DAND-D.P 13-1259

Reprinted from: METALLURGICAL EFFECTS AT HIGH STRAIN RATES Edited by R. W. Rohde, B. M. Butcher, J. R. Holland, and C. H. Karnes Book available from: Plenum Publishing Corporation 227 West 17th Street, New York, N.Y. 10011

CHARACTERISTICS OF THE SHOCK INDUCED TRANSFORMATION IN BaF,

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I. INTRODUCTION

Two of the several structure types commonly displayed by the solids with the formula AB_2 , in which B is fluorine at room temperature and one atmospheric pressure, are quasi-six-coordinated rutile and eight-coordinated fluorite. The rutile structure is tetragonal and the fluorite structure is cubic. In situ high pressure x-ray diffraction studies and related post mortem analyses of quenched materials of the AB_2 compounds have revealed a large number of polymorphic transitions in these compounds at high pressures.¹ Most of these studies have been carried out at room temperature and the transition pressures have been only roughly established. The situation is further complicated by varying rates of transformation in the different AB_2 compounds, which has made the study of these compounds by static high pressure methods difficult. Since the shock compression method had been successful in determining the pressure of transition in various materials,² it prompted us to use this technique to establish transition pressures in these compounds.

The starting material chosen was barium fluoride because the pressure of transition for it is one of the lowest among the fluorides studied so far.³ The shock compression experiments reported in this work were performed on the gas gun facility at Washington State University.

In order to make this paper self-contained, we first summarize the information available on barium fluoride from static compression studies and then present the results of our shock compression work.

II. RESULTS OF STATIC COMPRESSION IN BARIUM FLUORIDE

Phase transformations in barium fluoride (BaF₂) at elevated pressure under static conditions have been studied by several investigators. 1,4,5,6,7,8,9,10 Of these, the investigations of Seifert,^{5,6} and of Dandekar and Jamieson⁹ consisted in analyzing the quenched specimens of BaF₂ subjected to high pressure and temperature by the x-ray diffraction technique. The rest pertain to in situ high pressure investigations of BaF₂. Both types of investigations established that (1) BaF₂, which crystallizes in the fluorite structure (from now on identified as β -BaF₂) at ambient condition, transforms to the orthorhombic α -PbCl₂ structure (from now on also identified as α -BaF₂) at elevated pressures.¹¹ (2) The transition from β - to α -BaF₂ is extremely sluggish at room temperature, i.e. the transition is characterized by a large hysteresis. (3) α -BaF₂ is 10% to 11% denser than the fluorite phase at the ambient conditions.

The results of these investigations vary in three respects: (1) with regard to recovery of the high pressure polymorph of barium fluoride on release of pressure; (2) with regard to the magnitude and direction of change in pressure of transition with increasing temperature; and, (3) with regard to the pressure of transition at room temperature. These differences are described below in that order.

Under hydrostatic pressure, α -BaF₂ transforms back to β -BaF₂ on release of pressure.⁸ In anvil type pressure generating systems, α -BaF₂, once formed, is metastably recovered.^{1,5,9}

Samara⁸ reports that the pressure of transition decreases with increasing temperature. For example, whereas the transition pressure at 22°C is 26.8 kbars, the transition pressure at 200°C is around 20 kbars. The values of dP/dT are $\sim -2.6 \times 10^{-2}$ kbars/°C below 100°C and $\sim -2.2 \times 10^{-2}$ kbars/°C between 100° and 300°C. The results of ref. 9 indicate that the transition pressure tends to decrease with increasing temperature. However, Seifert's work⁵ indicates that the pressure of transition tends to increase with increasing temperature is increase of 22 kbars in transition pressure when temperature is increased from room temperature to 200°C. It is not clear if the increased pressure is an equilibrium pressure.

Values of transition pressure at room temperature reported by various investigators are listed in Table 1. It is seen that variations in transition pressure are quite large.

