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KINETICS OF SHOCK-INDUCED POLYMORPHIC PHASE TRANSITIONS*

Dennis B. Hayes
Detonating Components Division, 2513
Sandia Laboratories
Albuquerque, NM 87115

ABSTRACT

Shock-loading induces polymorphic phase transitions in some solids if the pressure exceeds that at which phase transition occurs under quasi-static compression. Volume changes in shock-induced transitions must occur very rapidly to produce the structured shock waves observed, so transition rates are large under these dynamic conditions. By contrast, the same transition might require minutes or hours under quasi-static loading. If shock-induced transition is so rapid that kinetic effects can be ignored, a steady two-wave structure is propagated. The first wave, of amplitude equal to the transition pressure, shocks the material to the phase boundary but produces no transition; the second, slower wave produces the transformed phase. When kinetic effects are important, this two-wave structure does not form immediately but by an evolutionary process which produces transients in the amplitudes and rise times of the stress waves.

By measuring these transient effects, some facts about the kinetics of phase transitions have been inferred. Comprehensive studies on phase-transition kinetics in antimony, iron, and potassium chloride are described, with emphasis on a thermodynamic description of the intermediate states during transition. Complicating effects such as shear strength and wave perturbations due to free surfaces are discussed.

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DISCLAIMER

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(1) KINETICS OF SHOCK-INDUCED POLYMORPHIC PHASE TRANSITIONS

Introduction

(2) Numerous phase changes have been observed under shock loading. For instance, a metal-to-insulator transition has recently been observed in lead sulfide under shock loading. Also, we are all familar with the ferromagnetic-to-paramagnetic phase changes which are known to occur in many materials. These are typically second-order phase changes.

Of the first-order variety, one can consider phase changes in materials which undergo chemical decomposition. An example of that might be the shock-induced detonation wave in a high explosive. Also, there have recently been several studies of shock-induced melting. Two that come to mind are melting in shocked aluminum and in shocked bismuth.

What I would like to talk about today is polymorphic phase transitions in which a reordering of the lattice is caused by the pressure-temperature excursion produced by the shock environment.

(3) I will consider transitions between states which are not in thermodynamic equilibrium.
(4) In fact, I want to talk about the rates at which these nonequilibrium states transform, so I will concentrate on kinetics. As you can see from this slide, we will cover specifically first-order, nonequilibrium phase-change kinetics under shock loading.

(5) There are really two parts to this talk. The first has to do with the theory of such phase changes. Within the theory, you can see that there are two distinct parts. The first is the influence of the phase change on the flow. In fact, as the volume changes associated with the phase change occur, the flow is perturbed and causes structured waves to propagate. The second part of the theory has to do with microscopic physical models of the phase change process itself. That is the influence of the flow on the phase changes.

The second part of this talk has to do with experiments that were done by various investigators on iron, antimony, potassium chloride, and quartz.

(6) During the course of preparing this talk, I made use of an unpublished source. It is very good and I would like to call it to your attention. It is an invited review by Duvall and Graham. It has been written and submitted to the Reviews of Modern Physics. Those following the field should watch for its publication. I think that it will become very useful as a source document for those who are working in the area of shock-induced phase changes.

(7) This slide shows the published experimental works which have shed light on phase-change kinetics. You can read the list over, and while you are doing that let me call your attention to the fact that several of the classical papers in shock wave physics that have to do with phase changes under shock loading are absent from this list. Bancroft, Peterson, and Minshall's paper on Armco iron, the first paper, in fact, on shock-induced phase changes, is absent. Others missing are Wackerle's paper on quartz and Duff and Minshall's paper on bismuth. The reason that those and others have been excluded from this list is that they do not deal specifically with phase-change kinetics, but only with the phase-change process itself. Each of those papers is more concerned with the final states than with kinetics. Also, let me point out that, in the case of boron nitride, Quintin Johnson of the Lawrence Livermore Laboratory has done work using x-ray spectroscopy. In fact, he has demonstrated that these reduced volume states which are achieved under shock loading are directly associated with a rearrangement of the lattice into the phase which we suppose was formed, based on our knowledge of what happens quasi-statically. That result is very significant.

(8) I do not have a list for the theory of polymorphic phase transitions that corresponds to the last slide which showed the experimental studies. What I have done is write down a list of those works to which I make reference. Let me point out that I am not going to mention the work of Forbes during this talk. The reason is that the next scheduled speaker is Dr. Forbes from NSWC who is going to talk about his theory of the kinetics of the $\alpha - \epsilon$ phase change in shocked Armco iron. For that reason, I will exclude any further discussion of that theory.

(9) Because of many diverse subjects, this is a complicated talk. For that reason, I have put together a road map to show you just what subjects will be covered. First of all, I am going to discuss the first portion of the theory; that is, the influence of the phase change on the flow. The most important part of this subject is to call to your attention the experimental observables. That is, what is it that the phase-change kinetics do to the flow which we can observe experimentally in order to back out or infer information about the rate of the phase-change processes? Next I want to cover the experimental studies on the four materials that I listed before. In the case of iron, the point that I want to make is that the case which has been made for kinetic effects to be present in Armco iron is still open, as far as I am concerned. The reason is that there are complications which arise because of shear-strength effects; transients produced in the observables because of the shear-strength effects complicate the interpretation of results. In the case of antimony, the point that I will make is that there are two different kinds of experiments which both lead to the same conclusion regarding the rates of the polymorphic phase change. Based on that similarity, antimony looks like a good example of a shock-induced phase change in which there is a single process occurring. Just the opposite will be shown in the case of potassium chloride. There we find very good evidence that there are two distinct rates: a very rapid one and a very slow one. In fact, I will discuss results on KCl that have been obtained by a rather different experimental technique. Finally we will consider the case of quartz, the only one of these four transitions

which is reconstructive. The fact is that the shock environment is producing temperature inhomogeneities. The hot areas arise from shear banding, stimulating or causing the phase change to occur more rapidly. So, in quartz, there is some evidence that thermally activated processes do occur under shock loading.

Finally, I will have some concluding remarks in which I will summarize the talk and point out directions of fruitful future research.

Theory

Let us begin then with the construction of a suitable constitutive equation under a set of specified conditions.

(10) If one makes the assumption that the transformed phase is composed of many small nuclei which remain in thermal and mechanical equilibrium with the surrounding matrix, then such a construction is possible. In fact, under those conditions you get the set of equations at the top. Those equations, if properly manipulated, lead to the matrix equation at the bottom. The vector $\underset{\sim}{x}$ is a vector with components equal to the mass factions of the constituents. By inspection, you can see that this matrix then relates variations in density, ρ, and variation in composition, $\underset{\sim}{x}$, to the variation in pressure and temperature. The coefficients in the matrix are well defined since all of these are thermodynamic properties which are defined for the mixture with frozen composition. Inspect the pressure equation. What we see is the rate of change of pressure, $\dot{P}$, as related to the variation in density in composition in the form of a Maxwell equation. In fact, $\dot{P}$ is $a^2\dot{\rho}$ plus some large thermodynamic term times $\dot{\underset{\sim}{x}}$. Subsequently, that large thermodynamic term is going to be referred to as F. In fact, we see this as an example of a Maxwellian material.

(11) Here I want to contrast the flow which is achieved by materials which are in thermodynamic equilibrium with a flow for material which obeys a Maxwellian form for a constitutive equation. On the left-hand side you see the procedure which we use for materials which remain in thermodynamic equilibrium. We construct a complete equation of state by generating the entropy function. We solve for the composition, x, by minimizing the Gibbs free energy. If we do that and there is a phase change, we find that the Hugoniot for such a material has cusps and kinks in it. In fact, if we attempt to propagate a wave through with a pressure amplitude above the cusp, we get a structured wave. That wave has a two-wave structure, a P_1 wave which has amplitude equal to the position of the first cusp and a P_2 wave which follows behind more slowly and continues to fall behind. The important thing is that the waves are steady; that is, they have the same shape at an early time as they have at a later time. They are just further separated. Contrast that with a nonequilibrium case for which we have the material with the constitutive equation of a Maxwellian form. For the purposes of instruction, suppose that we have a transformation rate law which is going to drive the material to thermodynamic equilibrium. In fact, for this example, suppose

that the transformation rate is proportional to the difference in specific Gibbs free energy of the two component phases. Transformation always proceeds so as to drive the difference to zero with some relaxation time, τ . For such a material we see a situation more like this (bottom right), where a two-wave structure evolves instead of being formed immediately. Let me point out now that it is not necessary to make an assuption regarding what the transformation law is. In fact, by measuring things having to do with the evolution of the wave we can back out the phase-transition rate. In the case of the leading wave (the P_1 wave), we can see that its time rate of change of evolution is related to that thermodynamic function F and the phase change rate at $x = 0$. What that means is, if we measure DP/Dt and we make a mathematical construction of F, then we can solve for the phase-transition rate experimentally.

(12) What I have done is used the method of Andrews to make an actual calculation of what the wave evolution for such material is. That calculation is shown on this slide. The stress waves are caused by the symmetric impact of one piece of phase-changing material onto another, producing a plane stress wave. Initially, the impact stress is as shown on the left hand margin. First track the evolution of the P_1 wave. Initially, if you follow P_1 from left to right and down, you can see that the P_1 amplitude evolution takes place. Results are shown in five different positions. Again, it is obeying this approximate decay equation, DP/Dt is equal to $F \cdot \dot{x} + 2$.

Let us look at the evolution of the P_2 wave. Initially, at impact, and as a matter a fact at the next two times, one sees that there is no P_2 wave--it has not formed. The stress is decaying at the impact interface and the stress of the P_1 wave is decaying. They are decaying together and there is but a single wave. Now at the third time one sees that the P_2 wave has formed. In fact, the P_2 wave formed only after the phase transition was complete at the impact interface. Stress would have continued to decay because of the decrease in volume associated with the phase change, and only stopped because the parent material was completely exhausted. Then the P_2 wave began to form, and one can see then that the propagation of the P_2 wave at the subsequent times is the point of reaction completion. So, an experimental observable then might be the delay of the formation of the P_2 wave.

Let us see what other observables appear on this graph. We mentioned that the stress continued to drop at the impact interface. In fact, initially it was P_1, followed by a drop down to its final value which is the value of the P_2 wave. Hence, if one measures the decay in stress or the rate of decay in stress at the impact interface, one can then infer from that the rate at which the phase change occurred. That decay rate is an experimental observable.

A fourth experimental observable is the structure which connects the P_1 wave to the P_2 wave. Notice that the P_1 - P_2 rise time stretches out, being very small initially. The reason it stretches out is that the entire phase change has to occur within that transition; and if the phase change is sluggish, it is going to make that transition region very wide. So we have the P_1 - P_2 rise-time stretch as another experimental observable.

(13) I have summarized these experimental observables for you on this slide. I will refer to [illegible] as we go through the experimental studies. We have P_1 decay, $P_1 - P_2$ rise time, loading interface transients, and the P_2 delay.

Experimental Studies

Iron

(14) These data are the P_1 decay data for Armco iron by the experimenters indicated above. There is obviously P_1 decay. The solid line is the line which would be drawn for the case when phase-change kinetics are not important, that is, the phase-change part of the flow is in thermodynamic equilibrium. The reason this line is not a constant line is as follows: It turns out that Armco iron is particularly complicated because, in front of this evolving P_1 wave, is an evolving elastic precursor. In fact, one obtains that line on the figure by assuming that the stress deviators in front of the P_1 wave are equal to the stress deviators behind the P_1 wave. Since the compressive stress of the precursor in the direction of propagation is a decaying function of distance, under the above assumptions, one finds that the P_1 amplitude, just based on the decaying precursor, is also a decaying function of distance. Well, clearly that solid line does not have enough variation of P_1 amplitude to describe the data. Barker has attributed this P_1 decay to phase-change kinetics. Examine the series of data represented by squares at about 6 mm specimen thickness. Note that there is a variety of P_1 amplitudes that have been observed by a very precise technique. Those experiments were for different initial loading stresses. The uppermost square was for a higher loading stress than the lowest loading square. That result is expected from kinetic effects.

(15) In this slide we have the model Barker used to fit these data. It is the model of Horie and Duvall, a phenomenological model, in which the phase change is approaching equilibrium exponentially with a exponential decay time, τ. One sees that, for this case, the stress is expected to decay along trajectories which depend upon the initial loading stress or driving stress, σ_D. At the top you see the three driving stresses of 16, 24, and 30 GPa. I have not attempted to key individual experiments to these graphs, but let me tell you that this model does a pretty good job of fitting the data. So, Barker attributes this P_1 decay to phase-change kinetics and determines that decay time τ to be about 0.2 μs. Well, 0.2 μs is a very long time; in fact, if we see transient effects lasting that length of time in P_1 evolution, then we ought to see the other experimental observables with effects which would be brought about by phase change which took as long.

Let us look at the case of $P_1 - P_2$ rise time.

