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Effects of High Shearing Stress Combined with High Hydrostatic Pressure

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Mean hydrostatic pressures up to 50,000 kg/cm^2 combined with shearing stresses up to the plastic flow point are produced in thin disks confined between hardened steel parts so mounted that they may be subjected to normal pressure and torque simultaneously. Qualitative and quantitative studies are made of the effects of such stresses. Among the qualitative effects it is found that many substances normally stable become unstable and may detonate, and conversely combinations of substances normally inert to each other may be made to combine explosively. Quantitatively, the shearing stress at the plastic flow point may be measured as a function of pressure. The shearing stress at plastic flow may rise to the order of 10 or more times greater at 50,000 kg/cm^2 than it is normally at atmospheric pressure; this is contrary to the usually accepted results in a narrower range of pressure. If the substance undergoes a polymorphic transition under these conditions of stress, there may be a break in the curve of shearing stress *vs.* pressure. This gives a very convenient tool for the detection of transitions. 57 elements have been explored in this way, and a number of new polymorphic transitions found.

INTRODUCTION

THE experimental study of high stresses has hitherto been confined almost exclusively to high hydrostatic pressure. The distortion produced by hydrostatic pressure is simply describable, and the physical effects are specifiable in terms of a few parameters. Greater complications may be expected if shearing stresses are allowed to act in addition to the hydrostatic pressure. It is, I think, the general feeling that these additional complications are probably of inferior physical significance, but that this may be too narrow a point of view is suggested by the fact that the forces between molecules are in general certainly not central forces, so that on the molecular scale any except the simplest solids must be the arena of shearing forces of high intensity. Furthermore, if such a phenomenon as molecular disintegration by high stress is possible, it is probable that shearing stresses will be much more effective than hydrostatic pressure.

The intensity of the shearing stresses hitherto realizable in practice has been restricted to a rather low value; there is no intrinsic upper limit to the hydrostatic pressure to which a substance may be subjected, but the shearing stress may not exceed a certain limit set by plastic yield of the material. The first plastic yield point in shear may be very low, as shown by the behavior of single crystals of many of the metals. The effect of initial plastic flow is to raise the resistance to plastic flow, a phenomenon described as "work hardening." It is known that this work hardening cannot proceed beyond a somewhat nebulously defined upper limit, and that there is a roughly defined "upper yield point" and a maximum shearing stress supportable by any material. In an ordinary tensile test the tension is accompanied, on planes at 45° to the direction of the principal tension, by a shearing stress numerically equal to one-half the tensile stress, so that under these conditions rupture or plastic flow occurs when the shearing stress reaches one-half the tensile stress limit. This quantity has been measured for many metals and rises higher than a few thousand kilograms per square centimeter for relatively few substances. Engineers have found that under the limited conditions of engineering practice the maximum shearing stress is not greatly affected by a superposed hydrostatic pressure, so that ordinary engineering experience would suggest that it would be impossible under any conditions to apply to a material a shearing stress of much more than one-half its ultimate tensile strength. This opinion is sometimes explicitly expressed in criteria of rupture.

This expectation, however, rests on a narrow range of experimental conditions, and it turns out that by sufficiently raising the mean hydrostatic pressure the maximum shearing stress may be very considerably increased. In the following are described experimental means by which this may be accomplished, as well as some of the effects of such high shearing stresses. This paper must be regarded only as a suggestive introduction to the subject; given the method of producing the stress, many sorts of experiment will occur to any one, some of which I have tried and will publish later, and some of which I have not yet had time to try. The results described in this paper fall into two parts; first a purely qualitative description of the behavior of a number of chemical compounds, and secondly a quantitative examination of the behavior of all the available elements. It is characteristic of the method that it is applicable to very small quantities of material, so that it has been possible to examine more of the elements than is often possible.

Description of Method

The principle of the method is suggested by Fig. 1. A represents a thin disk of the material under examination, squeezed between two cylinders B and C of hardened steel, with accurately ground plane ends. If the material A is softer than the hard steel it will, if its initial thickness exceeds a critical value, flow out laterally until the thickness of the disk is reduced to such a value that the friction against the steel near the outer edge of the disk is sufficient to balance the mean hydrostatic pressure exerted on the central parts of the disk. It is obvious that if friction is finite, lateral flow must eventually cease, no matter how great the pressure exerted by the cylinders B and C. When the equilibrium thickness has been reached for a given mean pressure, a couple is applied to the cylinders B and C with respect to each other. The initial effect of the couple is to produce a slight angular displacement, resisted by elastic distortion in the cylinders and in A, but if the couple is high enough, B rotates with respect to C with uniform angular velocity. There is thus applied to the disk A a shearing stress, the maximum magnitude of which is determined by the force necessary to produce uniform rotation of B and C. Under this maximum shearing stress there may either be slip at the surfaces of separation of A from B and C, or more usually plastic flow throughout the interior of A. In the following only the effects of the maximum shearing stress, that is, the effects when there is uniform rotation of B with respect to C, are studied.