Table 1 -- Transformation Pressure of BaF₂ from Fluorite to Orthorhombic Structure at Ambient Temperature (β to α phase)

Investigators		Transformation Pressure (kbars)
Minomura and Drickamer	(1961)	30.8
Chen and Smith	(1966)	36.0
Seifert	(1968)	25.0
Dandekar and Jamieson	(1969)	<20.0
Samara	(1970)	26.8
Kessler and Nicol	(1972)	23.0

If temperature of the press containing α -BaF₂ is quickly reduced from T to room temperature, and pressure is subsequently released, α -BaF₂ is found in the sample if T < 470°C but not for greater T.^{5,9} This temperature dependence of the effects of quenching is inexplicable on the basis of information given above.

It is very difficult to provide a clear explanation for disagreements among the investigators with regard to the pressure of transition at room temperature and its variation with temperature, and the variation in quenchability of α -BaF₂. However, one can easily think of a few of the variables which may have brought about those disagreements. For example the type of high pressure apparatus used in an investigation, the magnitude of hysteresis, impurities in the BaF₂ used could easily differ from one experiment to another and the experimental procedure to establish transition pressure, i.e. whether the pressure was observed by in situ examination of the sample or in a quenched sample. Inability to quench the orthorhombic phase at any pressure beyond 470°C tends to indicate that there may be a third phase of BaF2 present at high temperature but below the melting temperature of BaF2. That such a phase may exist even at one atmosphere is suggested by an observed transformation in the isostructural compound CaF₂ between 1047°C and 1100°C by Naylor.¹² The structure of this high temperature phase of CaF₂ remains undetermined.¹³

Finally the equation of state of the orthorhombic phase of barium fluoride is as yet undetermined.

III. SHOCK COMPRESSION EXPERIMENTS

Shock compression experiments were performed with the Washington State University gas gun. A detailed description of the gun and its operating characteristics are documented in ref. 14. Briefly, the gun is 44' long and four inches in diameter. It can propel a four inch diameter, 1 kg projectile with any velocity in



Fig. 1 -- An experimental assembly for measuring impact stress-time profiles. For measuring transmitted stress-time profiles a specimen is bonded to a quartz gage and mounted in the target. In recent experiments on BaF_2 , the back-up steel disk was found not to be necessary for the impact stress-time profile measurements.

the range of 0.1 mm/ μ sec to approximately 1.4 mm/ μ sec. Angular misalignment between the impacting surfaces of the projectile and target is of the order of 5 x 10⁻⁴ radians or less. The entire impact chamber is evacuated to 10⁻³ torr to prevent an air cushion forming between the two impacting surfaces. The electronic recording instruments consist of Tektronix 454, 585 and 519 oscilloscopes. Parameters measured in the experiments are projectile velocity, misalignment of the projectile and target, and stress history either at the impact interface or at the specimen surface opposite the impact surface. A schematic of a finished experimental assembly for measuring stress history at the impact face is shown in Fig. 1. The stress gages used were x-cut quartz disks with 1/2" diameter and 3.2 mm thickness. These gages were used in the shorted configuration.

Shock compression experiments were performed on single crystals of BaF_2 oriented along <111> and <100> directions.¹⁵ These specimens were in the shape of circular disks of diameter 22-25 mm and thickness ranging between 1.1 and 4 mm. Basically three types of experiments were performed. Experiments of the first type yielded stress history in the quartz gage after the shock wave was

transmitted through the specimen. Experiments of the second type measured the stress history at the impact surface of a BaF_2 specimen before reflections returned. Experiments of the third type were designed to recover a specimen of BaF_2 subjected to shock compression stresses well above the pressure of transformation at room temperature. The results of these experiments are described in the following section.