(16) These are two calculated free-surface velocity histories for Armco iron in which kinetic effects are not accounted for. That is, these are calculations of the flow for thermodynamic equilibrium being maintained. The dash line is the case for the phase change in iron in which

elastic-plastic effects were ignored. One sees in this calculation, which is the result of a finite difference calculation, that what is observed is a two-wave structure with nice crisp arrival times. Now, if one then does another calculation in which an equilibrium elastic-plastic effects are accounted for, one sees the elastic precursor precedes a nice sharp P_1 wave arrival. Then one notices that the $P_1 - P_2$ rise time is smeared out. The reason is that the free surface perturbs the flow. Even though the $P_1 - P_2$ rise time in situ in the calculations was sharp, when the elastic precursor reaches the free surface it reverberates back and forth, bringing the free surface to the final velocity in a series of steps. This series of steps then has the effect of smearing the wave out. So how does this $P_1 - P_2$ rise-time smearing for the equilibrium calculation compare with what is observed for the $P_1 - P_2$ rise time in a comparable Barker experiment?

(17) Here is a comparison between the calculation of the last graph and the corresponding experiment. We see that there is no $P_1 - P_2$ rise-time smearing beyond that which is accounted for by the equilibrium elastic-plastic effects. In fact, if there were phase change kinetic effects of the order of 0.2 μs then one would expect to see a smearing of the experimental values, rolling back about 0.2 μs farther back than this calculation shows. Well, so much for the $P_1 - P_2$ rise time.

There is another point I want to make for which I have no slide, and that is the arrival time of the P_2 wave. Recall there is a delay in the formation of the P_2 wave, which means that the arrival times of the P_2 wave when plotted against the thickness of the specimen, a straight-line fit, does not go through the origin. Now Barker did two experiments which were identical or nearly identidical in impact velocity. Hence, they produce P_2 waves of the same amplitude. One of these was for specimen thickness of about 6 mm, and the other was for a specimen thickness of nearly 18 mm. If one plots the arrival time of the P_2 wave as a function of specimen thickness and draws a straight line, using those data, it hits within 10 ns of the origin. So in this case, for kinetic effects which are supposed to be as large as 0.2 μs, we see no P_2 delay which even approaches that length of time. The P_2 delay is less than 10 ns.

I have summarized the conclusions for the experiments on Armco iron on Slide 18. These conclusions are as follows:

(18) You can fit P_1 decay with the existing phenomenological model; however, there is no P_2 delay. It turns out that the P_1 decay times are of the same order of magnitude as the elastic precursor decay times, but the elastic precursor decay correction is not enough to account for the magnitude of P_1 decay. It looks as if equilibrium elastic-plastic effects can account for the $P_1 - P_2$ rise time.

Antimony

Now I would like to turn to the experiments on antimony.

(19) On the left are the P_1 decay data of Warnes for this material. There are other experimental data which start with different driving stress (larger amplitude). Those data do not fall on top of these data so I have chosen for simplicity to just display Warnes'. The differential equation which is shown on the left-hand side describes all such available experimental data. In fact, the solid line is one solution to that differential equation. As you recall, there is a relationship between the pressure-decay rate, DP/Dt, and the phase-transition rate, $\dot{x}$. If the differential equation on the left is used to calculate the time rate of change P_1 decay, that along with the thermodynamic function F can be used to infer the values of the phase-change rate, $\dot{x}$. The formula shown on the right-hand side shows $\dot{x}$ is generally related to DP/Dx, the decay of pressure with position. If the phase-change rate remains constant during the entire phase transition, then one can use the equation on the right hand side to calculate a phase transition completion time. That time is just the reciprocal of the calculated $\dot{x}$. That calculated phase-change time can be plotted as the function of the applied load, which is what we see as the solid line. Again, that is the phase-transition time inferred from the P_1 decay data. It turns out that, at a pressure of 13 GPa, there is a one experimental datum for a phase-transition time. That was obtained by using a flash x-ray called PHERMEX in which an oblique shock was propagated in antimony and a flash x-ray was used to determine density profiles behind the oblique shock. I will show you shortly a schematic of the experimental result. The important thing is that, based on the flash x-ray experiment, by measuring the density behind the shock in antimony the experimenters, Breed and Venable, were able to infer a phase-transition time of between 2 and 3 μs. Using the simple analysis that I just described a moment ago, which is the solid line on the right-hand side, we see that the calculated or anticipated phase-transition time based on P_1 decay data is 2.3 μs--very close to that which was inferred by the experimenters. So, I judge this to be evidence that a single process is occurring. In fact, this is the only example where there has been agreement between P_1 decay and a phase-transition time obtained from a different technique, which leads me to believe that antimony is an example of a material which undergoes polymorphic phase change completion by means of a single mode. That is, there is a single mode of transformation.

(20) On this slide is the schematic of the experiment which I referred to on Slide 19. Near the top of this diagram is a region of high explosive. There is a detonation front propagating in baratol HE, going from right to left, producing a high pressure behind the detonation front. That pressure causes two oblique shocks to pass into the antimony, a P_1 shock and a P_2 shock. Now, in fact, the P_2 shock at late times forms a line which does not intersect the origin. An analysis of two-dimensional flow, of which this is an example, shows that such a lack of intersection arises from kinetic effects. That is, if kinetic effects were not important, the P_2 wave at late times would form a line which would intersect the origin. These notions were confirmed by different experiments in bismuth for which kinetic effects are known not to be important. That is, a very rapid transition was studied, and it was observed that the P_2 wave at late times formed a line which did intersect the origin. Thus, when the delay in the P_2 formation occurs in antimony, it infers transition delay. This is the result that is used by Breed and Venable to deduce the quoted 2 to 3 μs delay.

There is also shown on the same diagram a calculation by Duvall, using the P_1 decay data, of the flow pattern for an evolving two-dimensional wave, and there is good qualitative agreement between Duvall's calculation which does show the P_2 delay and the experimental result.

(21) The conclusions regarding kinetic effects in phase-changing antimony are as follows: Using the P_1 decay data, one can infer the initial phase-change rate. There is significant experimental error causing scatter in the data and, since one must use the slope of the P_1 decay data (i.e., differentiate the data in order to calculate the phase-transition rate), those errors are magnified. Nonetheless, using that calculated phase-transition rate, an anticipated P_2 delay has been calculated. That calculated P_2 delay agrees very well with measured value. Also, I would like to point out that the two-dimensional flow pattern qualitatively agrees with an experiment, as was shown on the last slide.

We are in the process of using the model shown during discussion of the constitutive equation in the early part of this talk. An existing two-dimensional code, the CSQ code, is being used to try to calculate the flow pattern. That is, an exact solution to the governing equations is being obtained to see what kind of agreement we can obtain between theory and experiment.

Potassium Chloride

(22) Several years ago a number of experiments were done in which quartz gages were impacted on potassium chloride. If you will examine the figure on the left, we can analyze what the anticipated results are, and I will describe the observed results.

First, look at the left-going Hugoniot for the quartz with initial velocity shown by U. Thick quartz was chosen so that it sees only left-going waves during experiment. Thus, all states which are produced in this impact experiment must lie on the left-going quartz Hugoniot UDB. The KCl was initially at rest. Now if the KCl undergoes no phase change, i.e., it always remains in its low-pressure phase (phase 1), then the shock state which is produced must lie on the Hugoniot for the low-pressure phase OABC. In fact, the result of the impact experiment would be, at impact time, a jump and stress to B and a constant stress at B for the duration of the experiment. On the other hand, if phase changes occur so rapidly that the material always maintains thermodynamic equilibrium after shocking, one expects the impact stress that is achieved to lie on the equilibrium Hugoniot which is shown as OAD. Thus, in an impact experiment, one would expect the stress to jump to D and remain constant for the duration of the xperiment. If, however, kinetic effects are such that the phase transition takes place during the recording time of the gage, then one expects to see the stress initially jump to B and decay to D during the phase-transition process.

In these experiments, this state, B, on the untransformed Hugoniot was never achieved. A state intermediate between B and D was always seen. In fact, it was first thought that stress B wasn't observed because of the bandwidth limitations of the recording system. When experiments were done using faster recording equipment, in which the rise time was made as short as 1 ns when the loads were applied in 1 ns, the states that were achieved were still intermediate between B and D. If those states in a mixed-phase region were achieved in less than 1 ns, and if during that time the mixed-phase region was half traversed, then the phase change must have occurred very, very rapidly initially--at greater than 500 μs^{-1}. On a much longer time scale, the observed stress relaxation brought the stress down to D, that point which is expected for equilibrium. Reiterating, the phase-change completion was observed to occur at a much lower rate than did the initial transformation. What we are faced with then is a very rapid transformation to some state in the mixed-phase region, followed by a very much slower rate of transformation completion.

(23) These were the states which were achieved before the stress relaxation of potassium chloride. What one sees is that, below the cusp, the states lie very close to the calculated equilibrium Hugoniot. Above the cusp, we see that the data all lie above the equilibrium Hugoniot, but they lie far below the stress that would be expected if the material did not change phase at all.

(24) Here we see these same states in stress/volume coordinates, where the slope of the observed instantaneous Hugoniot is quite steep. Now I would like to show you the states after the stress relaxation.

(25) Here we see the final or relaxed states. Within experimental error, the data lie on the calculated equilibrium Hugoniot. Because of uncertainties of gage response, the diamond-shaped data points have the smallest experimental uncertainty; the circles have the largest experimental uncertainty.

(26) Again we can look at the final relaxed states, i.e., the states after stress relaxation, and we see again they lie very close to the calculated equilibrium Hugoniot. The reason for the large scatter of the data is that, during the data-reduction process, one must divide by the difference between the stress of the observation and the stress of the cusp and that difference is small. That tends to magnify experimental uncertainties.

I would like to address the question of why the states representing the initial response in the mixed-phase region make such a steeply inclined angle in stress/volume space.

(27) On the left-hand side of this slide is seen the equilibrium PVT surface for potassium chloride. Equilibrium KCl has a zero entropy of formation, which means that the mixed-phase region forms a horizontal plane. Thus, any line in the mixed-phase region, including the Hugoniot curve lying in that plane when projected onto the P/V plane, forms a horizontal line. Consider the diagram in the upper right-hand corner of the slide. On the right-hand side of that graph we see a material, the low-pressure phase of which has the same PVT equation of state as the equilibrium material. The material near the left-hand side of that figure is a high-pressure phase which has the same PVT equation of state as the equilibrium material. The difference between this nonequilibrium high-pressure phase and the equilibrium high-pressure phase material is not its PVT response, but rather its entropy and energy of formation. Shown schematically then, on the right-hand side, is

the equation-of-state surface for an equilibrium phase 1 (low-pressure) material and a nonequilibrium high-pressure phase 2 material with a higher entropy and energy of formation than equilibrium potassium chloride. The mixed-phase region is tilted upward because of this nonzero entropy of formation of the high-pressure phase. In fact, the projection of the Hugoniot onto the P/V plane produces a representation of the mixed-phase region which is tilted upward. Methods have been established to calculate, based on the slope of the mixed-phase region, the entropy of formation of the high-pressure phase. When this is done, it is deduced that the entropy of formation of the high-pressure phase is 0.39 J/g/K. We can attribute this excess entropy of formation and the more energetic phase to the necessity to produce point defects or interfacial area of these very small nuclei which are formed of the transformed phase. In fact, if we attribute all of that excess entropy and energy of formation to surface energy and use reasonable estimates for the energy which is required to produce a surface, say a few hundred ergs per square centimeter, one can deduce estimates of the size of the nuclei. When that is done for these data, it is found that between 1 and $2 \cdot 10^5$ ion pairs must be involved in the formation of one nucleus.

(28) Now we look again at our data for the stress/particle velocity plane. We see that the data are very well represented by what I now tell you is a calculated nonequilibrium Hugoniot. The equilibrium phase transforms to a nonequilibrium phase with an entropy of formation of 0.39 J/g/K.

(29) Again we see the same data and the same calculation in the P/V plane. The agreement between the calculation and the experiment is quite good.

(30) As you have seen, the data for the initial response or the initial transformation of potassium chloride have been reported for different orientations of the crystallographic axes with respect to the direction of propagation of the shock. On this slide is a summary of the results of the experiments that were performed according to the crystallographic orientation of the shock. Experiments were done for the three different orientations shown. We see that the initial transformation rate was large, in each case too large to be measured. For the fastest response time experiments, initial transformation rate exceeded 500 μs^{-1}. We see that the initial states which were produced did not depend upon the orientation of the crystals. In fact, for each orientation the excess entropy of formation was the same number. However, the rate at which equilibrium was established varied considerably depending upon the crystallographic orientation. For experiments in which the shock propagated in the ⟨100⟩ direction, the rate of completion was estimated to lie between 2 and 5 μs^{-1}. At the other extreme, when the shock progressed along a ⟨111⟩ crystallographic axis, the phase change completion rate was much larger, being always the constant value of 25 ± 5 μs^{-1}. In each case, the state after the pressure transients were completed was close to the equilibrium surface. Now in a few minutes, when I describe to you the results on quartz, I am going to mention the way in which the phase change can be stimulated by finite shear strengths effects. So, in order to set the stage for that, I would like to mention (and I have shown at the bottom) the large difference,

more than a factor of 2 difference, in the shear strength for plane-wave shocks propagating in two crystallographic axes. In fact, the shear strength is smallest in the ⟨ 100 ⟩ direction; that is, the material is the softest. In that case, the phase-change rate was largest or the phase-change time was the longest. In the other case where there is a high shear strength, one finds the completion rate is a large number and that completion was achieved most rapidly.

