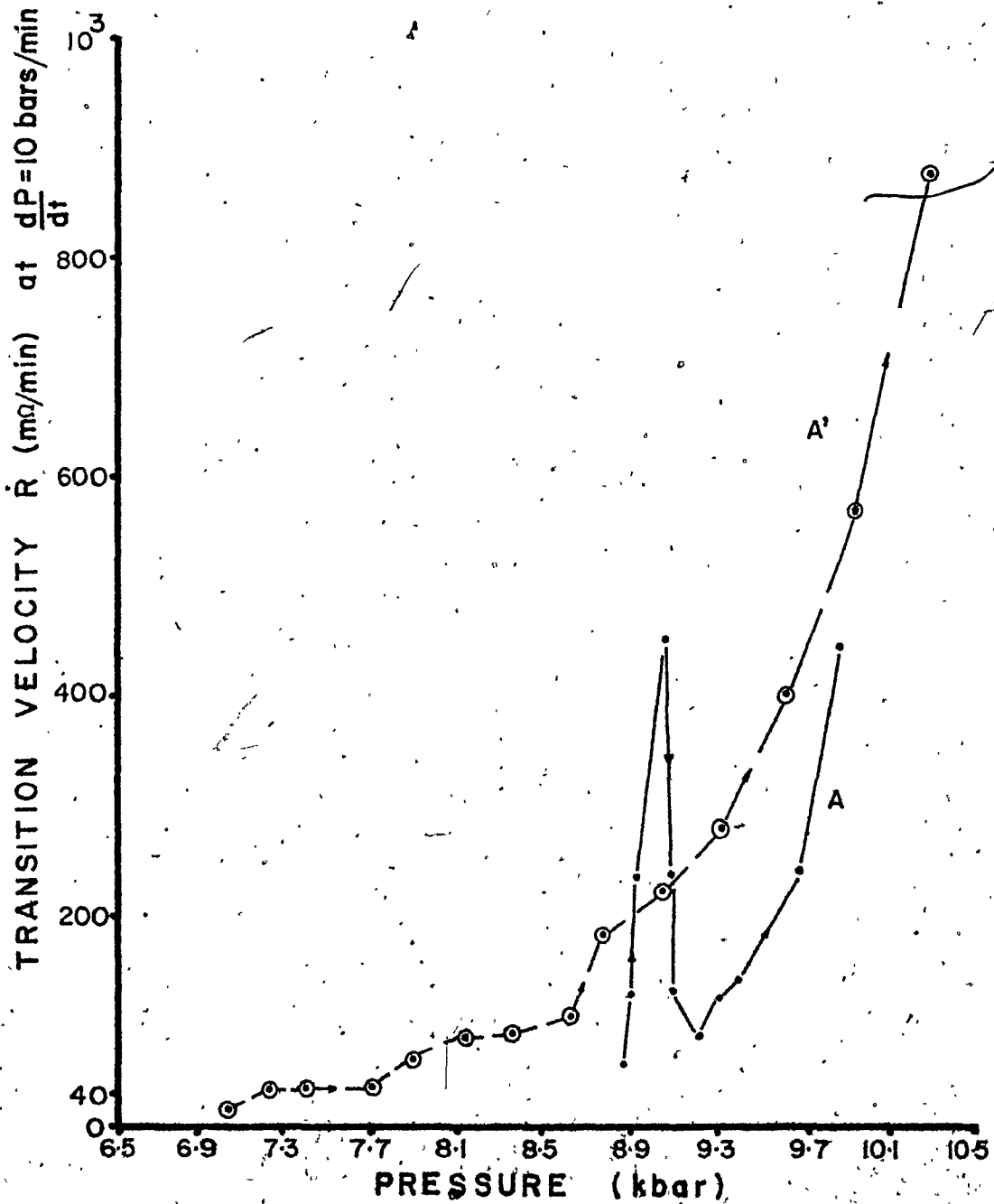


Fig. 23.--Normalized up-stroke transition velocity as a function of pressure for HgSe.