IV. EXPERIMENTAL RESULTS

Front Surface Impact

In these experiments a stress gage records the jump in stress (σ_i) impressed upon a specimen at the impact surface because the quartz gage impactor is also the transducer.^{16,17,18,19} The magnitude of this jump is calculated directly from the piezoelectric response of the gage.²⁰ For the configuration shown in Fig. 1, particle velocity in the quartz gage at the interface, is determined by the relation

 $u_{q} = \sigma_{i} / \rho_{q} D_{q}$ (1)

where ρ_q and D are density and elastic longitudinal velocity in quartz, respectively. Since both stress and particle velocity are continuous at the impact interface, the pair of values (σ_i, u_q) also apply to the BaF₂. However, since BaF₂ has the initial velocity, u_o , the physically significant velocity is

$$u_{s} = u_{0} - u_{0}. \tag{2}$$

Therefore the values tabulated as being characteristic of BaF₂ under the impact conditions are (σ_i, u_s) . The characterization of a material in the above manner is valid whether the profile of the wave is steady or not, or whether there are any rate effects present or not.

As shown by Hayes,¹⁹ in front surface impact the rate of stress relaxation at the impact surface immediately after impact is directly related to initial transformation rate at the impact surface. If a relaxation is present, the post-relaxation stress at the impact surface is propagated into the specimen with a steady profile.

In the present set of experiments, steady stress profiles were obtained only below ~ 24 kbars, i.e. probably below the stress at which β -BaF₂ transforms to α -BaF₂. At higher stresses, stress profiles obtained at the impact surface for specimens oriented along <111> show a unique type of profile never before reported. These show that the stress initially rises, then goes through a minimum,

and finally attains a steady state. A profile so obtained, with 40 kbar peak stress, is shown in Fig. 2, as recorded on two different oscilloscopes. Figure 2 also shows that the initial stress rise is very sensitive to the response of the electronic instrument used in the experiment. Figure 2(a) was recorded on a Tektronix oscilloscope Type 454 with 150 MHz bandwidth, and Fig. 2(b) was recorded on a Tektronix oscilloscope Type 519 with 1000 MHz bandwidth. This is important to remember because it implies that the initial record of a stress history does not necessarily reflect the mechanical property of the material. It may reflect the speed of the oscilloscope response to a signal. However, the magnitude of minima and subsequent steady state stress levels are insensitive to the type of oscilloscope used. Moreover, these stress profiles have been reproduced in identical experiments. Calculation of the impact stress for elastic compression of the β -phase indicates that the magnitude of initial stress is equal to the steady state value. However, the data present a difficult problem of interpretation because, on the basis of a standard stress-particle velocity $(\sigma-u)$ diagram for a material which exhibits a phase transition under high pressure, shocking up of the stress profile after an initial relaxation is impossible. For example, consider a typical σ -u diagram for a front surface impact experiment in which the specimen is stationary, (Fig. 3). Let OA and ABC, parts of the curve OABC, represent the stable and metastable part of the σ -u profile for phase I of a material. Let AB'C' represent a similar profile for stable phase II of the material. Let the transition stress be σ_A . If a quartz gage with a velocity uo is impacted on the specimen in phase I so as to generate a stress $\sigma_B,$ then if the transformation to phase II is instantaneous or faster than the rise time of the recording instrument, the impact stress profile would be of magnitude σ_{p_1} . However, if the rate of transformation is slower than



Fig. 2 -- Stress-time profile for shock compression of BaF₂ in <111> direction. The impact stress in both cases is 40 kbars. (a) The profile recorded on Tektronix Type 454 oscilloscope. (b) The profile recorded on Tektronix Type 519 oscilloscope.