I have not described to you what the numbers and brackets are under "Completion Rate." Gupta and Duvall did one experiment in which they preheated the specimen to 358 K and what they observed was as follows: The state that was produced initially did not seem to be different, but the completion rate was much larger; that is, equilibrium was established more rapidly in this experiment in which the material was preheated than in those experiments where no preheating was done. Based on this result, they have suggested tentatively that the second stage of phase-change completion might be a thermally activated process. They believe that they increased the phase change completion rate by preheating. I am not making a case that this secondary phase change is thermally activated but, if it is, one can make an estimate of the activation energy.

(31) This diagram shows the total phase-transition time vs the estimated homogeneous shock temperature in the shocked material. There are four data here. The one in the middle by Gupta is the one I just referred to--the preheated specimen. The one above it is an experimental result from my work which had the most similar experimental conditions with the exception that there was no preheating. The point at 10^{-11} s by Kormer is an estimate of the shock thickness transition time in an experiment where the index of refraction measurements behind the shock front indicated the phase change that already occurred. In other words, the phase change occurred within the shock front as judged by index of refraction experiments, and the shock front was 10^{-11} s thick. The lowest point on the graph is an estimate of the sound transit time across a spherical nucleus of KCl, where the spherical nucleus contains 10^{-5} ion pairs. One would expect that would be the lowest possible transition time. Well, if the process is thermally activated and some of these things are occurring more rapidly than others because of the background temperature, then one estimates the activation energy to be about 1/3 volt or 3600 K.

(32) These are the conclusions regarding the phase change in KCl. Metastable states are achieved very rapidly, far into the mixed-phase region. Hence, the phase rate must exceed 500 μs^{-1}. The shock states are characterized pretty well by an excess entropy of formation of 0.4 J/g/K. The initial states do not seem to depend upon the direction of the propagation of the shock, but the shock states do relax toward equilibrium and seemingly attain thermodynamic equilibrium at a rate that does depend upon the direction of propagation of the shock. If this secondary transmission is thermally activated, the estimates of the activation energy are about 3600 K.

Crystalline Quartz

I would now like to show you one slide of some very recent work which has been done on the alpha quartz-to-stishovite transition in quartz.

(33) The ideas for this analysis had their origin in some recovered specimens of quartz in which stishovite, a high-pressure phase of quartz, was recovered. Based on the equilibrium temperature on the Hugoniot, one would not have expected in these experiments pressures and temperatures high enough to produce stishovite. Nonetheless, in the recovered specimens, stishovite was found. In fact, a deformation pattern was observed, and the stishovite was all found in the area where this quartz showed evidence of local deformation. This localized deformation takes place in lieu of conventional plastic deformation. It is caused by what is now being described as adiabatic shear banding. Shear banding is deformation along planes in a regular spaced pattern. All of the irreversible work is done in a very localized region and very large temperatures are achieved. These planes of high temperature gradually heat the rest of the lattice, eventually causing the material to become more uniform in temperature. During this thermal diffusion time, while the hot planes are heating the rest of the lattice, in some regions the temperatures are large enough to stimulate the stishovite reaction. What Grady has done here is write down a couple of ordinary differential equations. The first one is an Arrenhius law of first order for the reaction rate, the second the diffusion equation with a source term which depends on the latent heat of transformation. By an approximate method, Grady has solved these equations to find out what the total extent of reaction--that is, the total mass fraction of phase change material--should be, depending on what is selected for the parameters and Arrenhius law. In fact, Grady is able to estimate an activation energy of about 210 kJ/mol based on this simple analysis, which is not in serious disagreement with what one would expect from low-temperature measurements.

That concludes my remarks on the four experimental studies.

Summary and Conclusion

(34) I would like to summarize the salient features of what has been said so far today.

In the area of theory, we have seen that the influence of the phase change on the flow was an understood phenomenon, with the possible exception of the influence of a decaying elastic precursor on the flow behind. On the other hand, we see that the microscopic physical models of the phase-change process are primitive, only in their earliest stage of development.

In the case of the four experimental studies, we have four different examples of response. We see in the case of iron the finite shear strength effects complicate the interpretation. In fact, the transients that are observed may not be due to phase-change kinetics, but might be related to plasticity kinetics. In the case of antimony, we have two different experimental results which lead to similar conclusions regarding the phase-change rates. In the case of KCl, we see a fast response and a slow response. The fast response seems to be independent of the details of the shock environment such as crystallographic axis directions. The slow response seems to be altered by those. In the case of quartz, we have the only reconstructive transformation of these four. It appears to be described quite well, at least by back-of-the-envelop calculations, as a thermally activated process.

(35) It seems after putting this talk together that it would be a wise idea for me to make recommendations for fruitful areas for future research. I have done that, and they fall into three separate categories. The first has to do with experimental observables. I believe an important area of research, one which has been ignored, is how plasticity kinetics affect the observables such as P_1 decay. It seems that this decaying elastic precursor complicates the interpretation, and there is a chance that it has caused us to draw the wrong conclusions. Also, we should keep our eye out for new experimental observables.

Now in terms of new modeling work I think there are two distinct areas. Again we see that the shock environment is not producing the homogeneous isotropic state that we think it is. In fact, we can have the heterogeneous heating from shear banding. I think that this is an important consideration. We can have in the case of an elastic deformation a great deal of damage done to the lattice, lots of point defects produced by the plasticity. This damage could certainly affect kinetics.

Finally there is the important area of stress deviator collapse. It seems reasonable for a crystalline material, which might have many equivalent directions, that when we are going to form a nucleus of a new phase by means of a coordinated shift of the lattice, all other things being equal, the lattice is going to shift in a direction which can minimize whatever free energy it can by transforming along certain directions. What I mean is that, given a choice of transforming and forming one nucleus in which the shear strain of the remaining lattice is made larger or transforming along another in which it causes the shear strain in the rest of the lattice to reduce, I think it would choose the latter. At least the latter would happen much more frequently. This means then that, along with the phase-change process, one expects a rapid reduction of shear energy. This I think is intimately related to the point of the influence of the yielding kinetics on observables. Not only do we have a decaying elastic precursor in front of the P_1 wave, but we have the potential for large transients in the stress deviator immediately behind the P_1 wave. This is a more complicated picture than can be understood at present. In the last column I think we see listed the four things that probably need the most attention. Three of them, the first, second and fourth, I think, are just those kinds of things that metallurgists have worried about, the microscopic processes of the very slow, quasi-static phase changes that are observed under hydrostatic pressure. The only one that may not be obvious, and that I would like especially to call your attention to, is the item marked martensitic, but in a hydrostatic mode. This kind of phase change has occurred in the potassium chloride. You see, the transformed cluster of 10^5 ion pairs may have some residual coherence with the old lattice; i.e., one expects the new P_2 lattice to be formed by an overall dilatation and a compression along one axis of the P_1 lattice. The two lattices are very closely related. When the transition occurs, we expect the new one and the old one to remain coherent. If this interpretation is right, we are seeing a very close similarity between martensitic transitions and this peculiar transition of potassium chloride. In fact, martensitic may not be the right word because, in the case of KCl, transition is not stimulated by shear stresses as is the case in the formation of martensite.

I hope this combination of analysis and experimental results will help bring the problems of the kinetics of phase transitions into perspective and stimulate further work in this area.

THE KINETICS OF SHOCK-INDUCED POLYMORPHIC PHASE TRANSITIONS

D B Hayes

Sandia Laboratories

PHASE CHANGES UNDER SHOCK LOADING

First Order	Second Order
Chemical	Electric
Melting	Magnetic
Polymorphic	

PHASE CHANGES UNDER SHOCK LOADING

First Order

- Polymorphic
  - Nonequilibrium
  - Equilibrium

PHASE CHANGES UNDER SHOCK LOADING

First Order

- Polymorphic
  - Nonequilibrium
    - Kinetics
    - Quasi-Statics

PHASE CHANGES UNDER SHOCK LOADING

First Order

Polymorphic

Nonequilibrium

Kinetics

Theory

- Influence of Phase Change on the Flow
- Models of the Phase-Change Process

Experiment

- Iron
- Antimony
- Potassium Chloride
- Quartz

"PHASE TRANSITIONS UNDER SHOCK-WAVE LOADING"

G. E. DUVALL AND R. A. GRAHAM

INVITED REVIEW FOR REVIEWS OF MODERN PHYSICS

EXPERIMENTAL STUDIES OF POLYMORPHIC PHASE TRANSITIONS SHOWING KINETIC EFFECTS UNDER SHOCK-LOADING

Armco Iron	Minshall	1961
	Loree, et al.	1966
	Novikov, et al.	1965
	Anan'in, et al.	1973
	Barker, et al.	1974
	Forbes	1976
Steel	Anan'in, et al.	1973
Iron-Silicon	Zukas, et al.	1963
Antimony	Minshall	1964 (McQueen)
	Warnes	1967
	Breed, et al.	1968
Carbon	Alder, et al.	1961
	Trunin, et al.	1969
	Pavlovskii, et al.	1966
	Dremin, et al.	1968
Silicon	McQueen	1964
Potassium Chloride	Kormer, et al.	1966
	Hayes -	1974
	Gupta, et al.	1975
Cadmium Sulfide	Kennedy, et al.	1966
Boron Nitride	Johnson, et al.	1972
Quartz	Al'Tshuler	1965

THEORY OF KINETIC EFFECTS IN SHOCK-INDUCED, POLYMORPHIC PHASE TRANSITIONS

Influence of the Phase Change on the Flow

Horie and Duvall	1966, 1968
Andrews	1973
Hayes	1975

Models of the Phase-Change Process

Hayes	1974
Forbes	1976
Grady	1977

SHOCK-INDUCED, POLYMORPHIC PHASE-CHANGE KINETICS

- Influence of Phase Changes on the Flow
    - Constitutive Equation
    - Approximate and Exact Treatments
    - Experimental Observables
- Experimental Studies of Phase-Change Kinetics
    - Armco Iron
        - P_1 Decay
        - Shear Strength
    - Antimony
        - P_1 Decay
        - 2-D Flow → P_2 Delay
    - Potassium Chloride
        - Loading Interface Transients
        - Fast and Slow Transformations, Rates
        - Thermodynamics of the Phases
        - Influence of Shear Strength on Rates
    - Quartz
        - Temperature Inhomogeneity
        - Thermal Activation
- Concluding Remarks

CONSTITUTIVE RELATION FOR PHASE CHANGING MATERIAL

$$E\,(P,\ T,\underset{\sim}{x}) = \underset{\sim}{x}\cdot\underset{\sim}{E}\,(P,\ T)$$

$$V\,(P,\ T,\ \underset{\sim}{x}) = \underset{\sim}{x}\cdot\underset{\sim}{V}\,(P,\ T)$$

$$\underset{\sim}{x}\cdot\underset{\sim}{1} = 1$$

$$\dot{E} + P\dot{V} = 0$$

$$\begin{pmatrix} \dot{P} \\ \\ \dot{T} \end{pmatrix} = \begin{pmatrix} a^2_{s,\underset{\sim}{x}} & \dfrac{K_{s,\underset{\sim}{x}}}{V\,Cp,\underset{\sim}{x}}\left[\left(\dfrac{\partial E}{\partial T}\right)_{P,\underset{\sim}{x}} \Delta\underset{\sim}{V} - \left(\dfrac{\partial V}{\partial T}\right)_{P,\underset{\sim}{x}} \Delta\underset{\sim}{E}\right] \\ \\ \dfrac{\bar{\gamma}\underset{\sim}{x}T}{\rho} & -\dfrac{K_{s,x}}{V^2Cp,\underset{\sim}{x}}\left[\left(\dfrac{\partial E}{\partial P}\right)_{T,\underset{\sim}{x}} \Delta\underset{\sim}{V} - \left(\dfrac{\partial V}{\partial P}\right)_{T,\underset{\sim}{x}} \Delta\underset{\sim}{E}\right] \end{pmatrix} \begin{pmatrix} \dot{\rho} \\ \\ \dot{\underset{\sim}{x}} \end{pmatrix}$$

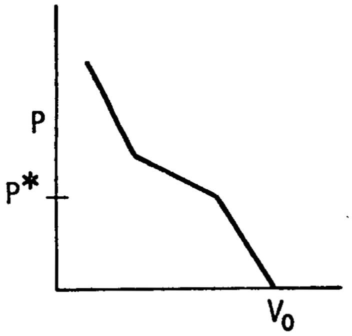
$$\Delta\underset{\sim}{V} = \underset{\sim}{V}\,(P,\ T) - \underset{\sim}{1}V_1\,(P,\ T),\ \text{ETC.}$$