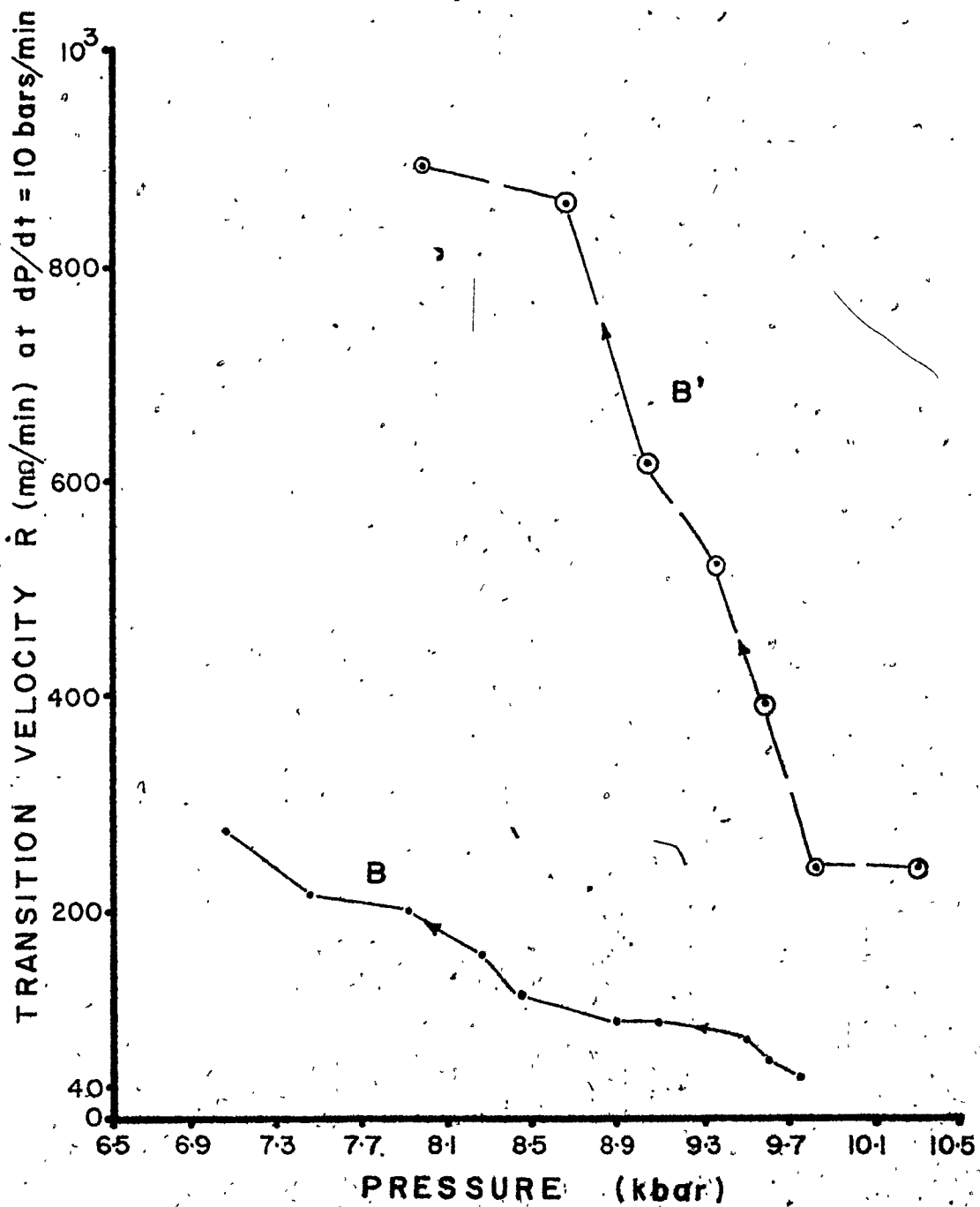


Fig. 24. -- Normalized down-stroke transition velocity as a function of pressure for HgSe.

rate of change of resistance of $10 \text{ m}\Omega/\text{min}$ versus pressure in Figures 25 and 26. As mentioned previously (p. 5) concerning the nature of the reaction, Bridgman has indicated that by measuring the acceleration of the reaction the existence of the ZOI could be just as easily located as from the velocity of reaction curves. We see in Figure 25 that during the first up-stroke transition (1 \uparrow) there exists a sharp double reversal in slope at 9.05 kbar. For the second up-stroke transition (2 \uparrow) there exists a flat region between 8.9 to 9.05 kbar. Also, in Figure 26, for the first down-stroke transition (1 \downarrow) there appears to be a pressure region from 8.45 to 9.05 kbar where the acceleration of reaction is essentially zero. Furthermore, for the second down-stroke transition (2 \downarrow) there exists a somewhat wide range of pressure where the rate changed slope. This pressure range is from 8.65 to 9.05 kbar. We also note that at both extremities of the graph the tendencies seem uniform.

Therefore, the results of our investigation have shown that by monitoring polymorphic transitions by resistance measurements, the "zone of indifference" as defined by Bridgman (4) can be determined. Bridgman had located the ZOI volumetrically.

R. Zeto and H. Vanfleet (10) (11) (12) have demonstrated that regions of indifference do exist and are most suitable for pressure calibration points. However, the relative resistance variation which they observed was only one order in magnitude, while we are concerned with a variation of 5 orders in magnitude.

Bridgman (4), in his investigation of polymorphic transitions, measured volumetrically the velocity of the reaction within zones of

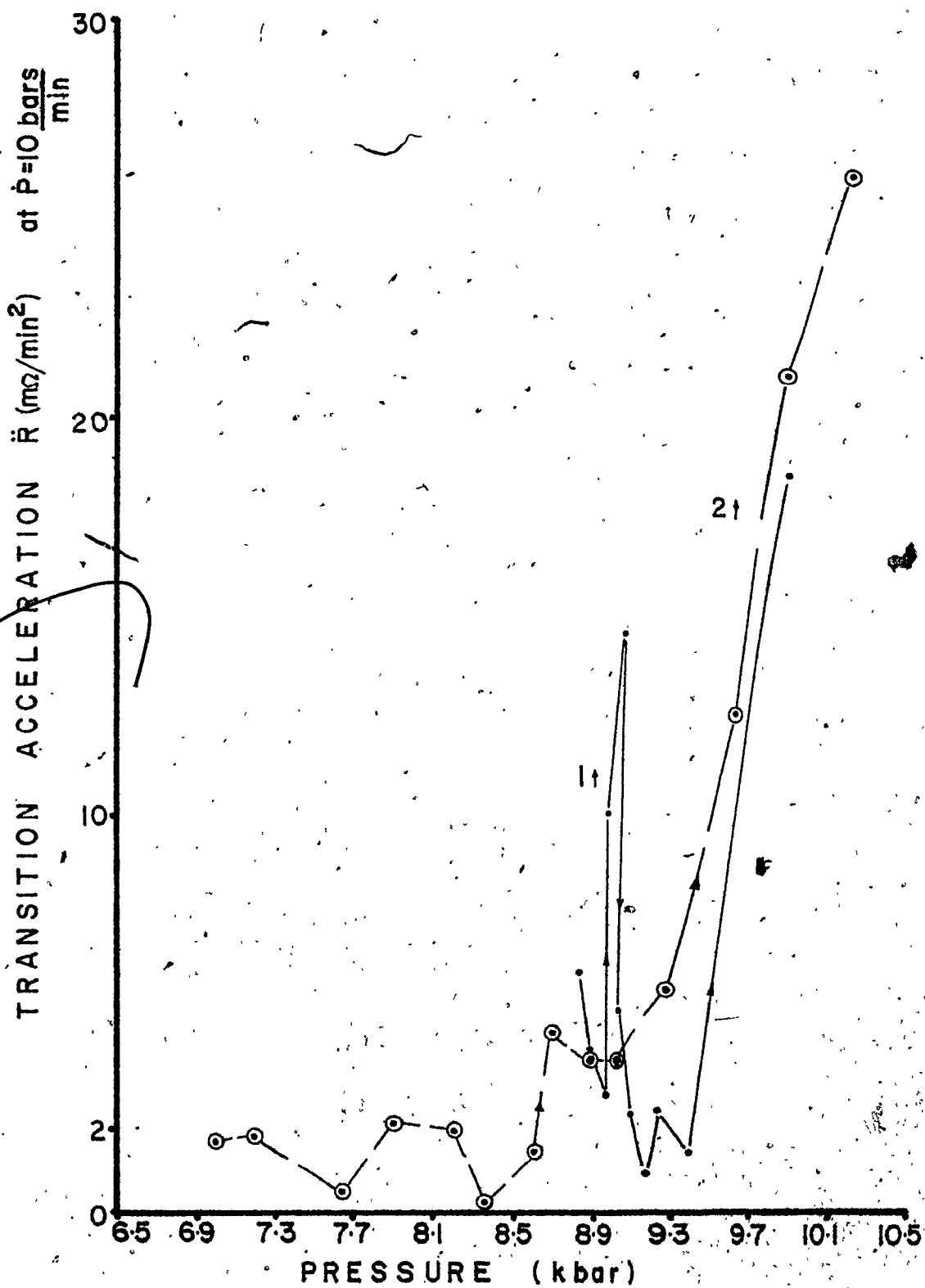


Fig. 25.--Normalized up-stroke transition acceleration as a function of pressure for HgSe.