Fig. 3 -- Stress-particle velocity diagram for a material which transforms to a new phase at stress σ_A , being shocked to a stress $\sigma_B > \sigma_A$ by an impactor, moving with a velocity u_0 . In the diagram impactor is a quartz gage.

the rise time of the recording instrument the impact stress would relax from σ_B to $\sigma_{B'}$ in some finite time. In no case would it shock up. Thus for a phase-transforming material impact stress cannot shock up as it does in our profile. Hence, the first question that arises is whether the profile represents a material property of BaF₂ or whether the quartz gage is behaving in a peculiar manner, since these shots develop a stress of 40 kbars in the gage, a value which is near or above the upper limit for reliable performance. Three experiments were performed to rule out one of the above mentioned alternatives. In the first of these experiments an aluminum 6061-T6 projectile was impacted on a quartz gage with a sufficient velocity to guarantee an impact stress of 40 kbars. The stress profile obtained was steady and showed no peculiarities whatsoever. In the second experiment, a projectile

generated 55 kbars in the gage. At this stress the quartz gage was found to break down. The profile obtained is shown in Fig. 4(a). The third experiment consisted of impacting a specimen of BaF_2 on a quartz gage to generate a stress of 55 kbars once more. The stress profile obtained in this experiment is shown in Fig. 4(b). It may be seen from Figs. 4(a) and 4(b) and the result of the first experiment that, except for distortions due to response time and nonlinearity of the quartz gage response, the total stress profile shown in Fig. 2 does represent the mechanical behavior of BaF_2 . The type of profile shown in Fig. 2 continues to be present at impact stress down to ~ 25 kbars. Below 25 kbars the impact stress profiles are steady, as shown in Fig. 5.

A plot of stress and particle velocity for BaF_2 specimens with <111> orientation (Fig. 6) shows that (1) the values of steady state stress and the corresponding values of particle velocity lie along the stress vs particle velocity curve of BaF_2 <111> in the β -phase,





Fig. 4 -- Stress-time profile at 55 kbars. (a) By impacting a quartz gage on aluminum. (b) By impacting a quartz gage on a BaF_2 specimen.



Fig. 5 -- Stress-time profile obtained for shock compression of BaF₂ in <111> direction for an impact stress below 25 kbars.



Fig. 6 -- Stress-particle velocity $(\sigma$ -u) plot of BaF₂ as obtained from the front surface impact experiments. The line marked <111> denotes the estimated σ -u dependence of β -BaF₂ in <111> direction. It is identical with σ -u plot for <100> direction. • steady state stress realized in the experiments. x the pair of σ , u values corresponding to minima in the experiments. • the steady state (σ, u) values for <100> shots.

as obtained from the elastic constant data of BaF_2 .²¹ In the same vein, if we plot the magnitude of the stress corresponding to minima and related particle velocity, these two sets of data form a cusp at 22 to 24 kbars.

The stress profiles obtained for BaF₂ specimens oriented along the <100> direction show that a steady state stress is reached immediately. A plot of stress and particle velocity indicates that these pairs of points lie along the curve of elastic compression of the β -phase of BaF₂. A stress profile obtained around 40 kbars for the <100> orientation is shown in Fig. 7.



Fig. 7 -- Stress-time profile obtained for shock compression of BaF_2 in <100> direction with an impact stress of 40 kbars.

Transmission Experiments

Only three transmission experiments have been performed. A representative stress profile recorded by a quartz gage at 38 kbars is shown in Fig. 8. Stress profiles obtained around 20 kbar show the same character as that shown in Fig. 5. The nature of the profile obtained at higher stresses makes it difficult to analyze in a straightforward manner, and no further transmission experiments have been performed as of this date.

Recovery Experiments

Two recovery shots were performed. The details of design and construction, being of only ancillary interest, are not described here. Both experiments were performed at 35 to 40 kbars, well above the stress at which the minimum occurs in the stress profile.



Fig. 8 -- Transmitted stress-time profile for BaF_2 in <111> direction with an impact stress of 40 kbars.

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Post mortem examination of the shocked BaF₂ specimens by x-ray diffraction techniques showed that the materials were in the β -BaF₂ phase. There was no trace of the α -BaF₂ in either specimen.

V. DISCUSSION OF EXPERIMENTAL RESULTS

In the previous section we established that (1) stress profiles observed in BaF_2 reflect its mechanical properties within the limitation of the recording instruments, (2) shock recovered specimens of BaF_2 were found to be in the β - phase and (3) information from the transmission shots is too meagre to yield any significant insight in interpreting the data.²² In light of the above, we shall try to elucidate the behavior of BaF_2 on the basis of experimental observations resulting from front surface impact and recovery experiments.