TWO PHASE FLOW: EQUILIBRIUM VS NON-EQUILIBRIUM

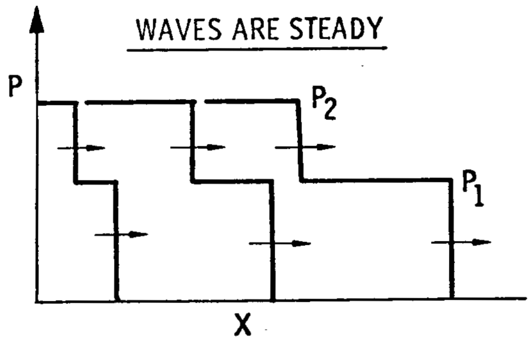
EQUILIBRIUM

$S(E,V,x)=0$

G IS MINIMIZED



WAVES ARE STEADY



NON-EQUILIBRIUM

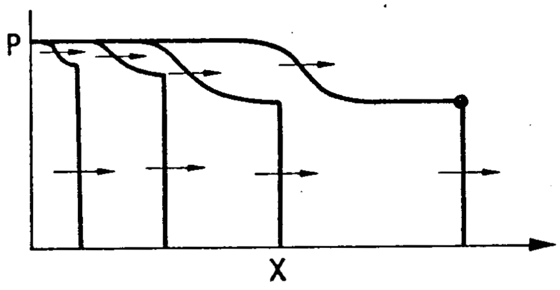
$\dot{p} = a^2_{S,x}\,\dot{\rho} + F\dot{x}$

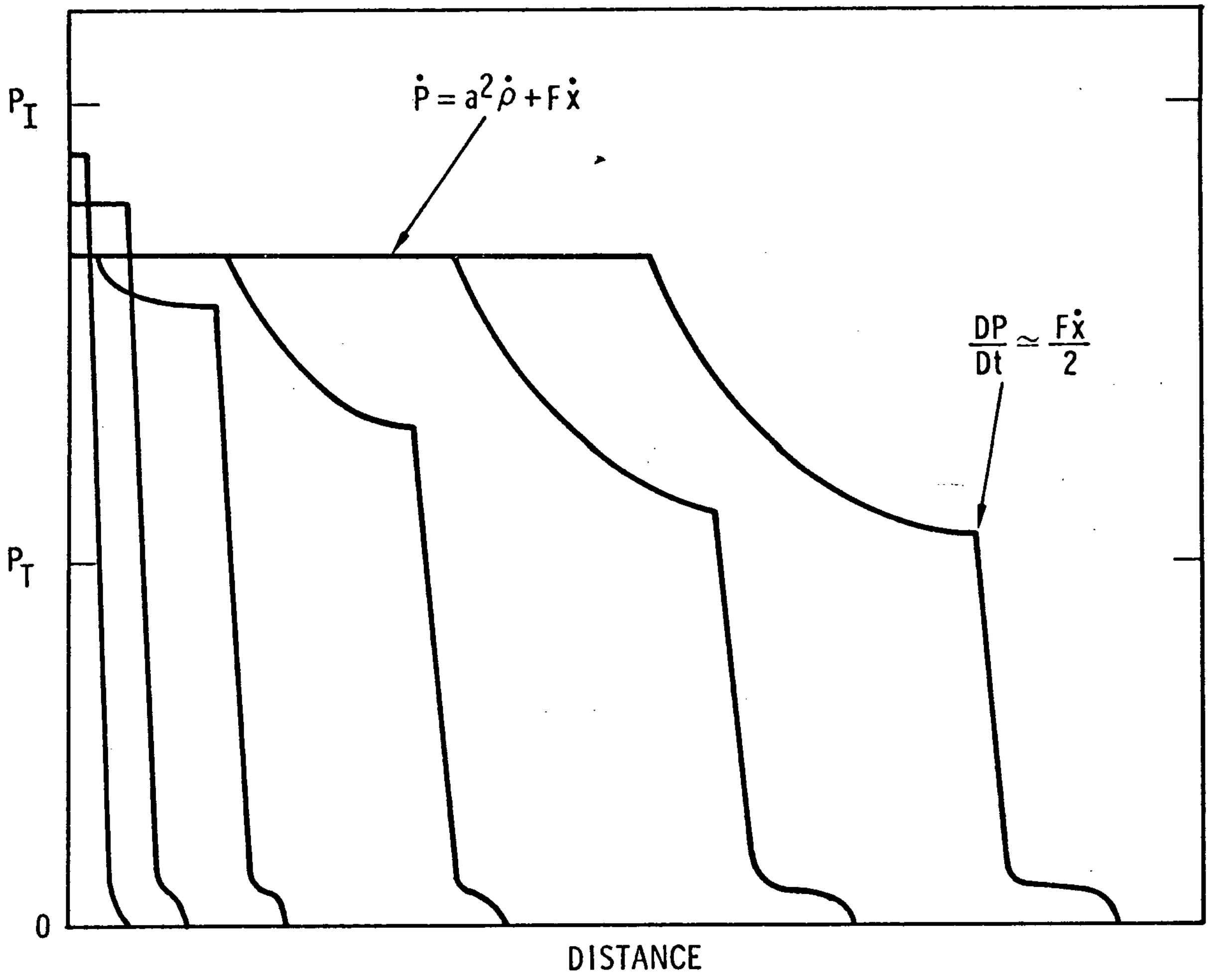
$\dot{x} \sim -\frac{\Delta G}{\tau}$

SHOCK ENTERING UNTRANSFORMED MATERIAL DECAYS ACCORDING TO:

$$\frac{DP}{Dt} \simeq \frac{F}{2}\,\dot{x}\Big|_{x=0}$$

WAVES EVOLVE





STRESS DISTRIBUTIONS DURING WAVE EVOLUTION FOLLOWING A SYMMETRIC IMPACT.