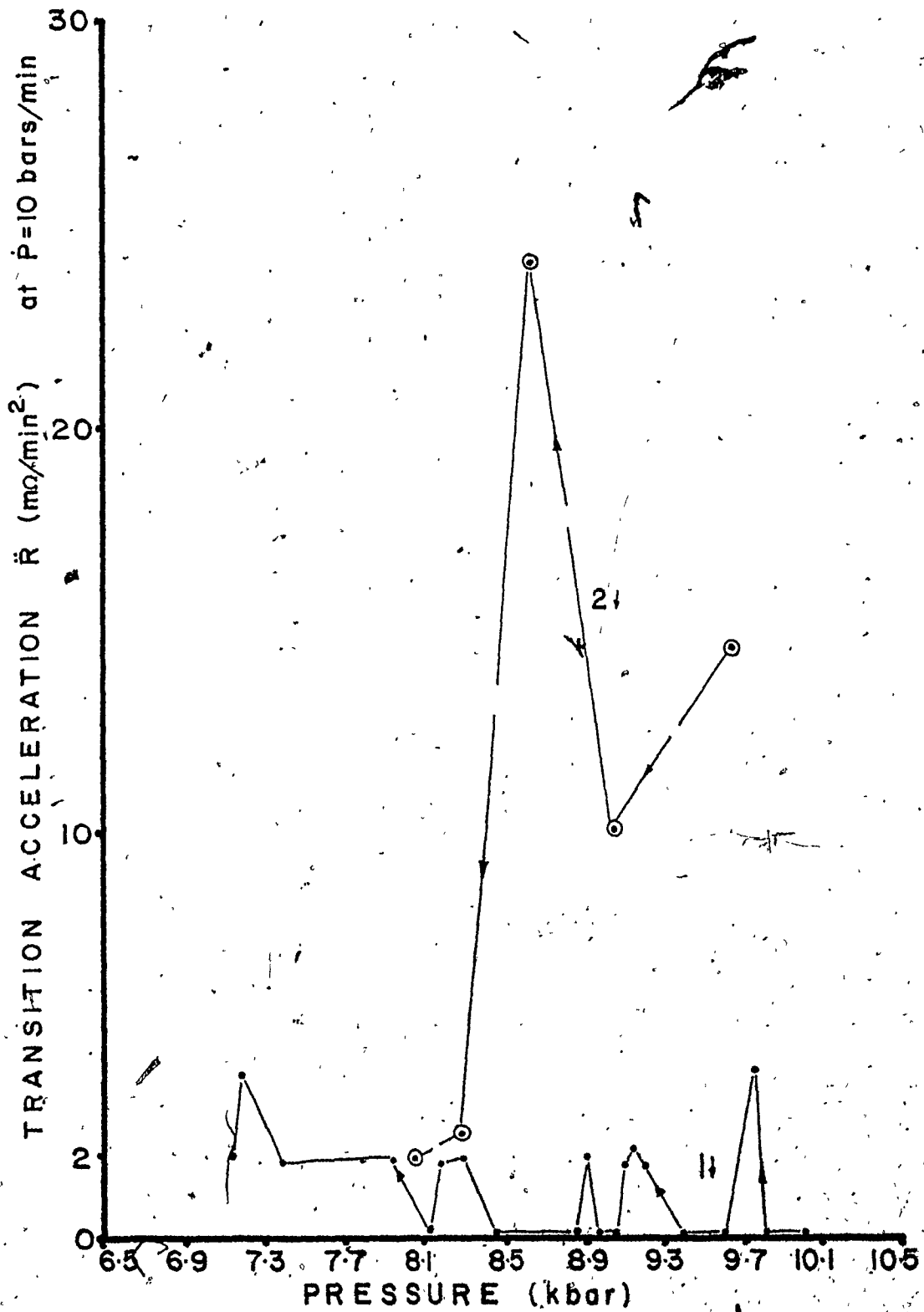


Fig. 26.--Normalized down-stroke transition acceleration as a function of pressure for HgSe.

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indifference and showed that the width of the ZOI was temperature and pressure dependent. Following Bridgman's technique, Zeto and Vanfleet (11) were able to locate (for bismuth and other elements) regions within the hysteresis curve where the relative rate of change of resistance proceeded at a rate of less than $3 \times 10^{-4} \%$ transition per second. This they called the region of indifference. They also showed that the equilibrium point, at the center of their ZOI, was reproducible both in solid and liquid pressure mediums, and could be arrived at along any portion of the hysteresis curve.

Now, let us return to Figure 22 where we observed the sluggish nature of the reaction within the hysteresis curve itself. After the up-stroke transition initiation pressure was encountered, the reaction proceeded quickly as the high pressure phase was nucleated. During the first pressure plateau (B) the reaction progressed along the up-stroke transition line. However, when pressure was decreased, the reaction slowed down and stopped within a 1 kbar range which indicated that both the high pressure and the low pressure phase existed mutually within the sample. The same phenomenon was observed when the reaction proceeded along the down-stroke transition line and pressure was increased. This behavior was again repeated higher along the transition lines during the second cycle. From the velocity curves of Figures 23 and 24 we noted that these above-mentioned plateaus were static equilibrium conditions. The reaction did not, however, stop when we artificially applied pressure within this region, but the pressure change produced a state of uniform harmonic oscillation between both polymorphic phases within the sample. This state ceased as pressure was further increased or decreased when sufficient energy was applied.

or removed from the crystal lattice to alter the energy balance between both phases. Now, from the velocity curves we noticed that during the first up-stroke transition the reaction changed direction twice, and we noticed that during the first down-stroke transition, a zero change in velocity existed. Both these phenomena took place around 9.05 kbar. This observation is significant in that the nature of the reaction in the vicinity of 9.05 kbar either stops or passes through an inflection point.

In Figure 27 we have extracted the pressure region from 8.25 to 9.25 kbar from Figures 25 and 26. From the first cycle we see an overlapping of a zero acceleration curve (1 ↓) and a double change in direction acceleration curve (1 ↑). Likewise for the second cycle, the slope of the up-stroke acceleration curve (2 ↑) changed direction at 8.73 kbar, experienced a zero slope between 8.89 and 9.05 kbar, and then increased positively again beyond 9.05 kbar. For the second down-stroke acceleration curve (2 ↓), at 9.04 kbar a change in slope occurred until 8.66 kbar at which point the initial trend repeated itself.