It is useful to make some remarks about the time scale of the events recorded in these experiments. The minima occur between 5 and 12 nsec after impact, and their times of occurrence decrease with increasing impact pressure. These minima are sharp and have no temporal spread. The times taken to reach steady state bear no relation to the value of the steady state impact stress. The steady state stress is reached within a time interval of 23-62 nanoseconds for impact stresses above 25 kbars. These time intervals which add to less than 80 nsec, are well within the time at which the disturbing effects of using shorted quartz gages would seriously affect the recorded stress-time profile in these experiments.

If the presence of a cusp is taken to indicate the onset of a transition in BaF_2 , one may conclude that the observed transition in BaF_2 is shear induced. This is because in a fluorite structure shear stresses developed in specimens oriented along the <111> and the <100> directions are equal to 26,1 and 0.0 per cent of the applied normal stress, respectively.²³,²⁴,²⁵ Since recovered specimens of BaF_2 were found to be in β -phase, one may conclude that the transition is a reversible one. Thus, in this regard, the response of BaF_2 to shock compression is like the response of BaF_2 to a hydrostatic stress environment.

Information available from experiments reported here is not enough to enable us to characterize the BaF_2 under these conditions. We do note, however, that the upturn of stress following its initial decay, shown in Fig. 2, is consistent with a simple relaxation model of the material. To see this, consider the configuration in which a stationary quartz gage is struck by a moving BaF_2 sample. Let the constitutive relation for BaF_2 be of the form²6

$$\frac{d\sigma_x}{dt} - a^2 \left(\frac{d\rho}{dt}\right) = -F$$
(3)

where a is the speed of elastic compression in material of density ρ , σ_X is the longitudinal stress, and F is a function characterizing the rate at which an equilibrium stress is reached in the shocked material. The specific form of F depends upon the type of process or processes through which the material relaxes. In general F can be a function of static as well as rate dependent variables. Let h be the Lagrangian space coordinate for the problem. Then for arbitrary h, equation (3) becomes

$$(\partial \sigma_{\rm X}/\partial t)_{\rm h} - a^2 (\partial \rho/\partial t)_{\rm h} = -F.$$
(4)

The equations expressing mass and momentum conservation, in Lagrangian coordinates are, respectively

$$(\rho_0/\rho^2) \cdot (\partial \rho/\partial t)_h + (\partial u/\partial h)_t = 0,$$
 (5)

$$(\rho_0/\rho) \cdot (\partial u/\partial t)_h + (1/\rho) \cdot (\partial \sigma_x/\partial h)_t = 0.$$
 (6)

Combining Eqs. (5) and (4) we obtain

$$(\partial \sigma_{\rm X}/\partial t)_{\rm h} = -(a_{\rm P})^2 \cdot (1/\rho_{\rm O}) \cdot (\partial u/\partial h)_{\rm t} - F.$$
 (7)

At the interface, we have, referring to Fig. 1,

$$(\partial \sigma_x / \partial t)_{h=0} = Z_q (\partial u / \partial t)_{h=0}$$
(8)

where $Z_q = \rho_q D_q$. Substituting the value of $(\partial \sigma_x / \partial t)_{h=0}$ from Eq. (8) into Eq. (7) we obtain

$$Z_q(\partial u/\partial t)_h = -(a_\rho)^2 \cdot (1/\rho_o) \cdot (\partial u/\partial h)_t - F.$$
 (9)