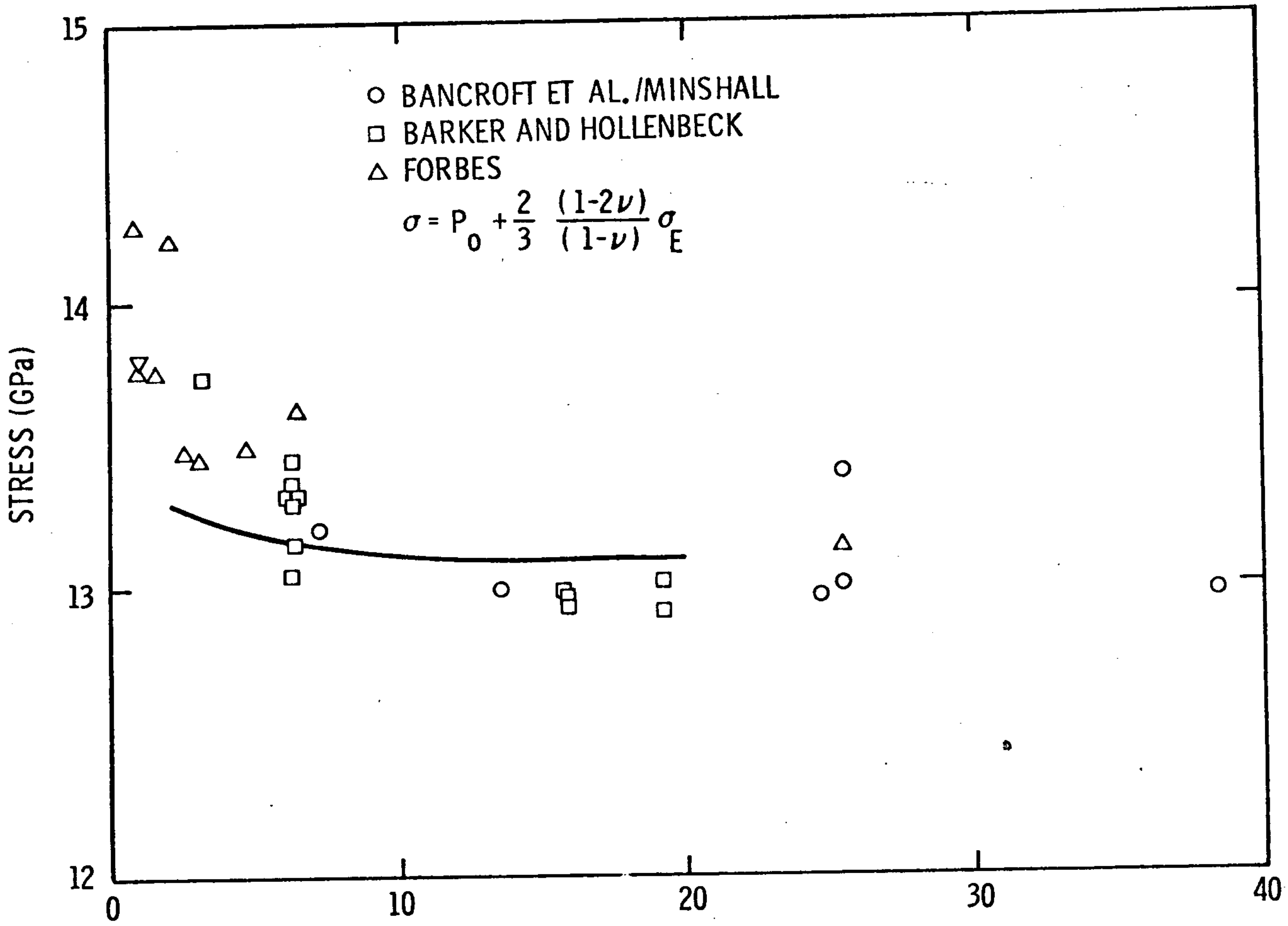
EXPERIMENTAL OBSERVABLES IN SHOCK-INDUCED POLYMORPHISM

P_1 DECAY

P_1 - P_2 RISETIME

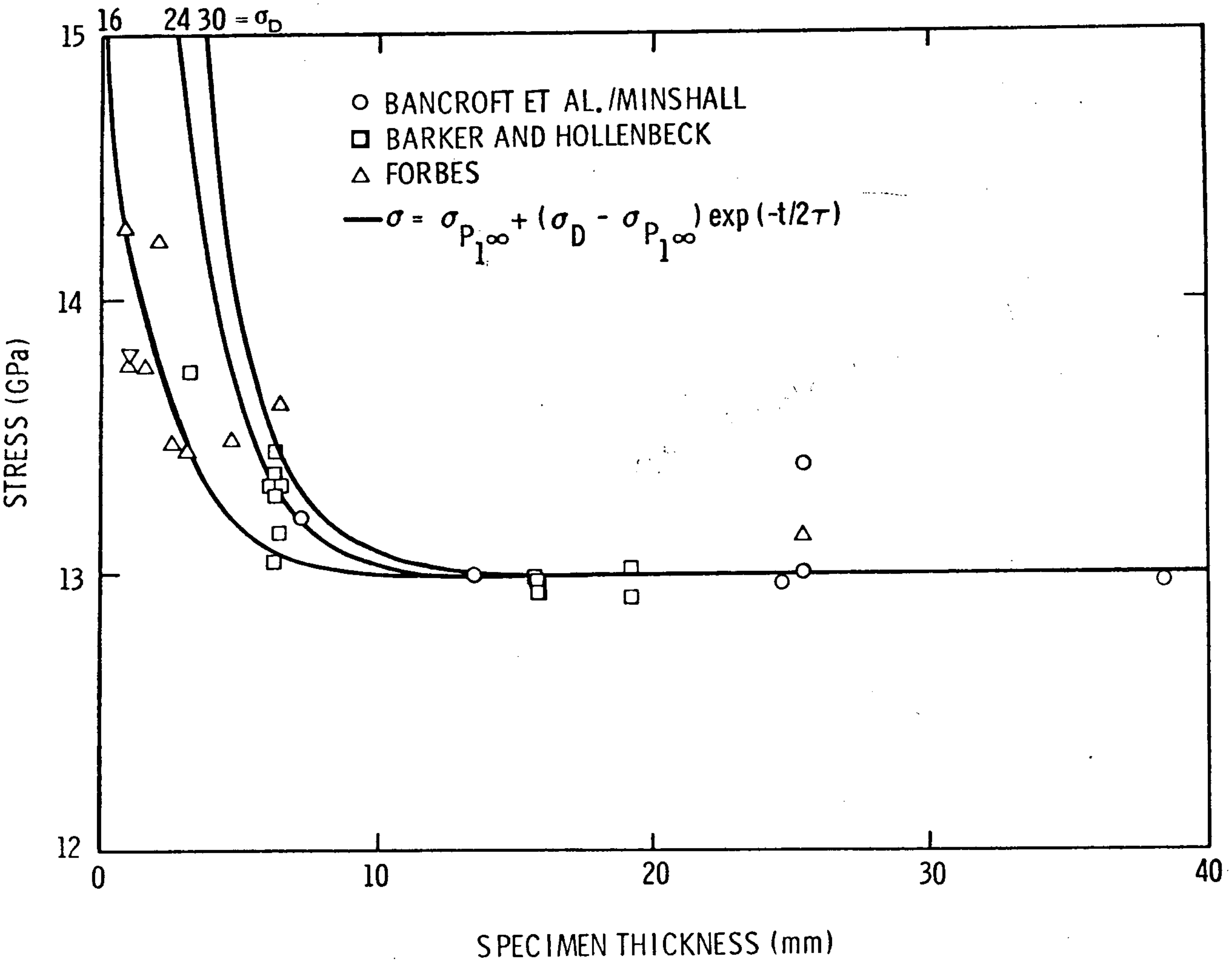
LOADING INTERFACE TRANSIENTS

P_2 DELAY



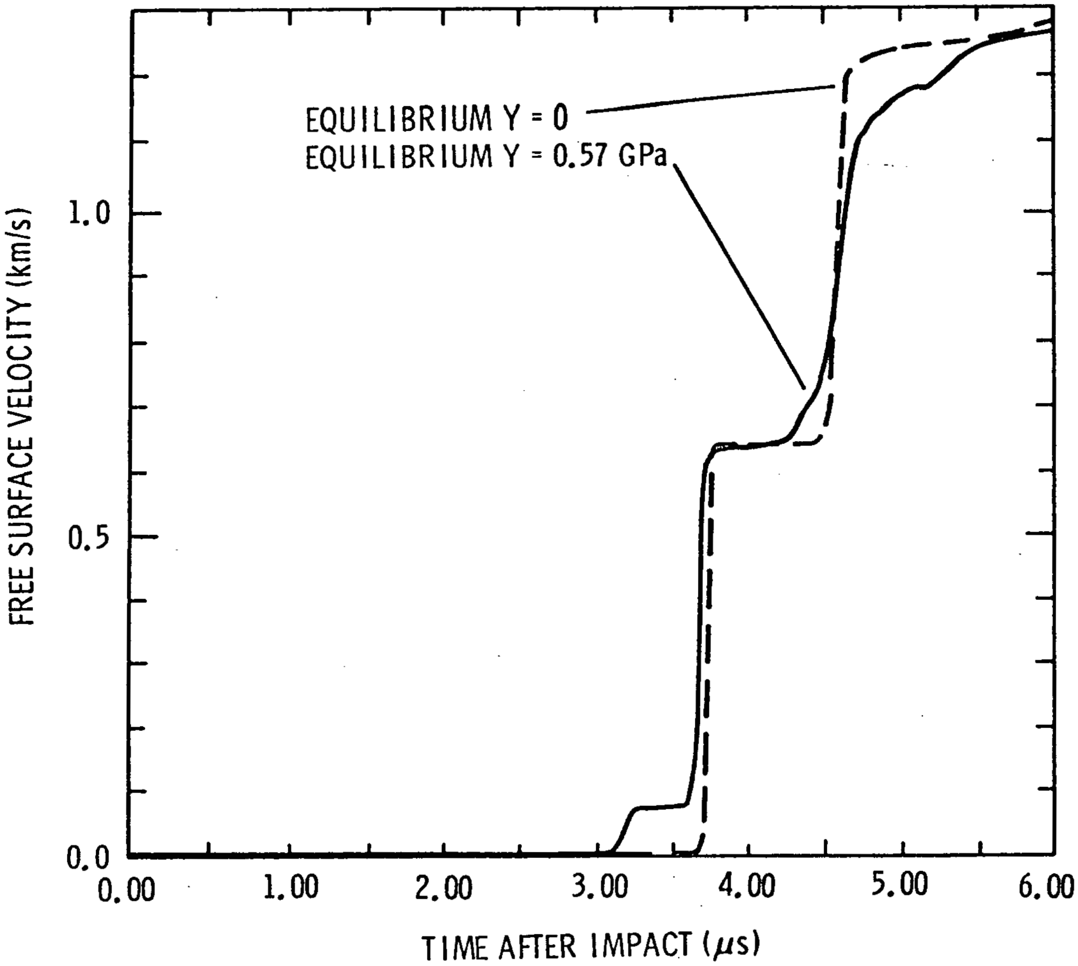
SPECIMEN THICKNESS (mm)

P_1 STRESS IN ARMCO IRON



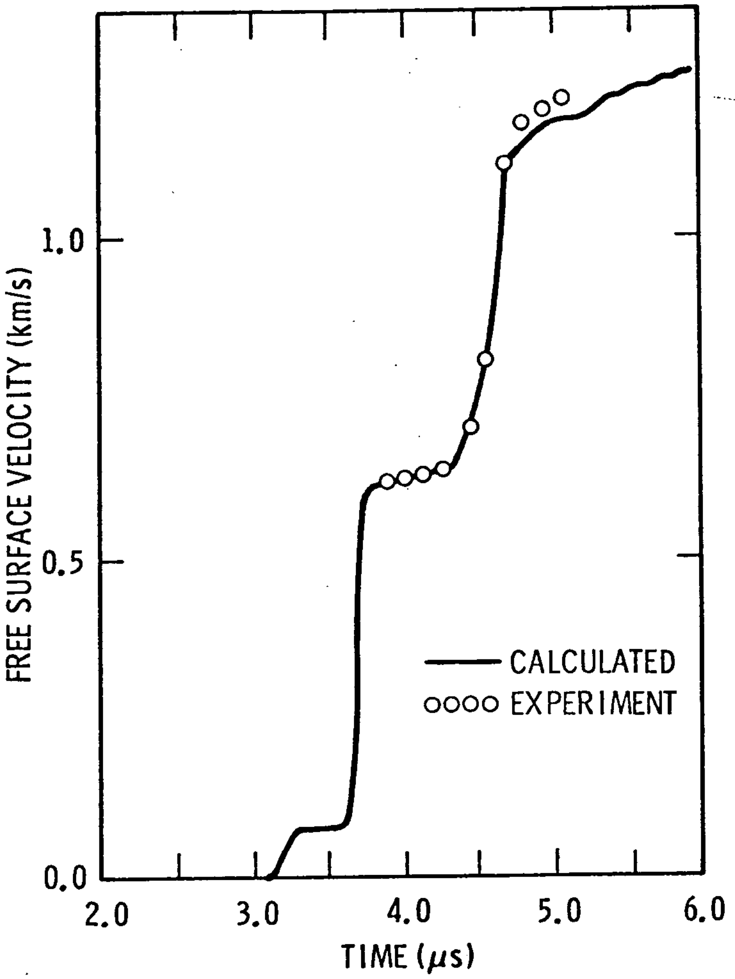
P_1 STRESS IN ARMCO IRON

Slide 15



EQUILIBRIUM CALCULATION OF FREE SURFACE VELOCITY IN IRON

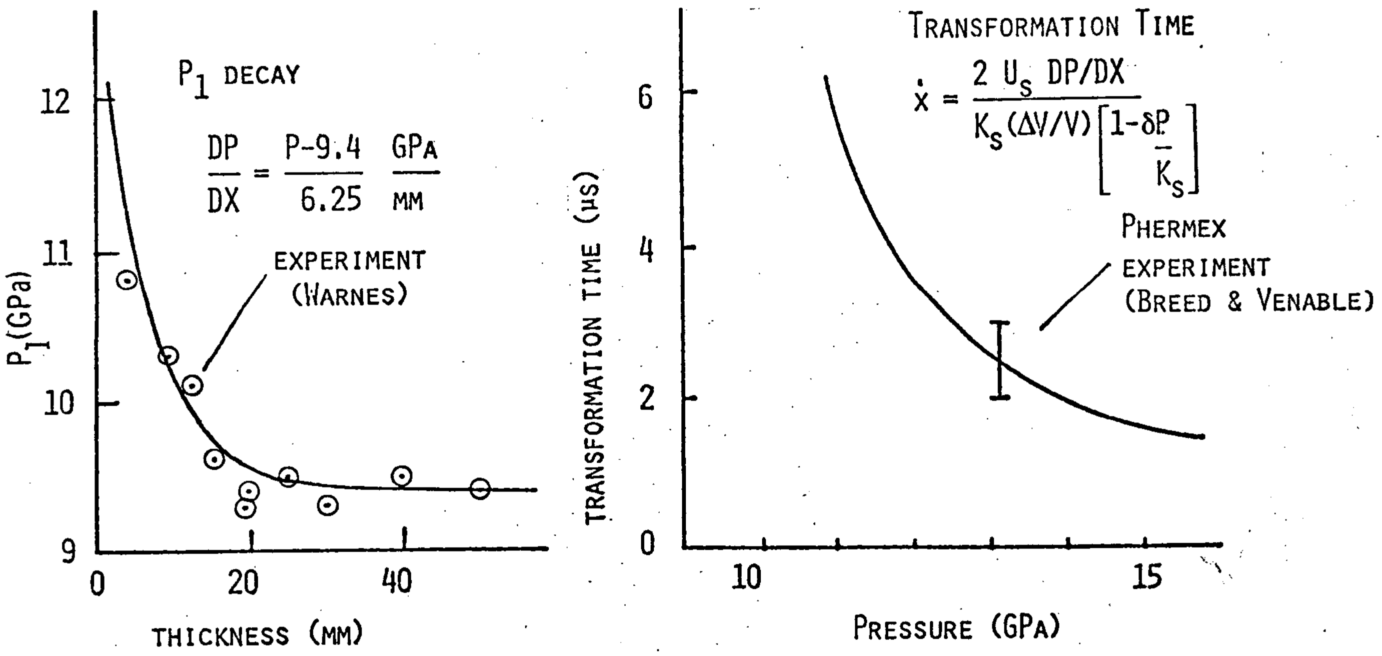
FREE SURFACE MOTION IN IRON



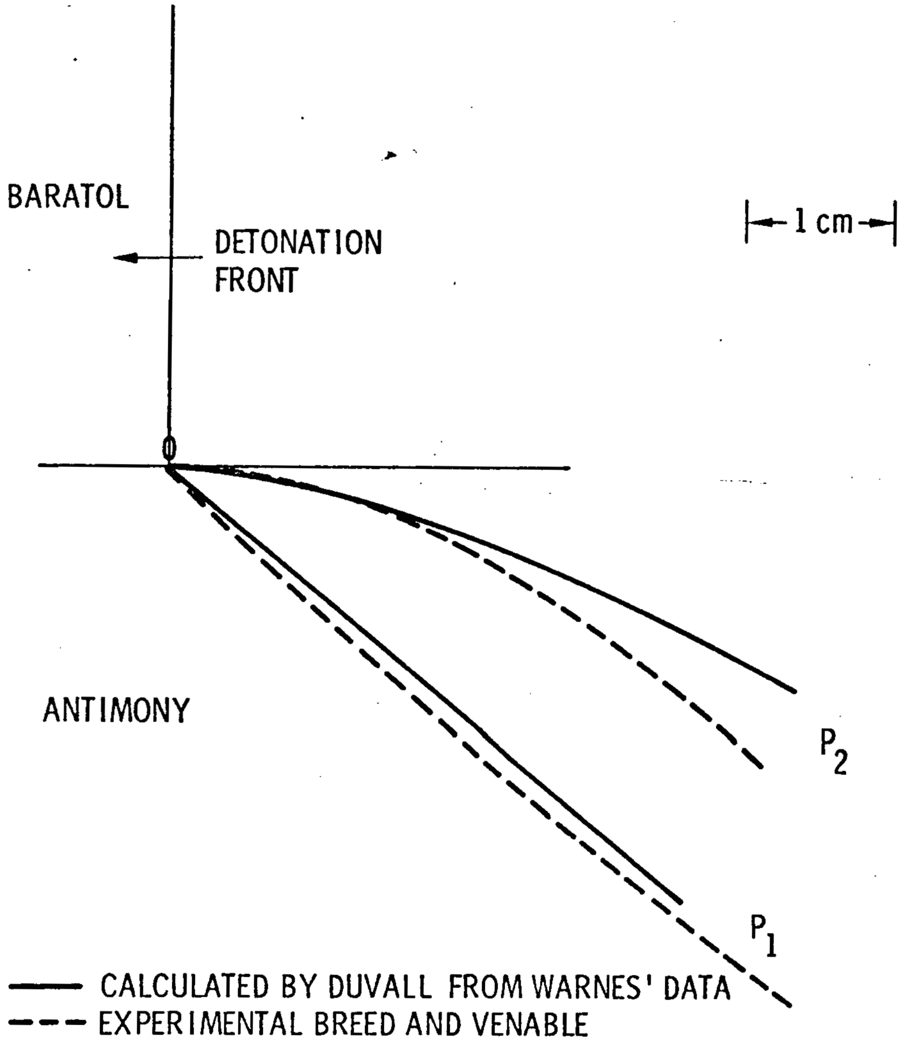
Slide 17

KINETICS OF THE SHOCK-INDUCED PHASE TRANSITION IN ARMCO IRON

- THE HORIE - DUVALL MODEL FITS THE P_1 DECAY DATA WITH A RELAXATION TIME OF 0.16 - 0.18 μS
- NO P_2 DELAY
- PRECURSOR DECAY TIMES ARE OF ORDER 0.2 μS, BUT MAGNITUDE OF OFFSET NOT CORRECT TO ACCOUNT FOR OBSERVATIONS
- EQUILIBRIUM ELASTIC-PLASTIC EFFECTS DESCRIBE P_1 - P_2 RISETIME