We can therefore argue that, during a polymorphic transition, there may exist an inflection point within the hysteresis curve which can be approached during either the up or down-stroke transitions along any part of the transition line. Furthermore, this inflection point may be considered as being an equilibrium point. Since constant rates of change of pressure were applied to the sample, its behaviour-- i.e. the reaction proceeded and entered a region where the velocity of the reaction supposedly ceased and then left this region--could

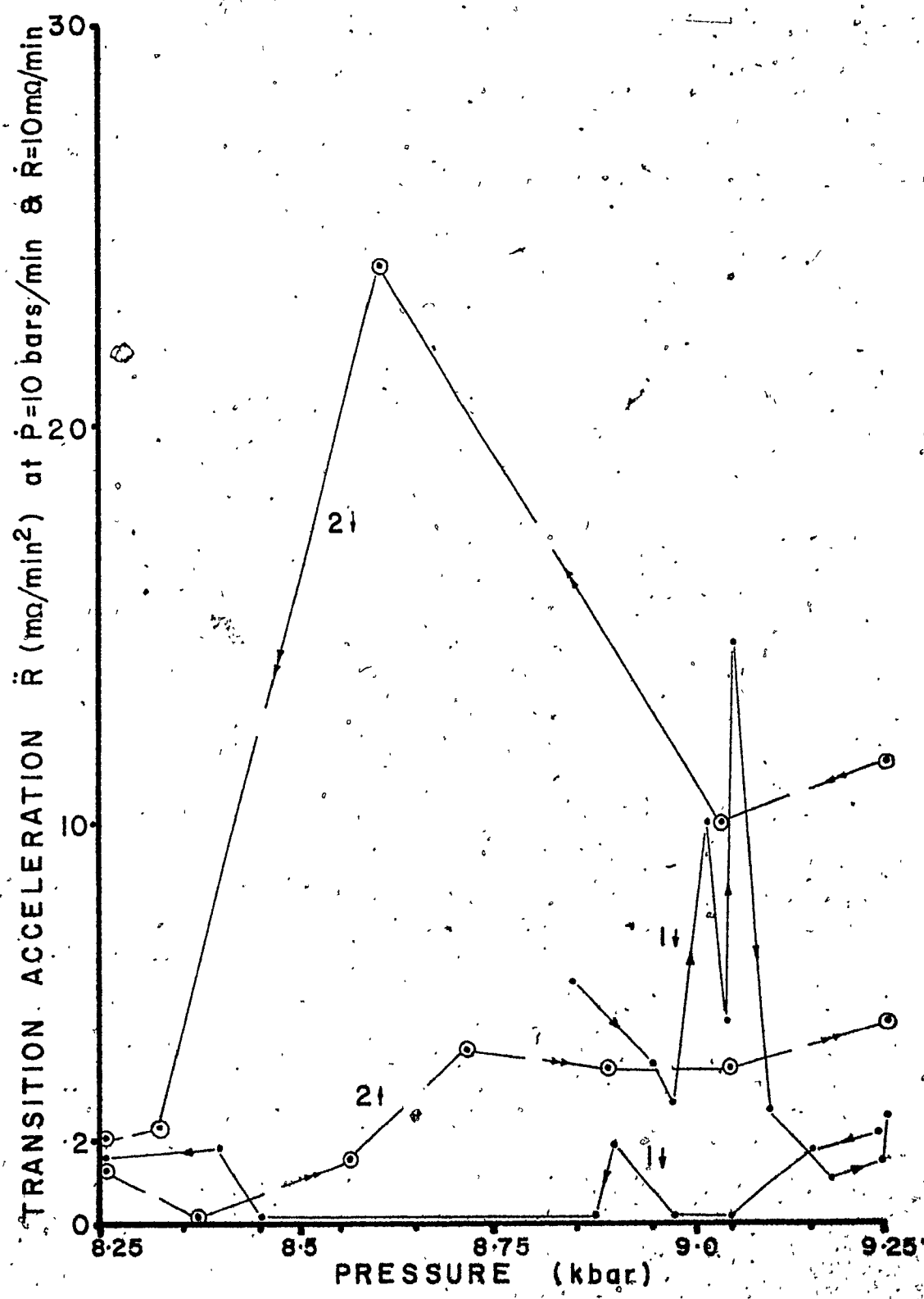


Fig. 27.--Normalized up-stroke and down-stroke transition accelerations in the pressure region between 8.25 and 9.25 kbar for HgSe.

only be characterized as being an inflection point. From our experimental results (an inflection point was measured for HgSe, and within our experimental conditions, this point lies very close to the up-stroke transition initiation pressure--between 8.98 and 9.06 kbar. This band of pressure where the inflection point was found for HgSe may correspond to the existence of Bridgman's zone of indifference. Therefore, our interpretation may have shown an adequate method of determining equilibrium pressures by resistance measurement techniques.

CONCLUSION

In this investigation of polymorphic transitions for the HgSe - HgTe system, it has definitely been shown that, by monitoring solid-solid transformations by electrical resistance techniques, the study of the mechanism governing such transformations is possible. Furthermore, it has been shown that one can characterize this mechanism by activation volumes. Also, a new means of locating the equilibrium pressure within Bridgman's "zone of indifference" in HgSe has been presented.

At the approach of a polymorphic transition, there is a weakening of the bonds in the low pressure crystalline form and a strengthening of the bonds in the high pressure crystalline form. Therefore, by studying the nature of the phase transitions some information concerning the complex properties of mercury chalcogenides has been revealed.

Experimentally it has been shown that there was a linear dependence upon the transition pressures as the amount of selenium decreased in the alloys. A similar behaviour was observed for the activation volumes of the alloys. This linear behaviour can only be attributed to a linear variation of the nearest-neighbours distance. The results of this study have shown that the width of the hysteresis curve for HgSe was twice that of HgTe, but that the activation volume for HgSe was only half that for HgTe.

By measuring rates of transition, it has been demonstrated that the polymorphic transitions studied were governed by a first-order type kinetic mechanism. By detecting the motion of an "interface" which is believed to be separating both polymorphs, it has been concluded that the transformations were initiated by a mono-nucleonic reaction.

In high pressure measurements, the direct calculation of pressure is not always possible and therefore a calibration based on fixed-point pressures is necessary. These calibration points are usually arrived at by determining the pressure at which sharp polymorphic transitions occur. These transitions are characterized by abrupt changes in volume and/or electrical resistance of the calibrant. Due to the inherent variations of these pressure points, large errors result in the calculation of pressure. Recently, the equilibrium pressures have proven to be more reliable as pressure calibration points. The investigation of Bridgman's "zone of indifference" has revealed within the hysteresis curve for HgSe a pressure range of between 8.98 and 9.06 kbar where the velocity of the reaction appears to go through an inflection point. It has been shown that the inflection point in the acceleration curve could be approached along any portion of the transition line, and it appears to be asymmetrically located toward the high pressure side within the hysteresis curve. Therefore, on the premise that the existence of a "zone of indifference" is characterized by an inflection point obtained while monitoring the velocity of the reaction by resistance measurements, a tentative equilibrium pressure for ²⁰⁰HgSe at 9.02 kbar

is reported.

In conclusion, some recommendations regarding future research on mercury chalcogenides can be made.