The stress profile obtained for BaF₂ indicates that after the initial rise, say at time t = 0, stress and particle velocity decrease up to a time τ_1 where they both attain an extremum value. From time τ_1 to some time τ_2 , stress and particle velocity increase and beyond τ_2 the stress and particle velocity are constant. For these time intervals, we have

$$(\partial u/\partial t)_{h=0} < 0 \qquad 0 \le t < \tau_1$$
 (10a)

$$(\partial u/\partial t)_{h=0} = 0$$
 $t = \tau_1$ and τ_2 , and (10b)

$$(\partial u/\partial t)_{h=0} > 0 \quad \tau_1 < t < \tau_2$$
 (10c)

Since F is always positive, it implies that in order to obtain the observed profile one must have for

$$0 \le t < \tau_1$$
, $(a_\rho)^2 \cdot (1/\rho_0) \cdot (\partial u/\partial h)_{t,h=0} < F$ (11a)

$$t = \tau_1 \text{ or } \tau_2 \qquad (a_p)^2 \cdot (1/\rho_0) \cdot (\partial u/\partial h)_{t,h=0} = F \qquad (11b)$$

$$\tau_1 < t < \tau_2$$
 $(a_p)^2 \cdot (1/\rho_0) \cdot (\partial u/\partial h)_{t,h=0} > F$ (11c)

In the derivation of the conditions expressed by Eq. (11), it has been assumed that particle velocity decreases with increasing propagation distance. These conditions do not seem to violate any fundamental relations. In terms of the rate of change of density, the above sets of conditions imply that during the time interval 0 and up to τ_1 , the rate of change of density at the interface may be positive or negative. In the case it is positive, its magnitude must be less than the value of F/a². During the time interval τ_1 and up to τ_2 , the rate of change of density must be positive and its magnitude must be larger than the value of F/a². At the time points τ_1 and τ_2 either both the rate of change of density must be positive and F are identically zero or the rate of change of density must be positive and balance with the value of F/a². None of the situations described above violates any physical conditions, especially since a negative rate of change of density is observed in an elastic-plastic relaxing material as a shock compression wave propagates in it.

In BaF₂, the situation may be more complicated if above 25 kbars it behaves both plastically and starts to transform to its α -phase. We plan to pursue the present study of polymorphic behavior of BaF₂ further by performing the following experiments. (1) Experiments where stresses generated would be such that β -BaF₂ would almost instantaneously transform to α -BaF₂, i.e., probably at stresses in excess of 70 kbars; (2) experiments on the samples at high temperatures; (3) experiments measuring stress profile at various depths in the specimens of BaF₂ at varying initial temperatures; and (4) the above type of experiments will permit us to build a model for the behavior of BaF₂ under shock compression.

ACKNOWLEDGMENT

This work was supported by the United States Air Force Office of Scientific Research Contract Number 71-2037A.

REFERENCES

1. D. P. Dandekar and J. C. Jamieson, <u>Proceedings of Symposium on</u> <u>Crystal Structures at High Pressures</u>, American Crystallographic Association (1969) pp. 19, and the references in the article.