TRANSPORTATION TIME FROM P_1 DECAY DATA IN ANTIMONY

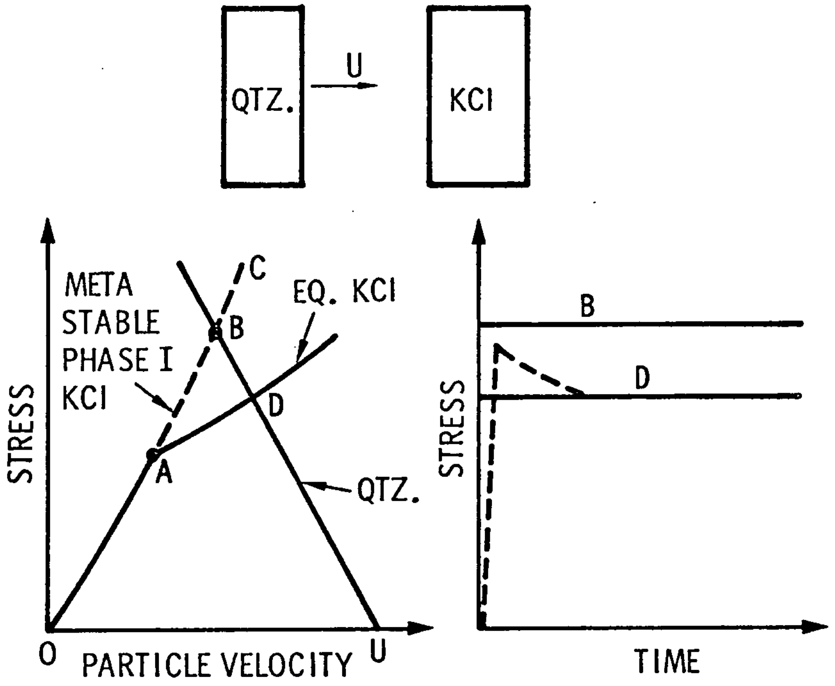


Slide 20

KINETICS OF THE SHOCK-INDUCED PHASE TRANSITION IN ANTIMONY

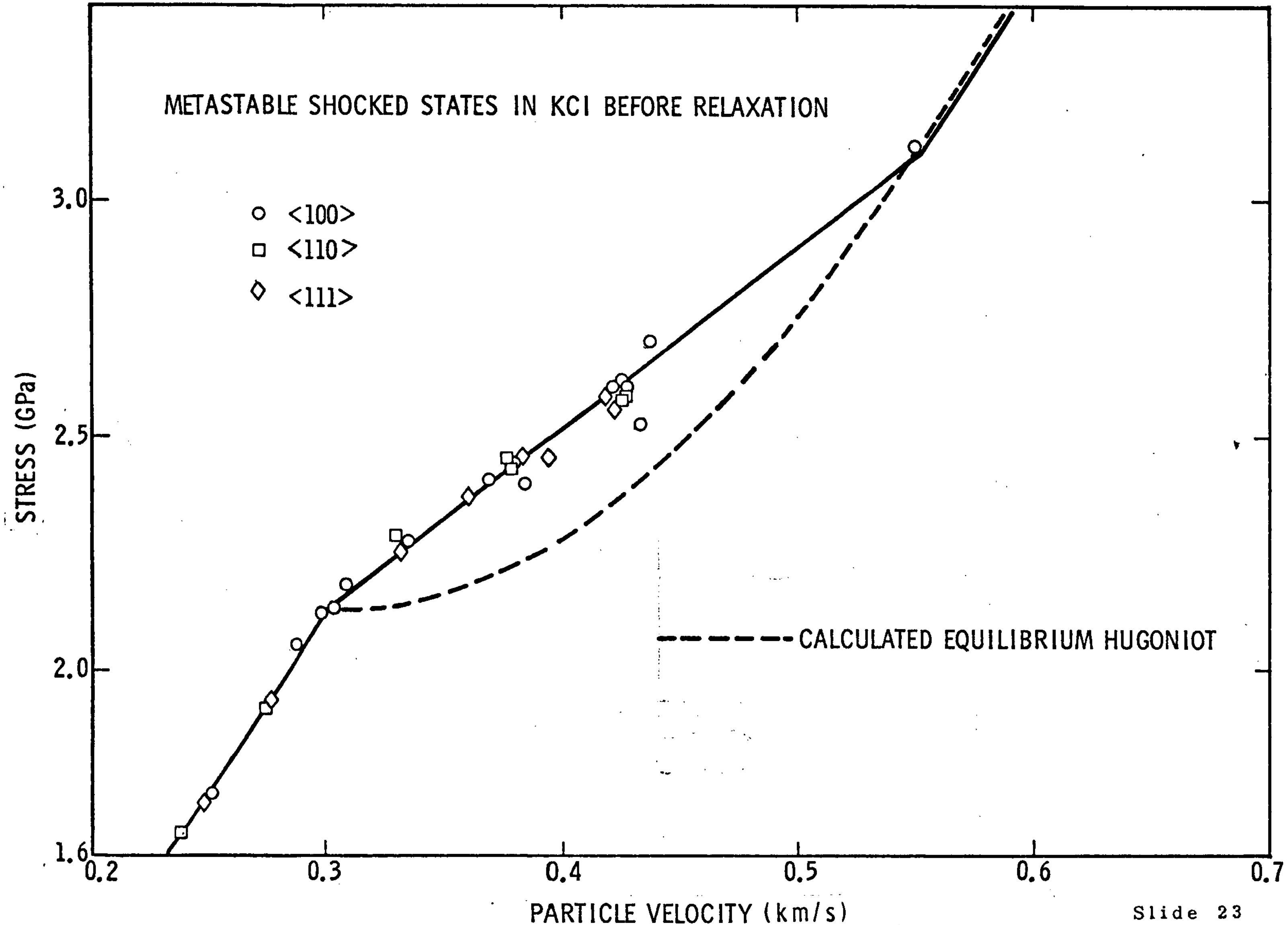
- P_1 Decay Data are Sufficient to Deduce the Initial Phase Transformation Rate
- P_2 Delay has been used to Infer a Transformation Time Which Agrees with that Deduced from P_1 Decay
- 2-D Flow Analytical Model Agrees with Experiment