By repeating on the entire HgSe - HgTe system the same procedure as that carried out in this study on HgSe for determining the equilibrium pressure, one would be able to not only provide a reliable series of high pressure calibrants, but also to determine the effects of alloy composition on the equilibrium pressures. Also, the effects of different pressurization rates on the equilibrium pressure should be investigated in an attempt to locate distinctly the region where the equilibrium pressure exists, and to possibly outline a procedure which would facilitate its location.

It is also felt that the region prior to the initiation of the high pressure phase warrants further investigation with respect to possible identification of the band structure of the alloys. The nature of the zero slopes observed in the resistivity data reported suggests that this behaviour may be characteristic of band overlapping. More sensitive measurements are required which may confirm or disprove this concept. Also, with improved sensitivity, the motion of the interface would be better analyzed.

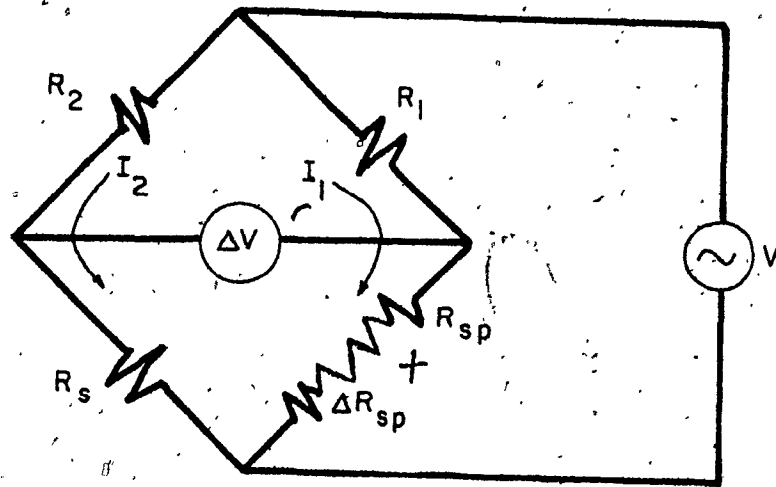
Finally, it is realized that the results reported herein would be confirmed by ultrasonic measurements. With these and other available results, one would be in a position to explain the hysteresis effect in general.

Also, it is fully realized that the above-detailed limitations to this study make it but a contribution toward the better understanding

of the nature of polymorphic transitions. It has been reaffirmed that Bridgman's intuitions in this field were correct, and an attempt has been made to present--with the "inflection point"--a new concept regarding the nature of the hysteresis curve.

APPENDIX A -

RESOLUTION OF PRESSURE SENSOR



To determine the resolution of the pressure sensor the above circuit is used, where

V = power supply (bridge voltage)

ΔV = deflection voltage (output of high impedance voltmeter)

R_1 & R_2 = low temperature coefficient resistors

$R_s = R_{sp}$ = atmospheric resistance of manganin coil ($\Delta R_{sp} = 0$)

ΔR_{sp} = change of resistance of manganin coil due to pressure

Note that R_{sp} and ΔR_{sp} are contained within the high pressure instrument.

Now, applying Kirchoff's law, we have:

$$V = (R_1 + R_{sp} + \Delta R_{sp})I_1 = (R_s + R_2)I_2$$

and, $\Delta V = R_1 I_1 - R_2 I_2$

$$\begin{aligned} &= - (R_{sp} + \Delta R_{sp})I_1 - R_s I_2 \\ &= R_1 \left(\frac{V}{R_1 + R_{sp} + \Delta R_{sp}} \right) - R_2 \left(\frac{V}{R_2 + R_s} \right) \end{aligned}$$

$$\Delta V = V \left(\frac{R_1}{R_1 + R_{sp} + \Delta R_{sp}} - \frac{R_2}{R_2 + R_s} \right)$$

Letting $R = R_1 = R_2$, we can write

$$\Delta V = V \left(\frac{1}{1 + \frac{R_{sp}}{R} + \frac{R_{sp}}{R} \frac{\Delta R_{sp}}{R_{sp}}} - \frac{1}{1 + \frac{R_s}{R}} \right)$$

Letting $\frac{R_{sp}}{R} = \alpha$, and remembering that $R_s = R_{sp}$ we obtain

$$\Delta V = V \left(\frac{1}{\alpha + 1 + \alpha \frac{\Delta R_{sp}}{R_{sp}}} - \frac{1}{\alpha + 1} \right)$$

$$\Delta V = \frac{V}{\alpha + 1} \left(\frac{1}{1 + \frac{\alpha}{\alpha + 1} \frac{\Delta R_{sp}}{R_{sp}}} - 1 \right)$$

By using the first two terms of the Binomial Expansion, we obtain

$$\Delta V = \frac{V}{\alpha + 1} \left[1 - \frac{\alpha}{\alpha + 1} \frac{\Delta R_{sp}}{R_{sp}} + \frac{1}{2} \left(\frac{\alpha}{\alpha + 1} \right)^2 \left(\frac{\Delta R_{sp}}{R_{sp}} \right)^2 - 1 \right]$$

$$\Delta V = \frac{V}{(\alpha + 1)} \left[\frac{\alpha}{\alpha + 1} \frac{\Delta R_{sp}}{R_{sp}} + \frac{1}{2} \left(\frac{\alpha}{\alpha + 1} \right)^2 \left(\frac{\Delta R_{sp}}{R_{sp}} \right)^2 \right]$$

$$\Delta V = \frac{\alpha V}{(\alpha + 1)^2} \frac{\Delta R_{sp}}{R_{sp}} + \frac{V}{2} \frac{\alpha^2}{(\alpha + 1)^3} \left(\frac{\Delta R_{sp}}{R_{sp}} \right)^2 \quad (\text{App. A, 1})$$

Now, choosing $R = 5 \text{ K}\Omega$ and $R_s = 128 \Omega$

$$\therefore \alpha = \frac{R_{sp}}{R} = \frac{128}{5} \times 10^{-3} = 25.6 \times 10^{-3}$$