- O. E. Jones and R. A. Graham, <u>Accurate Characterization of the High-Pressure Environment</u>, National Bureau of Standards Special Publication 325, U.S. Government Printing Office, Washington, D.C., 1971, pp. 229 and references therein.
- 3. Lead fluoride which is isostructural to BaF₂ transforms at 4.8 kbars at 23°C. Hence, lead fluoride would have been the ideal material to start with, but for the unavailability of a good large single crystal of the same. On the other hand BaF₂ crystals are readily available and economical to perform experiments with.
- 4. S. Minomura and H. G. Drickamer, J. Chem. Phys. <u>34</u>, 670 (1960).
- 5. K. F. Seifert, Ber. Bunsenger, Physik. Chem. 70, 1041 (1966).
- 6. K. F. Seifert, Fortschrift Miner. 45, 214 (1968).
- J. H. Chen and H. I. Smith (Report AFCRL-66-601), (1966) and Bull. APS <u>11</u>, 414 (1966).
- 8. G. A. Samara, Phys. Rev. B1, 4194 (1970).
- 9. D. P. Dandekar and J. C. Jamieson (Unpublished).
- 10. J. R. Kessler and M. Nicol, Bull. APS II, 17, 123 (1972).
- 11. Both structures contain 4 molecules per unit cell. In the fluorite structure (space group Fm3m-05) barium atoms are in a cubic close-packed type of arrangement with fluorine atoms occupying all the tetrahedral sites. Each fluorine atom is surrounded by 4 barium atoms disposed tetrahedrally, and each barium atom by 8 fluorine atoms disposed toward the corners of a cube. In the α -PbCl₂ structure (space group Pbnm-v¹⁶) each barium atom is surrounded by 9 fluorine atoms, but all of these atoms are not equidistant from the cation they surround. This structure may be considered as a distorted close-packing of fluorine atoms with the barium atoms accommodated in the same plane with them. For details see: R. W. Wyckoff, Crystal Structures, Vol. 1, (Interscience, New York, 1963). Chapter IV.
- 12. B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945).
- 13. A similar transition has been observed in SrCl₂, BaCl₂, SrBr₂ below their respective melting points. These compounds are isostructural to CaF₂ and BaF₂. The possible nature of this transition may be inferred from the x-ray diffraction work of Croatto and Bruno on SrCl₂. They suggested that the resulting high temperature structure shows a disordering in the anion

semilattice. For further information see the following references. (1) U. Croatto and M. Bruno, Gass. Chem. Ital. 76, 246 (1946), and (2) A. S. Dworkin and M. A. Bredig, J. Physical Chem. 67, 697 (1963).

- 14. G. R. Fowles, G. E. Duvall, J. Asay, P. Bellamy, F. Feistman, D. Grady, T. Michaels and R. Mitchell, Rev. Sci. Instr. <u>41</u>, 984 (1970).
- 15. BaF₂ crystals were bought from Harshaw Chemical Co., Solon, Ohio and Optovac Inc., North Brookfield, Mass. These crystals were of optical quality and free from any visual defects. Back reflection x-ray pattern indicated that misorientation of specific specimen could be accurately represented by $\theta = \pm 0.5^{\circ}$ and $\phi = \pm 0.5^{\circ}$.
- 16. A. R. Champion, J. Appl. Phys. 42, 5546 (1971).
- W. J. Halpin and R. A. Graham, "Shock Wave Compression of Plexiglass from 3 to 20 kbars," in Fourth Symposium on Detonation, Office of Naval Research Report #ACR-126 (1965).
- W. J. Halpin, O. E. Jones and R. A. Graham, "A Submicrosecond Technique for Simultaneous Observation of Input and Propagated Impact Stresses," in Dynamic Behavior of Materials, ASTM Special Technical Publication #336 (1963).
- 19. D. B. Hayes, Ph.D. Thesis, Washington State University (1972).
- R. A. Graham, F. W. Nielson and W. B. Benedick, J. Appl. Phys. <u>36</u>, 1775 (1965).
- C. E. Wong and D. E. Schuele, J. Phys. Chem. Solids <u>29</u>, 1309 (1968).
- 22. This conclusion is not based on the three shots reported in here alone but includes the transmitted stress profiles obtained previously in this laboratory by a graduate student in 1969-70.
- J. N. Johnson, O. E. Jones and T. E. Michaels, J. Appl. Phys. <u>41</u>, 2330 (1970).
- 24. An independent way of confirming the conclusion that the transformation in BaF_2 from fluorite to orthorhombic structure is shear induced would be to subject a small sample of either BaF_2 or preferably lead fluoride to a prolonged grinding in a mechanical mortar.

- 25. J. R. Kessler (private communication) finds that β -BaF₂ is relatively easily and reasonably completely transformed to α -BaF₂ phase at 23 kbars where the pressure is applied normal to <111> direction in β -BaF₂.
- G. E. Duvall, in <u>Stress Waves in Anelastic Solids</u>, H. Kolsky and W. Prager, Eds., Springer-Verlag, Berlin (1964), pp. 20-32.