Slide 21

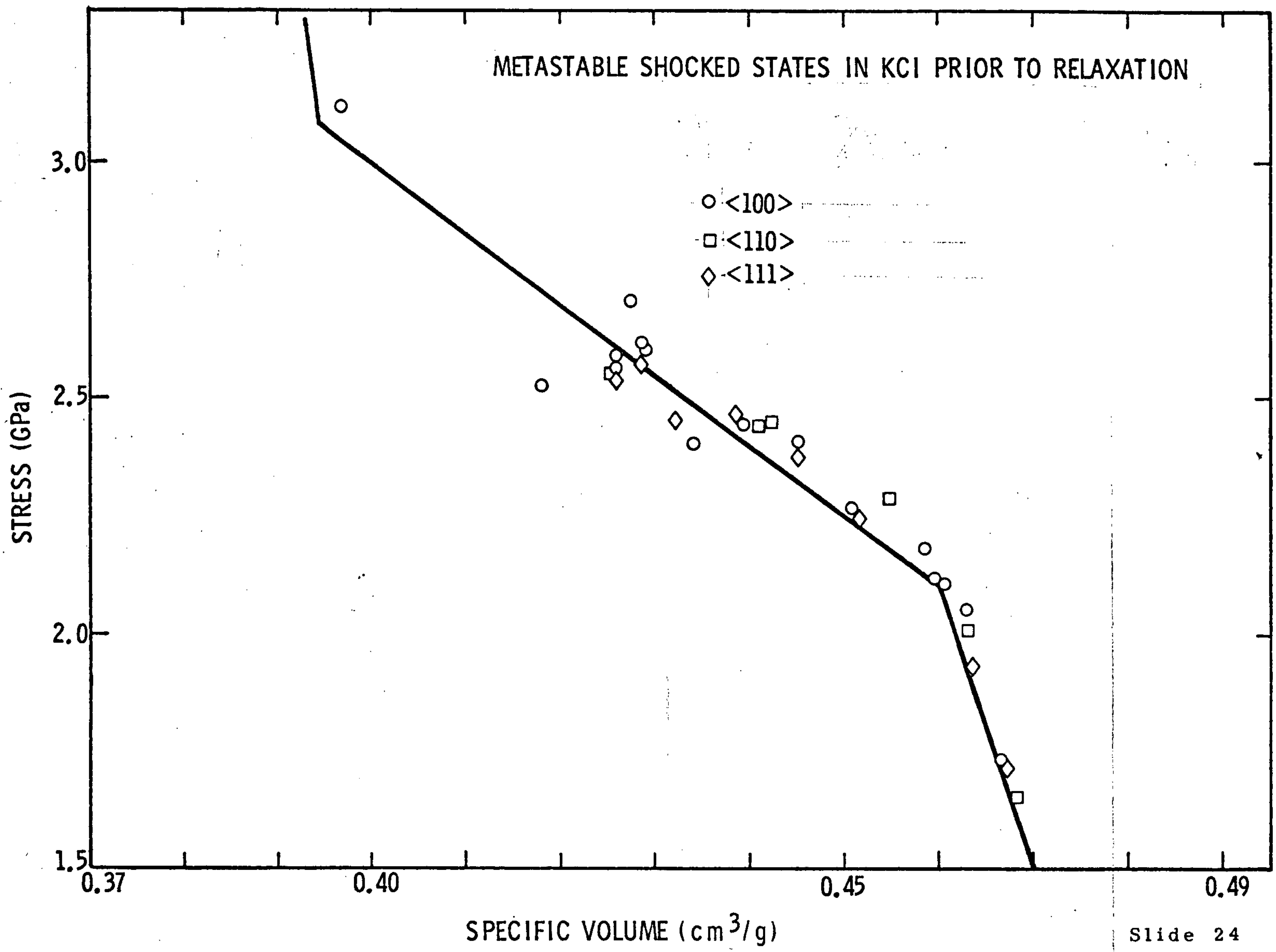

QTZ.
U
KCl
STRESS
META STABLE PHASE I KCl
C
B
EQ. KCl
D
A
QTZ.
0
PARTICLE VELOCITY
U
STRESS
B
D
TIME

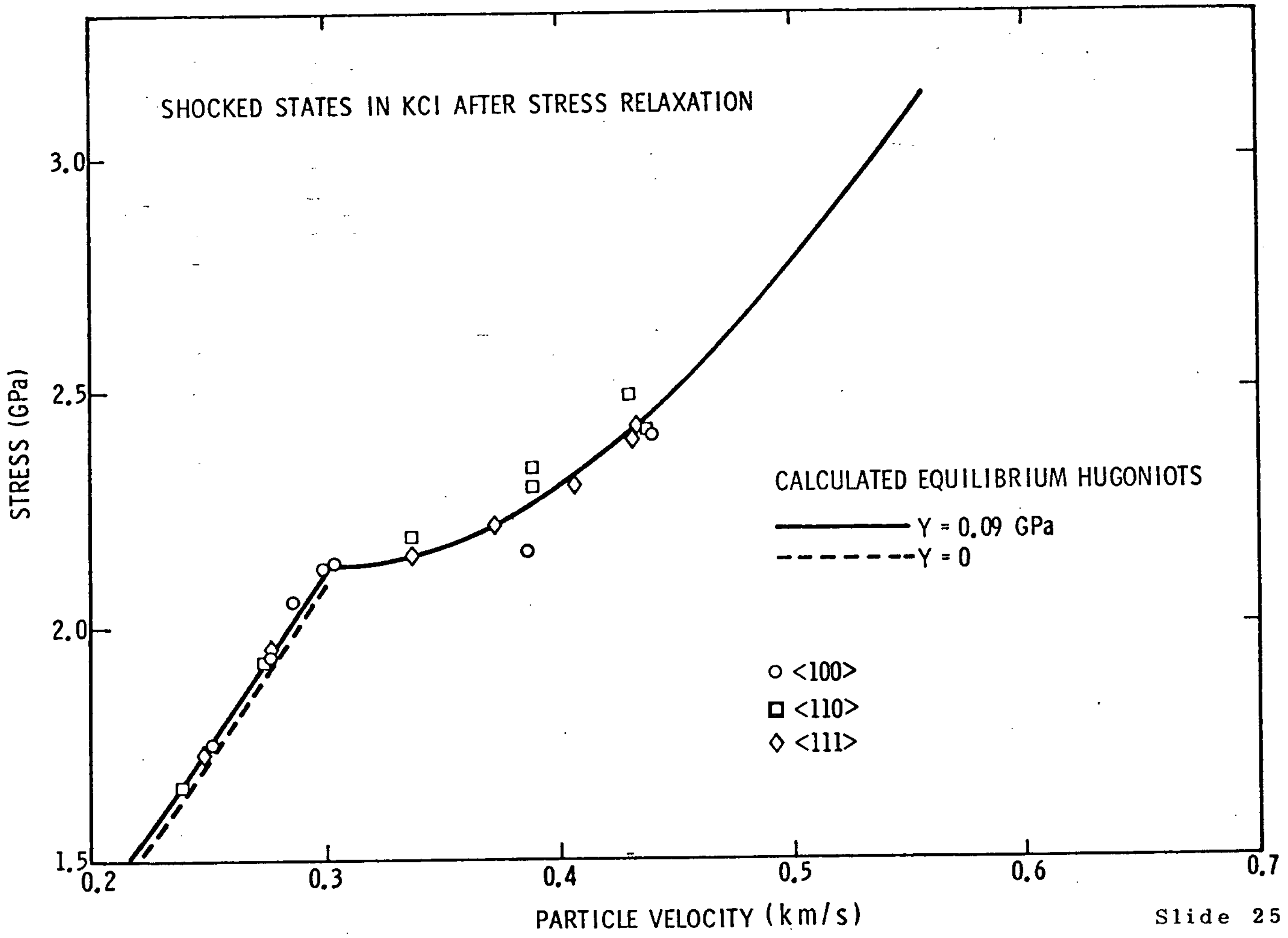
Slide 22

METASTABLE SHOCKED STATES IN KCl BEFORE RELAXATION

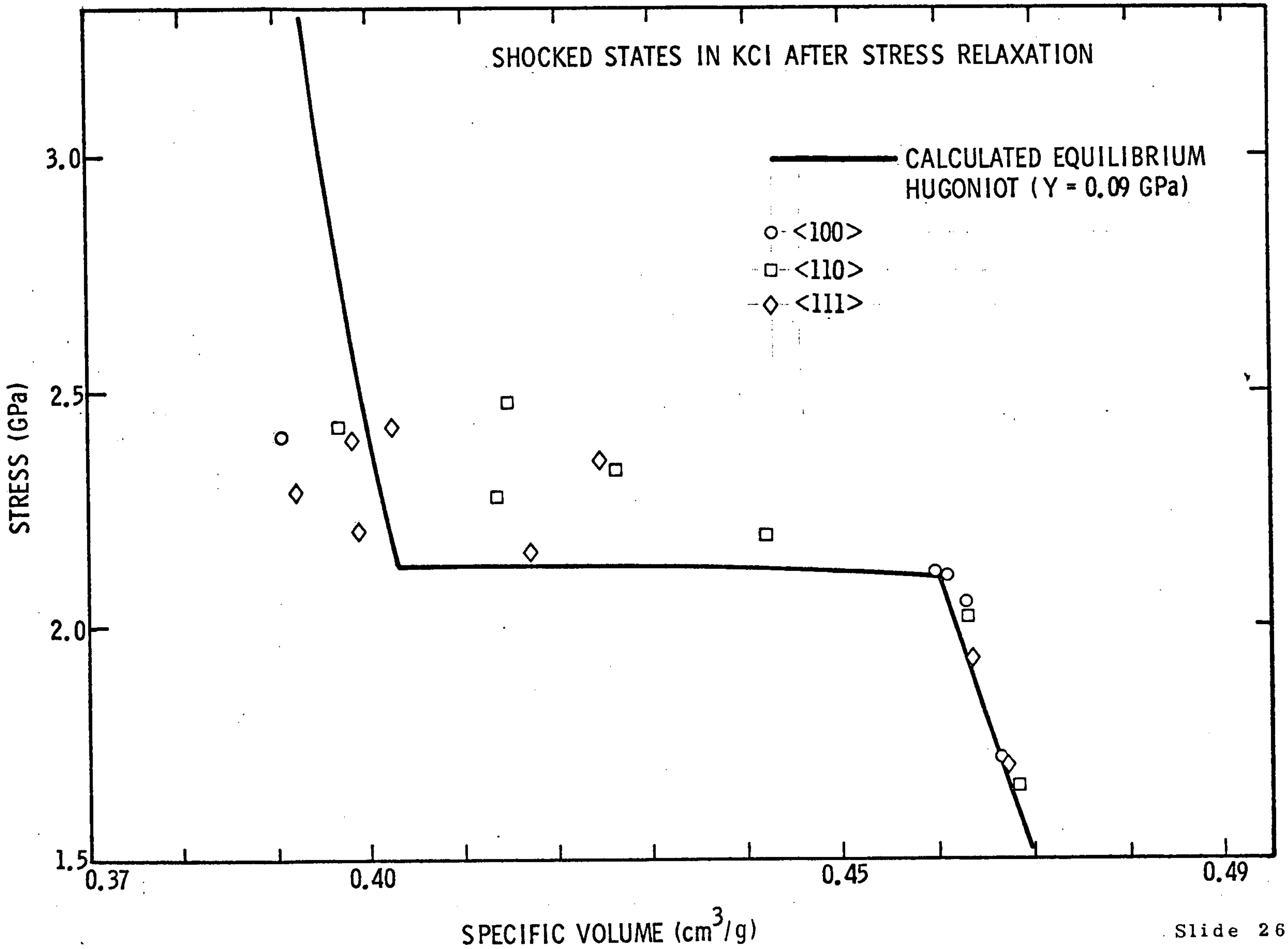


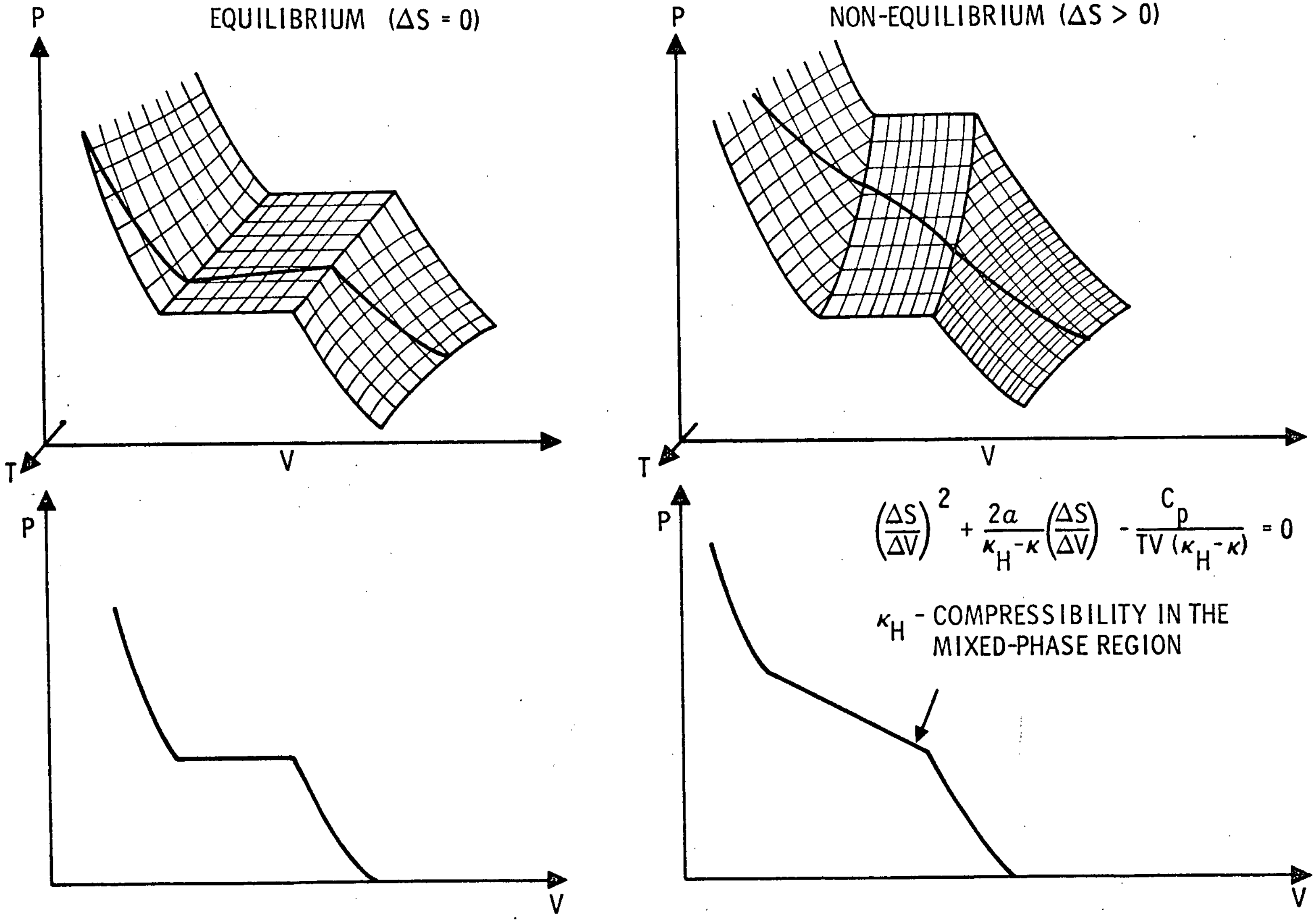
slash


METASTABLE SHOCKED STATES IN KCl PRIOR TO RELAXATION
○ <100>
□ <110>
◇ <111>
STRESS (GPa)
3.0
2.5
2.0
1.5
0.37
0.40
0.45
0.49
SPECIFIC VOLUME (cm³/g)


SHOCKED STATES IN KCl AFTER STRESS RELAXATION
STRESS (GPa)
1.5
2.0
2.5
3.0
0.2
0.3
0.4
0.5
0.6
0.7
PARTICLE VELOCITY (km/s)
CALCULATED EQUILIBRIUM HUGONIOTS
Y = 0.09 GPa
Y = 0
○ <100>
□ <110>
◇ <111>

Slide 25

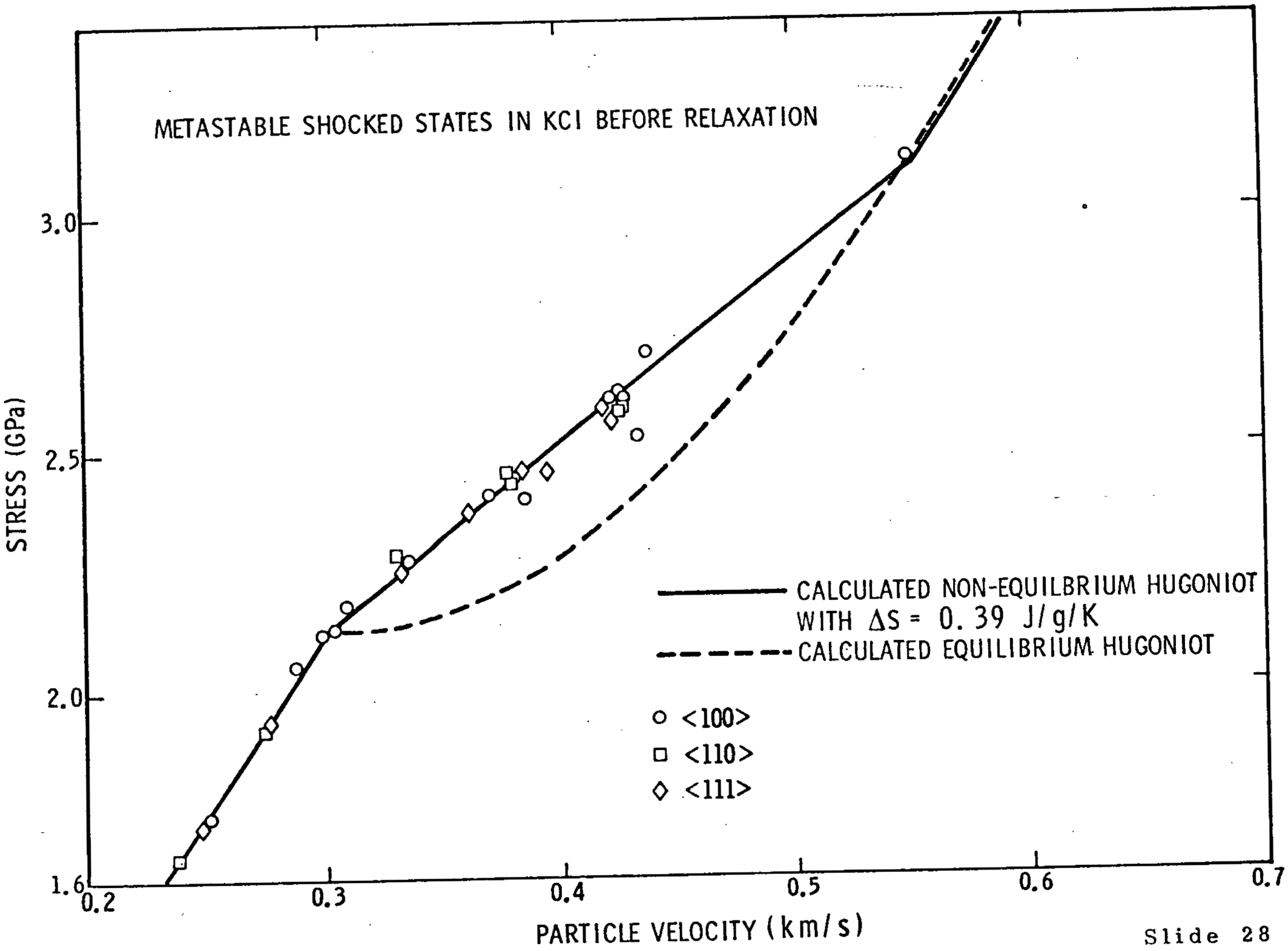

SHOCKED STATES IN KCl AFTER STRESS RELAXATION
CALCULATED EQUILIBRIUM HUGONIOT (Y = 0.09 GPa)
○ <100>
□ <110>
◇ <111>
STRESS (GPa)
3.0
2.5
2.0
1.5
0.37
0.40
0.45
0.49
SPECIFIC VOLUME (cm³/g)