\(\therefore\) the second term can be neglected and,

$$(\alpha + 1)^2 \approx 1 + 2\alpha = 1.0412$$

also, $\frac{(\alpha + 1)^2}{\alpha} = 40.67$

From (App. A, 1) above we obtain

$$\frac{\Delta R_{sp}}{R_{sp}} = \frac{\Delta V (\alpha + 1)^2}{V \alpha} = \frac{\Delta V (40.67)}{V}$$

or $\Delta V = \frac{V}{40.67} \frac{\Delta R_{sp}}{R_{sp}}$

Now, for $V = 15$ volts

$$V = (R + R_s) I$$

or $I = \frac{V}{R + R_s} \approx \frac{V}{R}$

$$\therefore I = \frac{V}{5} \times 10^{-3} = 3 \text{ ma}$$

$$\therefore \Delta V = 0.3688 \frac{\Delta R_{sp}}{R_{sp}}$$

Nominally $R_{sp} = 128.65 \Omega$

$$\therefore \Delta V = 2.87 \times 10^{-3} \Delta R_{sp}$$

Therefore, for $1 \text{ m}\Omega$ change of resistance the deflection voltage is

$$\Delta V = 2.87 \times 10^{-6} \text{ volts}$$

$$\therefore \text{RESOLUTION} = 2.87 \mu\text{V}/\text{m}\Omega$$

(For $\Delta R_{sp} = 0.2 \Omega$, $\Delta V = 574 \mu\text{V}$. Observed $\Delta V = 600 \mu\text{V}$. \therefore % error =

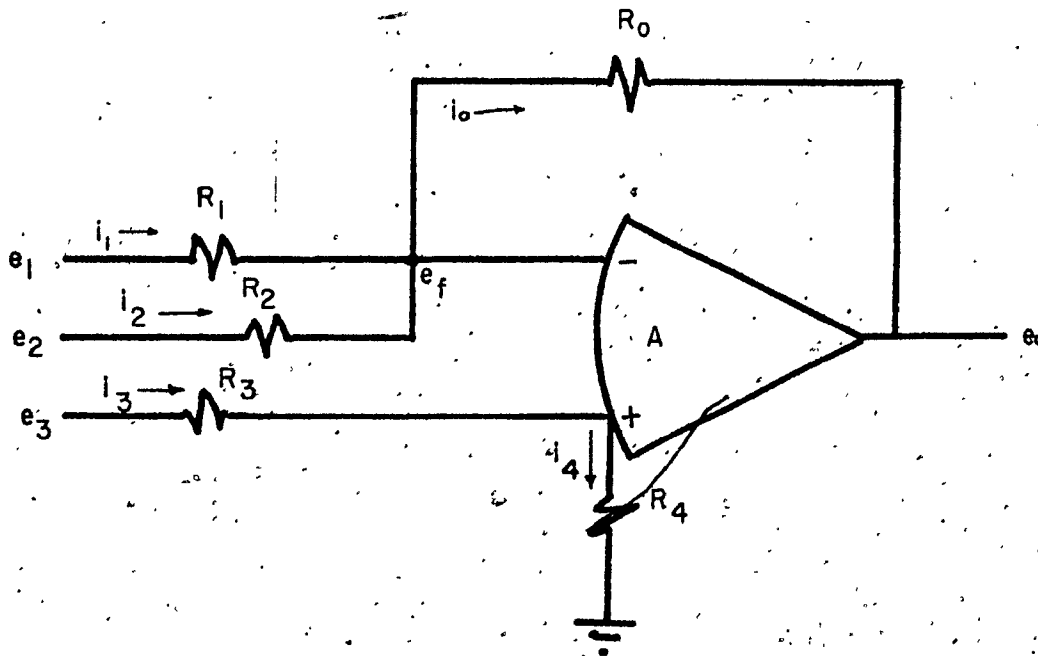
$$4.5. \therefore \text{Maximum sensitivity} = 0.045 \times 8.160 \text{ (p.23)} \approx 0.5 \text{ bars}$$

APPENDIX B

DESIGN OF ADJUSTABLE D.C. BIASING FOR GREATER
SENSITIVITY MEASUREMENTS

Let A represent an operational amplifier with infinite input impedance and infinite gain.

Thus, for a differential input we proceed with the following circuit.



$$i_1 + i_2 = i_0$$

$$\frac{e_1 - e_f}{R_1} + \frac{e_2 - e_f}{R_2} = \frac{e_f - e_0}{R_0}$$

or

$$\frac{e_0}{R_0} = e_f \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_0} \right) - \frac{e_1}{R_1} - \frac{e_2}{R_2}$$

$$e_0 = e_f \left(1 + \frac{R_0}{R_2} + \frac{R_0}{R_1} \right) - \frac{R_0}{R_1} e_1 - \frac{R_0}{R_2} e_2$$

$$\therefore i_3 = i_4 \text{ and } e_f = i_4 R_4$$

$$e_f = \frac{R_4}{R_3 + R_4} e_3$$

$$\therefore e_0 = \frac{R_4}{R_3 + R_4} \left(1 + \frac{R_0}{R_1} + \frac{R_0}{R_2} \right) e_3 - \frac{R_0}{R_1} e_1 - \frac{R_0}{R_2} e_2$$