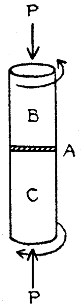

Fig. 1.

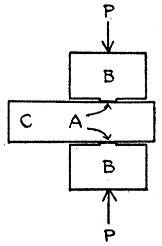

Fig. 2.

Fig. 1. Idealized apparatus for exerting pressure and shearing stress simultaneously on the thin disk at A.

Fig. 2. Scheme of the actual apparatus. The material in the form of a thin disk at A is squeezed by a hydraulic press pushing the steel cylinders B against the anvil C, which is rotated, while the cylinders B are held stationary by friction against the press.

In actual application, the apparatus is considerably modified from the simple scheme represented in Fig. 1. In the first place the maximum pressure attainable with the scheme of Fig. 1 would be limited to very materially less than the maximum compressive strength of the steel as given by ordinary compressive tests because of longitudinal splitting of the cylinders due to friction of A as it flows out laterally. By proper design of the steel parts, it is possible, however, to exceed very materially the ordinary compressional limit of the steel.

Local intensities of stress, which are very much greater than the intensities attainable under more normal conditions, are often reached in parts of a system which receive proper support from surrounding parts. Consider, for example, the Brinell method of measuring hardness by measuring the dimensions of the indentation produced by a hardened steel ball. Formulas will be found in the engineering handbooks for the stresses in the ball under working conditions. It appears that steel balls are regularly used on hard materials up to a compressive force at the point of contact of 75,000 kg/cm^2, about twice the compressive strength under ordinary conditions of test. It is obvious in this case that the area of the ball receiving the maximum thrust is supported by surrounding parts of the ball and of the material with which it is in contact, and rupture prevented.

The arrangement adopted in the following by which the surrounding parts support the most highly stressed parts, is something like that of the Brinell hardness test. The upper cylinder B of Fig. 1 is replaced by a very short boss projecting from a very much larger piece of steel. This boss is referred to in the following as the "piston"; in most of the experiments the diameter of the face of the piston was 0.25 inch, although 0.375 and 0.50-inch pistons were also sometimes used. The lower cylinder C of Fig. 1 is replaced by a large block of steel with a perfectly flat face, referred to in the following as the "anvil," and the material A is placed between the two. Finally, in order to eliminate frictional resistance to the rotation when the couple is applied, the whole arrangement is doubled, as shown in Fig. 2, and the anvil is rotated between the two pistons, which themselves do not rotate. The two pistons are compressed together with any desired force with a hydraulic press, and the force required to rotate the anvil is measured with a simple strain gauge on the handle of the rotating wrench. By doubling the apparatus, not only is end thrust eliminated, but each experiment is made virtually the mean of two, with a corresponding greater certainty in the results.

In setting up the apparatus it was necessary to use various auxiliary devices to ensure accurate centering and proper placing of the material of the disk, which need not be described in detail. Suffice it to say that the apparatus must be well made; all the parts must be accurately centered and aligned.

As a matter of routine the mean pressure exerted by the pistons was carried in all the following experiments to a maximum of 50,000 kg/cm^2. The success of the piston in withstanding this pressure depends to a certain extent on the nature of the compressed material; many of the softer materials produce no perceptible effect on the piston except a slight rounding of the very outer edge, whereas the harder materials may produce much greater damage, grinding scratches in the surface, and sometimes chipping pieces off the edge along shear planes at approximately 45°. There was almost always some perceptible permanent alteration of the piston, so that a fresh set of pistons was used for every experiment, either completely new pistons or pistons reground after a former experiment. A freshly ground part of the anvil was also always used for each new experiment. The necessity of fresh parts for every experiment makes the small size of the apparatus a very real advantage.

The maximum force to produce rotation, and therefore the maximum shearing stress applicable to the disk, varied greatly from substance to substance; the maximum reached for any substance was 18,000 kg/cm^2; the force on the end of a 1-meter lever to produce this was about the limit of what one man wanted to exert.