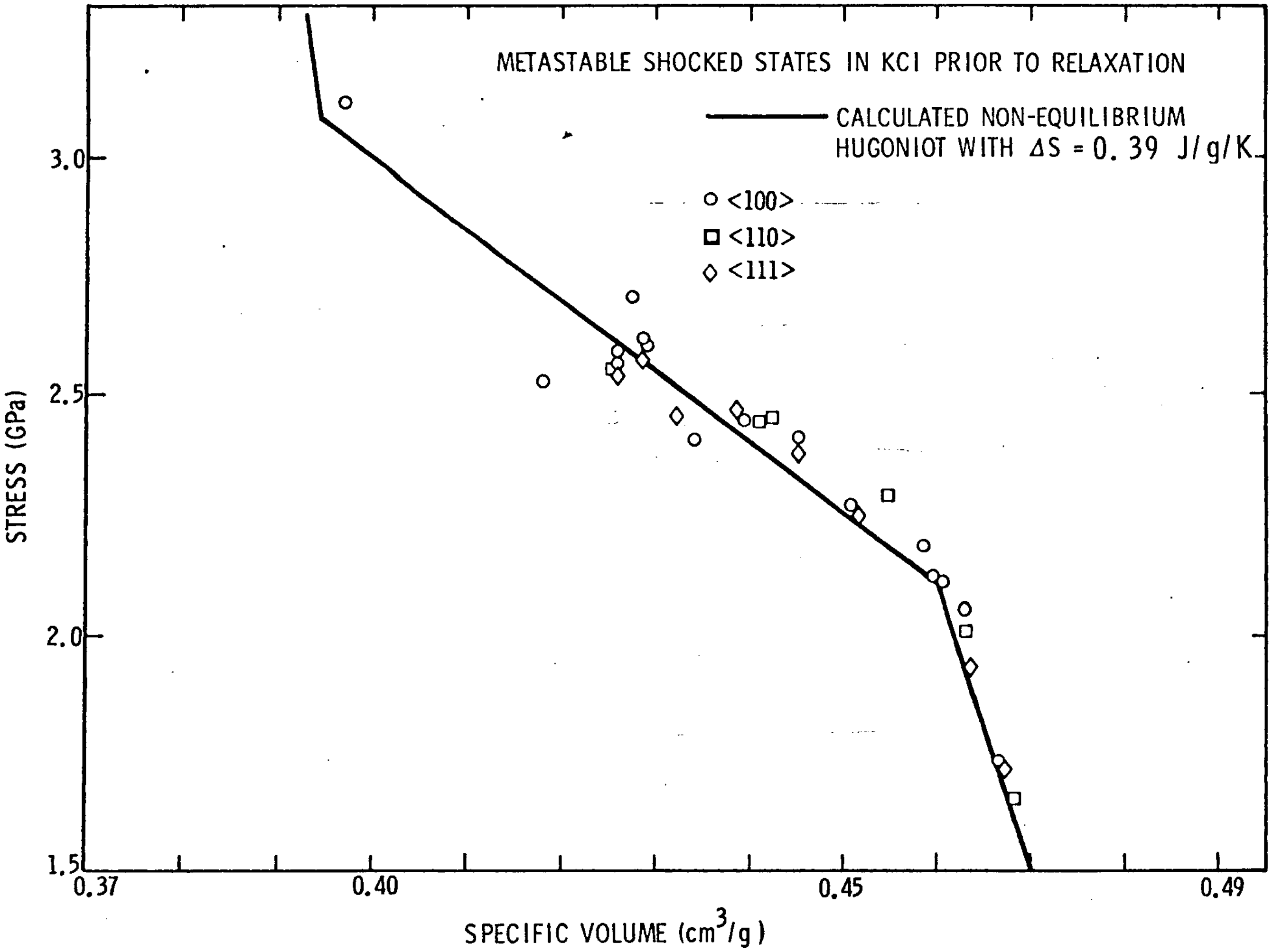
$$\left(\frac{\Delta S}{\Delta V}\right)^2 + \frac{2a}{\kappa_H - \kappa}\left(\frac{\Delta S}{\Delta V}\right) - \frac{C_p}{TV\,(\kappa_H - \kappa)} = 0$$

κ_H - COMPRESSIBILITY IN THE MIXED-PHASE REGION

RELATIONSHIP BETWEEN ENTROPY OF FORMATION AND SLOPE OF HUGONIOT IN MIXED-PHASE REGION

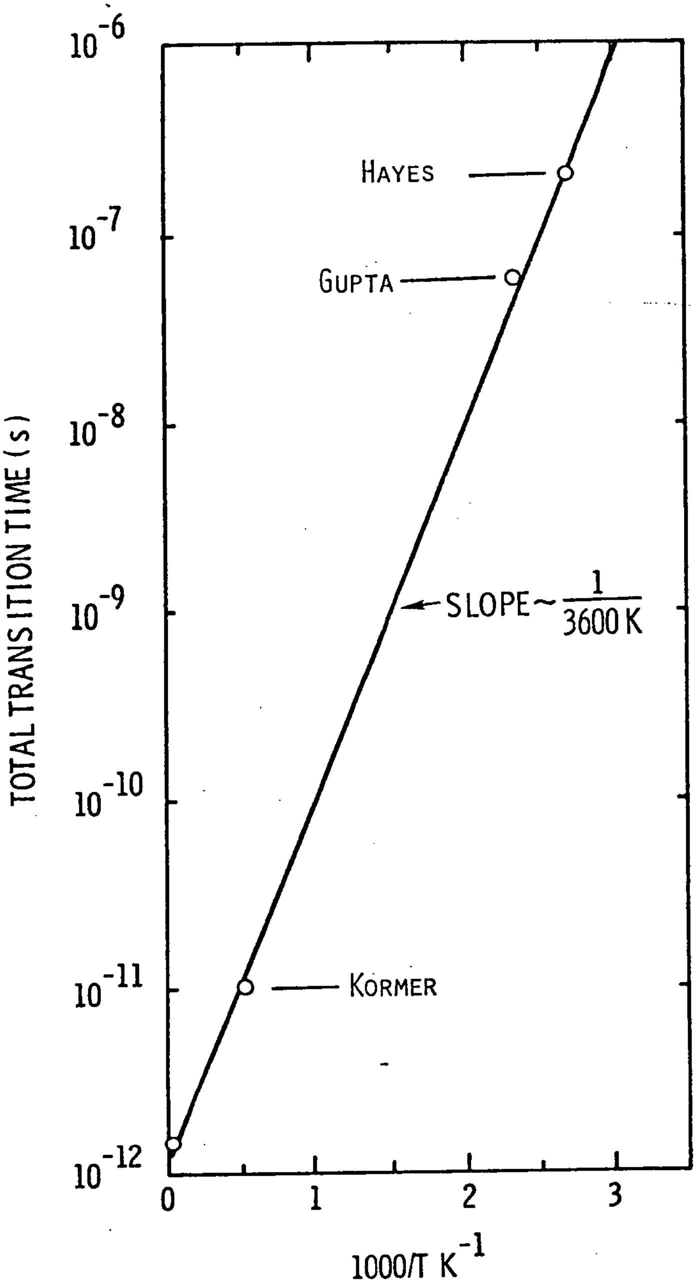

METASTABLE SHOCKED STATES IN KCl BEFORE RELAXATION
STRESS (GPa)
3.0
2.5
2.0
1.6
0.2
0.3
0.4
0.5
0.6
0.7
PARTICLE VELOCITY (km/s)
CALCULATED NON-EQUILBRIUM HUGONIOT WITH ΔS = 0.39 J/g/K
CALCULATED EQUILIBRIUM HUGONIOT
○ <100>
□ <110>
◇ <111>

Slide 28



DATA SUMMARY ON KCl EXPERIMENTS

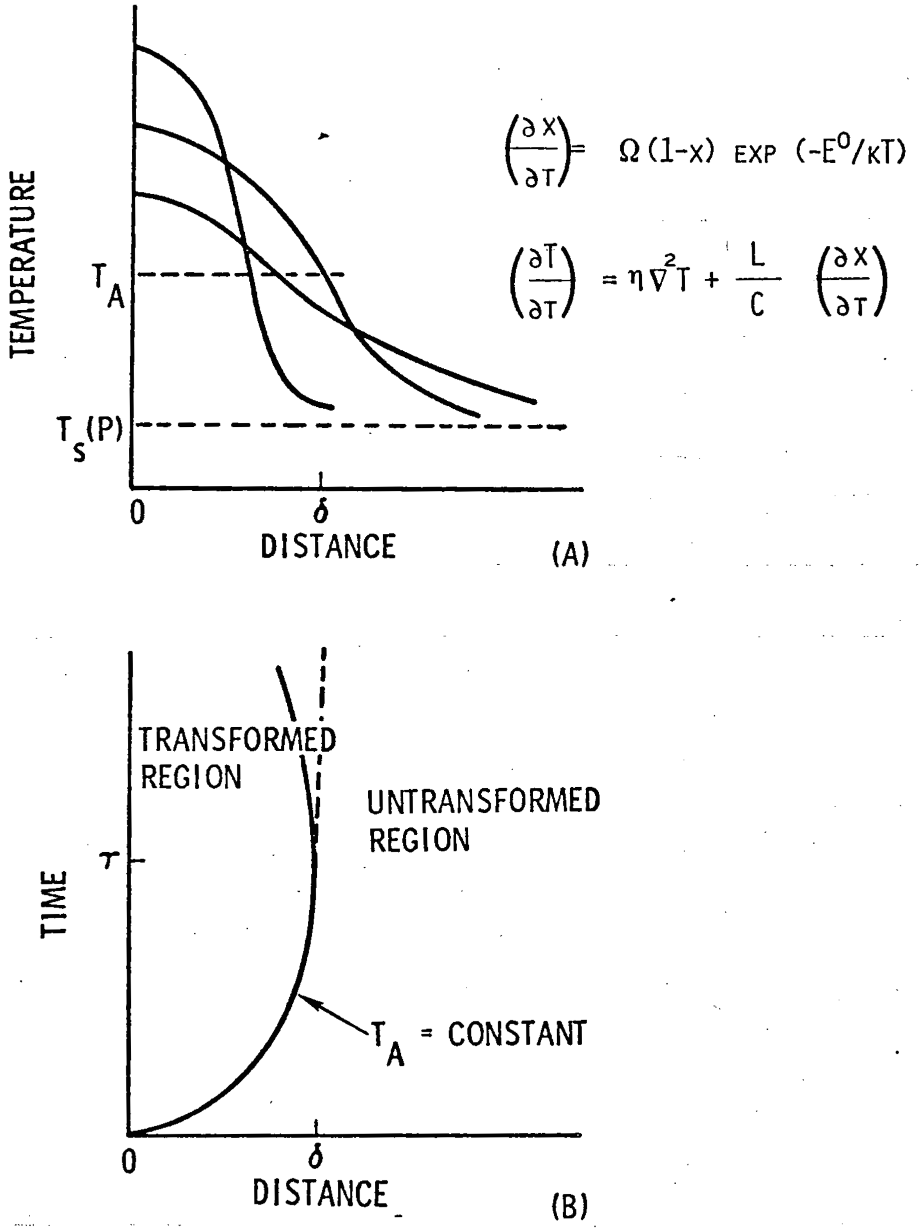
	⟨100⟩	⟨110⟩	⟨111⟩
Initial Transformation Rate (μs^{-1})	>500	>50	>500
Initial State, Δs (J/g/K)	0.39	0.39	0.39
Completion Rate, 300 K (μs^{-1}) (358 K)	2-5 (8)	15	25±5
Completion State	Equilibrium ←	—	→ Equilibrium
Shear Strength (GPa)	0.04	-	0.09



TRANSITION TIME IN SHOCKED KCl

KINETICS OF THE SHOCK-INDUCED PHASE TRANSITION IN KCl

- METASTABLE STATES IN THE MIXED PHASE REGION ARE ACHIEVED IN LESS THAN 1 ns, $\dot{x} > 500\ \mu s^{-1}$
- SHOCKED STATES IN THE MIXED PHASE REGION ARE NON-EQUILIBRIUM $\Delta S = 0.39$ J/g/K
- SHOCKED STATES ACHIEVED IN THE MIXED PHASE REGION ARE INDEPENDENT OF THE APPLIED SHEAR STRESS
- SHOCKED STATES RELAX TOWARDS EQUILIBRIUM AT RATES WHICH DEPEND ON THE APPLIED SHEAR STRESS
- IF TRANSFORMATION FROM THE METASTABLE PHASE TO EQUILIBRIUM IS THERMALLY ACTIVATED, THEN $E°/\kappa \simeq 3600$ K



$$\left(\frac{\partial x}{\partial T}\right) = \Omega(1-x)\ \mathrm{EXP}\ (-E^0/kT)$$

$$\left(\frac{\partial T}{\partial T}\right) = \eta\nabla^2 T + \frac{L}{C}\left(\frac{\partial x}{\partial T}\right)$$

SUMMARY

THEORY:
- INFLUENCE OF PHASE CHANGE ON FLOW WELL UNDERSTOOD
- MODELS OF PHASE CHANGE PROCESS ARE PRIMITIVE

EXPERIMENT:
- COMPLICATIONS OF SHEAR STRENGTH (IRON)
- P_1 DECAY, P_2 DELAY AGREEMENT (ANTIMONY)
- COMPLICATED RATE LAW (KCl)
- THERMALLY ACTIVATED PROCESS (QUARTZ)

RECOMMENDATIONS: Areas for Future Research

OBSERVABLES

- INFLUENCE OF YIELDING KINETICS ON OBSERVABLES
- NEW OBSERVABLES

SHOCK ENVIRONMENT

- HETEROGENEOUS SHOCK HEATING
- INELASTIC DEFORMATION
- STRESS DEVIATOR COLLAPSE

MICROSCOPIC PROCESSES

- SHEAR ACTIVATION
- THERMAL ACTIVATION
- MARTENSITIC NATURE (HYDROSTATIC)
- NUCLEATION AND GROWTH

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