Letting $R_0 = R_1 = R_2$ we get

$$e_0 = \frac{R_4}{R_3 + R_4} (3) e_3 - e_1 - e_2$$

and choosing $R_3 = 2R_4$

$$\therefore e_0 = \frac{R_4}{3R_4} (3) e_3 - e_1 - e_2$$

$$\text{or } e_0 = e_3 - e_1 - e_2$$

$$\therefore e_0 = - [e_1 + (e_2 - e_3)]$$

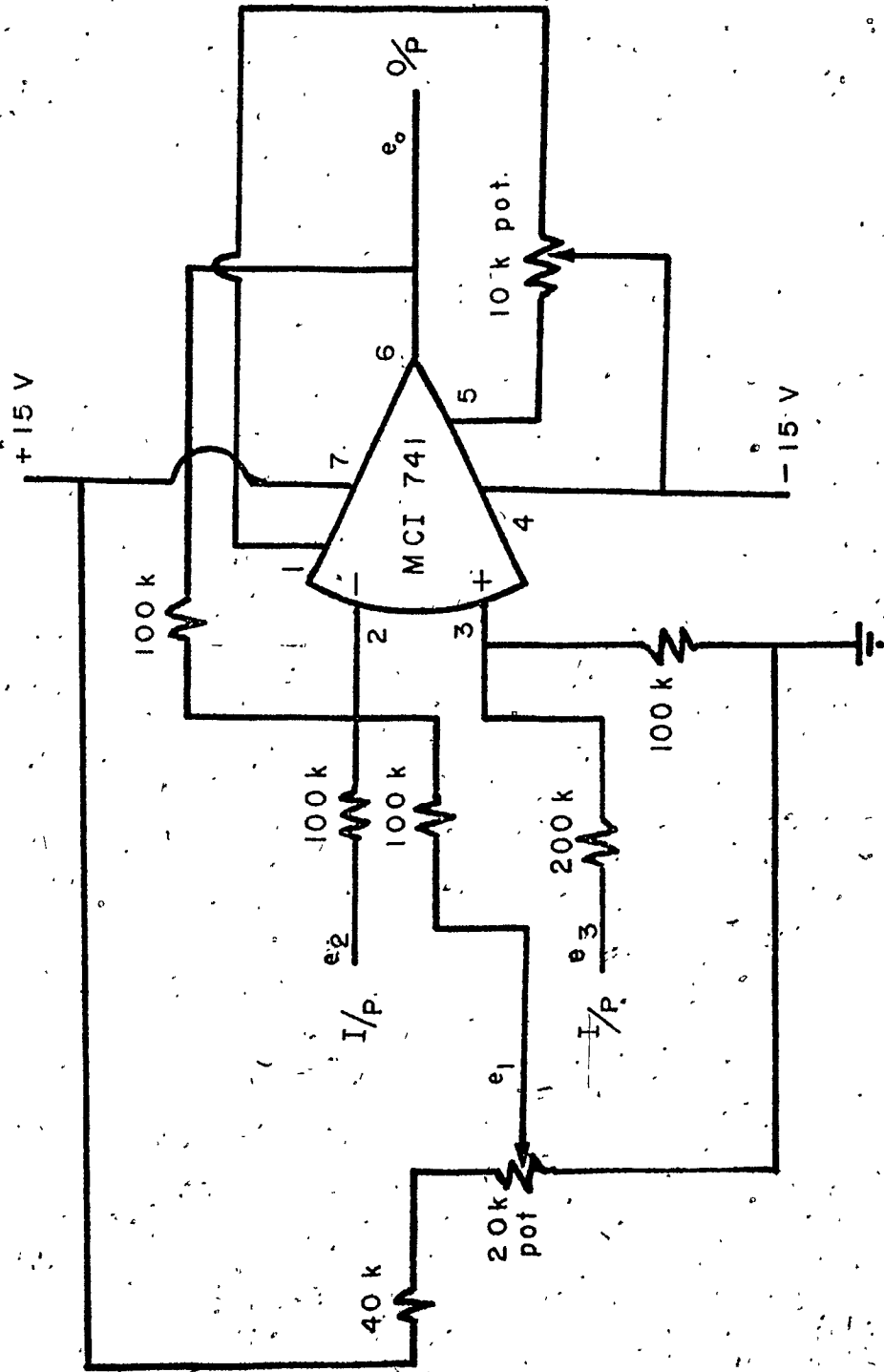
where

e_1 = bias input voltage

and

$e_2 - e_3$ = differential input voltage

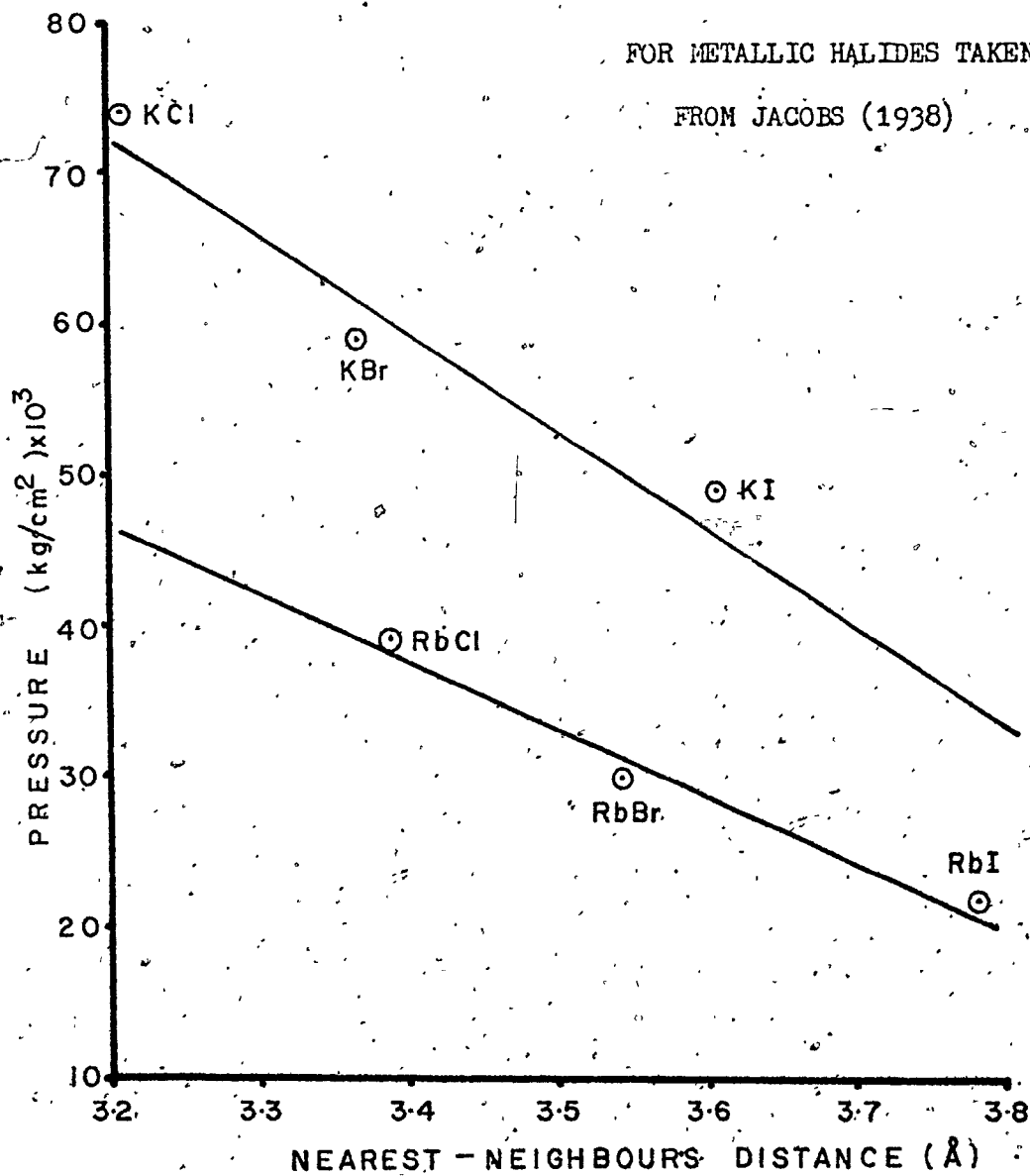
The complete schematic of the device to provide 5 volts of bias is given on the next page.



(Adjustable 5 volt D.C. Bias.)

APPENDIX C.