The actual distribution of stress and strain in the disk is evidently very complicated, and must differ greatly from the mean values just discussed. An exact solution of the problem would be impossible to give, both because of mathematical difficulties arising from the finite size of the strains, and because of physical difficulties arising from the fact that the constants of the material vary in an unknown and important way at such high stresses. However, some qualitative idea of the distribution of stress and strain can be obtained from the conventional solution of Hertz by the methods of classical elasticity theory, assuming small strains and unaltered elastic constants. This solution will be discussed in more detail in another paper, which will go into all questions of technique in greater detail. The solution shows that the originally plane surfaces of the anvil do not remain plane, but it becomes relatively depressed at the center, so that under stress the disk assumes the shape of a double convex lens, sometimes as much as five times as thick at the center as at the edges. The actual thickness of the disks in these experiments after exposure to a mean pressure of 50,000 kg/cm^2 was of the order of a few thousandths of an inch, being greater than 0.005 inch at the center only for a few of the hardest materials. Not only is the strain distribution far from uniform, but the normal pressure is not uniform, being greatest near the outer edge of the disk. Since the greater part of the area is concentrated near the outer edge, the assumption of mean values for normal pressure and also for shearing stress, the latter calculated on the assumption of a constant coefficient of friction all the way across the disk, gives a rough idea of what is happening. The attempt to get more accurate values than that corresponding to mean values must be left until later, if indeed it proves feasible at all.

EXPERIMENTAL RESULTS

1. Qualitative results

This whole study of the effect of shearing stresses was the outgrowth of the extension of measurements on polymorphic transitions to 50,000 kg/cm^2, which will be described in a subsequent paper, and in particular was at first directed to the attempt to produce in other substances irreversible and permanent changes analogous to the change from white to black phosphorus. It seemed not unreasonable that if the atoms or molecules could be forced to slide over each other by a shear they might take up new positions which they would be less likely to assume under the uniform distortion of a hydrostatic pressure. It seemed that perhaps sulfur was the most likely candidate for an irreversible change to a metallic modification, because of its chemical similarity to phosphorus. An irreversible transition from graphite to diamond was also an attractive possibility, made plausible by the magnitude of the volume change, and the fact that the diamond structure can be approximately obtained from the graphite structure by a shear and an axial compression. The anticipated permanent changes were not produced, however. It then suggested itself that substances in which the molecular and atomic forces are not as intense as in sulfur and carbon, as in the more loosely knit organic compounds, might show permanent changes; the first substance tried of this kind was rubber. Positive results were at once obtained; rubber is derubberized to a hard translucent material, not unlike horn in appearance. Paper was also transformed into a translucent horn-like mass. By control experiments it was established that the paper was not transformed by the action of a pure hydrostatic pressure of 50,000, but the rotation was necessary for the effect. Wood and linen cloth next showed a similar sort of transformation. Celluloid was then tried; it detonated violently, blowing off the edges of the piston. One disk detonated spontaneously when a pressure of 25,000 was reached without rotation, but the full 50,000 and rotation in addition was necessary to detonate the other disk. This result was perhaps not surprising in view of the known unstable character of celluloid.

The detonation of celluloid brings up the question of temperature changes, there must of course be a local rise of temperature during rotation; the question is whether it is large enough to be important. An upper limit to the rise of temperature can at once be found from the known solution of the following problem in one-dimensional heat flow: The X axis is maintained at temperature 0 for all negative values of time. At the origin of time a source emitting unit quantity of heat per unit time is installed at the origin and constantly maintained for positive times. The known solution gives for the temperature at the origin $(t/\pi\kappa\rho)^{\frac{1}{2}}$, where κ is thermal conductivity, ρ specific heat, and t the time.

In the shearing experiments the rate of generation of heat by friction was of the order of 5 g cal. per sec. Taking for the specific heat of steel 0.1×0.28, and for the thermal conductivity 0.15×0.28, in appropriate units, where 0.28 is the cross section of the piston, the rise of temperature at the end of five seconds, the maximum time of rotation, is 37°C. This value must be too large by a factor of several-fold, because actually heat flow takes place from the region of generation three-dimensionally into a practically infinite mass, instead of one-dimensionally as assumed here. The thermal factor thus appears to be of absolutely no importance in the following results.

After the experiments already described, NH_4NO_3 was tried, with the expectation that it would detonate even more readily than celluloid, but no effect could be obtained by the full 50,000 and repeated rotation. Red phosphorus was then tried; this was irreversibly transformed into black, a result which was checked by determining the density by the flotation method, and was also kindly checked by Dr. Jacobs, who found that the x-ray structure is the same as that of the high density black phosphorus. There are at least two varieties of black phosphorus.[1] Previous attempts to transform red to black phosphorus by the application

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[1] R. Hultgren, N. S. Gingrich and B. E. Warren, J. Chem. Phys. 3, 351 (1935).

of hydrostatic pressure alone up to 50,000 had not been successful. The cooperation of the shearing stress is apparently necessary for the transition, and is the sort of thing that I had been looking for in the beginning.