CALCULATED TRANSITION PRESSURES
FOR METALLIC HALIDES TAKEN
FROM JACOBS (1938)



LITERATURE CITED

- (1) Blair, J., and Smith, A. C. "Phase Transition in Mercury Telluride." Physical Review Letters, VII (Aug., 1961), 124-5.
- (2) Kafalas, J. A.; Gatos, H. C.; Lavine, M. C.; and Banus, M. D. "High Pressure Phase Transition in Mercury Selenide." Journal of Physics and Chemistry of Solids, XXIII (1962), 1541-44.
- (3) Bridgman, P. W. The Physics of High Pressure. London; G. Bell and Sons Ltd., 1952.
- (4) Bridgman, P. W. "The Velocity of Polymorphic Changes between Solids." Proceedings of the American Academy of Science, LII (1916), 57-88.
- (5) Lacam, A.; Lombos, B. A.; and Vodor, B. "Kinetic Aspect of Polymorphic Transitions Induced by High Pressure." Proceedings of the 1st International Conference on Calorimetry and Thermodynamics. Warsaw, 1969.
- (6) Lacam, A.; Lombos, B. A.; and Vodor, B. "Pressure Effect on the Rate of Phase Transition in Mercury Telluride." Physics of the Earth and Planetary Interiors, III (1970), 511-2.
- (7) Jacobs, R. B. "Polymorphic Transitions in Metallic Halides." Physical Review, LIV (Sept., 1938), 468-74.

- (8) Evans, M. G., and Polani, M., "Some Applications of the Transition State Method to the Calculation of Reaction Velocities, especially in Solution." Transactions of the Faraday Society, XXXI (1935), 875-94.
- (9) Lacam, A., and Peyronneau, J. "Transition Polymorphique Induite par la Pression dans le Chlorure de Rubidium. Effet d'Hystérésis." Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Paris, 1971.
- (10) Vanfleet, H. B., and Zeto, R. J. "Comparison of the Bismuth I-II Phase Transformations in Liquid and Solid High Pressure Systems." Journal of Applied Physics, XLII (Nov., 1971), 4955-60.
- (11) Zeto, R. J., and Vanfleet, H. B. "Pressure Calibration to 60 kbar Based on the Resistance Change of a Manganin Coil under Hydrostatic Pressure." Journal of Applied Physics, XI (April, 1969), 2227-31.
- (12) Zeto, R. J., and Vanfleet, H. B. "Interpretation of Initiation Pressure Hysteresis Phenomena for Fixed-Point Pressure Calibration." Journal of Applied Physics, XLII (March, 1971), 1001-010.
- (13) Pearson, W. B. Handbook of Lattice Spacings and Structures of Metals and Alloys. International Series of Monographs on Metal Physics, 1958.
- (14) Harman, T. C., and Strauss, A. J. "Band Structure of HgSe and HgSe - HgTe Alloys." Journal of Applied Physics, XXXII Supplement (Oct., 1961), 2265-70.

- (15) Rodot, A.; Rodot, H.; and Triboulet, R. "Some Properties of HgSe - H₂Te Solid Solutions." Journal of Applied Physics, XXXII Supplement (Oct., 1961), 2254-56.
- (16) Harman, T. C. "Properties of Mercury Chalcogenides." Physics and Chemistry of II-VI Compounds. Edited by H. Aven and J. S. Prener. New York: John Wiley and Sons Inc., 1967.
- (17) Giriat, A. "Mixed Crystals of Mercury Compounds." Physics Letters, XVI A (May, 1968), 639-40.
- (18) Abrokosov, N. K.; Bankina, V. F.; Poretskaya, L. V.; Shelimova, L. M.; and Skulnova, E. V. Semiconducting II-VI, IV-VI, and V-VI Compounds. New York: Plenum Press, 1969.
- (19) Lawson, W. D.; Nielsen, S.; Putney, H.; and Young, A. S. "Preparation and Properties of HgTe and Mixed Crystals of HgTe - CdTe." Journal of Physics and Chemistry of Solids, IX (1959), 325-29.
- (20) Harman, T. C.; Logan, M. J.; and Goering, H. L. "Preparation and Electrical Properties of Mercury Telluride." Journal of Physics and Chemistry of Solids, VII (1958), 228-35.
- (21) Barnett, J. D., and Bosco, C. D. "Technique for Obtaining True Hydrostatic Pressures to 60 kbar." The Review of Scientific Instruments, XXXVIII (1967), 957ff.
- (22) Birch, F. Handbook of Physical Constants. Edited by S. P. Clark, Jr. Geological Society of America, Memoir 97, 1966.

- (23) Lacan, A.; Peyronneau, J.; Engel, L.; and Lombos, B. A. "Pressure Induced Phase Transitions in Mercury Chalcogenides." Chemical Physics Letters, XVIII (Jan., 1973), 129-31.
- (24) ASTM. Standard Methods of Test for Resistivity of Semiconducting Materials. P43-70.
- (25) Bridgman, P. J. "The Compression of 46 Substances to 50,000 kg/cm²." Proceedings of the American Academy of Science, LXXIV (1940), 21-51.
- (26) Jayaraman, A.; Klement, W.; and Kennedy, G. U. "Melting and Polymorphic Transitions for some Group II-VI compounds at High Pressure." Physical Review, CXXX (June, 1963), 2277-83.
- (27) Mariano, A. N., and Warcenais, E. P. "High Pressure Phases of some Compounds of Groups II-VI." Science, CXLIII (1963), 672.
- (28) Groves, S., and Paul, W. "Band Structure of Gray Tin." Physical Review Letters, XI (Sept., 1963), 194-96.
- (29) Groves, S., and Paul, W. Proceedings of the 7th International Conference on the Physics of Semiconductors. Paris, 1964.
- (30) Giriat, W. "On some Properties of Mercury Chalcogenides." Electron Technology (Warszawa), IV, 1/2 (1971), 37-43.
- (31) Vérie, C., and Martinez, G. "Transition Semi-métal → Semi-conducteur Induite par une Pression Hydrostatique dans Cd₁₁Hg_{9.89}Te." Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Paris, 1968.

- (32) Piotrkowski, R.; Porowski, S.; Dziuba, Z.; Ginter, J.; Gariat, W.; and Sosnowski, L. "Band Structure of HgTe." Physica Status Solidi Short Notes, VIII (1965), K135-39.
- (33) Edwards, A. L.; Slykhouse, T. D.; and Drickamer, H. G. "The Effect of Pressure on Zinc Blende and Wurtzite Structures." Journal of Physics and Chemistry of Solids, XI (1959), 140-48.
- (34) Minomura, S., and Drickamer, H. G. "Pressure Induced Phase Transitions in Silicon, Germanium and some III-V Compounds." Journal of Physics and Chemistry of Solids, XXIII (1962), 451-56.
- (35) Samara, G. A., and Drickamer, H. G. "Pressure Induced Phase Transitions in some II-VI Compounds." Journal of Physics and Chemistry of Solids, XXIII (1962), 457-61.
- (36) Paul, W., and Warschauer, D. H., ed. Solids under Pressure. New York: McGraw-Hill, 1963.
- (37) Onodera, Akifumi. "Kinetics of the Polymorphic Transitions of Cadmium Chalcogenides under High Pressure." The Review of Physical Chemistry of Japan, XLI (1971), 1-17.