One of the obvious difficulties of these experiments was to determine with the very small amounts of material available whether there really was any important permanent change. A determination of density by the flotation method offered possibilities, but unfortunately the density of most of the substances is outside the range of this method. It seemed to me that color changes might afford a sensitive indication, particularly in the case of certain organic substances like the dyes, and the next substance tried was accordingly thymol blue. This showed no change of color, but did show a striking change of solubility, becoming so insoluble in slightly acidified water as to color the water by only a barely perceptible amount. Rosanilin, on the other hand, showed no perceptible change. Professor Forbes of the Chemistry Department then suggested to me that PbO_2 would be an interesting substance because of the different colors of the different oxides. To my great surprise this detonated violently, leaving a residue of metallic lead. The yellow oxide, PbO, was next tried; on compression to 50,000 it rotated quietly, but on releasing pressure it was found completely decomposed to a film of metallic lead.

It thus appeared that important effects of shearing stress were not confined to complicated organic compounds, and a number of inorganic compounds which suggested themselves for one reason or another and which were readily available in the casual laboratory stock, were rapidly tried. These experiments were superficial to the extent that I made no attempt to analyze the resulting product, but in most cases recorded only whether there was a detonation or not. These experiments will be summarized presently.

The question next presented itself whether certain compounds could not be synthesized. The first attempt was made with copper and sulfur, it having been found previously that CuS is not affected. The results were at once positive; there was a detonation at about 20,000 without rotation, and the product was apparently the ordinary black sulfide. A few other syntheses were next tried. First the thermite reaction, Fe_2O_3+Al; there was a very violent detonation between 20,000 and 30,000, without rotation, and with much damage to the steel parts; the product of the reaction was apparently metallic iron. $K_2C_2O_4+Al$ was compressed to 50,000 and after considerably more rotation than usual one of the disks detonated, but the other could not be made to detonate by prolonged rotation. Examination showed that the detonation had been confined to the peripheral parts of the disk, where the intensity of stress is greatest, and that the central parts were unaltered. Ground quartz, SiO_2, $+Mg$ filings, in the ratio of 24 Mg to 60 SiO_2 by weight, detonated on one side after several rotations at 50,000, but the other disk did not detonate. The whole behavior was much like that of $K_2C_2O_4+Al$. Finally a mixture of powdered silicon and MgO was similarly detonated on one side, the other side being obdurate; this detonation was of more than usual violence, about one-half the piston being blown away. This completes the list of syntheses attempted to date; the subject is a most inviting one and nearly inexhaustible. I have now made provision to continue this sort of exploration, with micro-analysis of the resulting products.

The various qualitative experiments to date are briefly summarized in Table I.

TABLE I. *Summary of qualitative experiments on effects of high shearing stress and high hydrostatic pressure.*

I. Substances giving negative results

Graphite, both amorphous and single crystal, mica, NH_4NO_3, sugar, rosanilin, CuS, SiO_2, tremolite, NH_4F, CuO, MgO, Ag_2S, Fe_2O_3, LiF, AgCl, $K_2C_2O_4$, $NaBrO_3$, Si, Rochelle salts, $HgNO_3$, $K_2Cr_2O_7$.

II. Substances which detonate

Celluloid, CHI_3, PbO_2, $KMnO_4$, Ag_2O, MnO_2, $(NH_4)_2$-Cr_2O_7, $AgNO_3$, $Sr(NO_3)_2$, $Cr_2(SO_4)_3K_2SO_424H_2O$, $Cr_2(SO_4)_3$-K_2SO_4, $Al_2(SO_4)_3$, $CuCl_22NH_4Cl2H_2O$.

III. Substances showing other sorts of positive results

Rubber, changes to a horn-like substance; "Duprene," somewhat like rubber; wood, changes to a horn-like translucent substance; paper, changes to a horn-like translucent substance; linen cloth, changes to a horn-like translucent substance; Brom thymol blue, no change in appearance, but becomes insoluble; Se, amorphous variety partially changed to metallic; S, crystalline variety probably changes to amorphous; PbO, no detonation, but decomposes to metallic Pb; HgO, the red modification changes to black; P, red changes to the dense black modification.

IV. Combinations with detonation

$Cu + S$, Fe_2O_3+Al, SiO_2+Mg, $K_2C_2O_4+Al$, $Si+MgO$.

2. Quantitative experiments

The quantitative experiments consisted of a determination of the force required to rotate as a function of mean normal pressure, and were restricted to those substances which showed no permanent change. Interesting information may be expected from the curve plotting rotating force against pressure, both because this sort of phenomenon has previously been very little studied, and because the pressure range is considerably greater than that yet open to experiment. The most obvious and immediate information from curves of this kind is with regard to polymorphic transitions; if the shearing strength of one polymorph is different from that of the other a break in the curve may be expected on passing the transition pressure. Great advantages of this method of exploring for polymorphic transitions are that the quantities of material necessary are very small, 0.1 g or less, and that it is very rapid, a complete exploration up to 50,000 and back to zero in steps of 2000 occupying less than one hour. Further, the method does not depend on the volume change, so that transitions with too small a volume change to detect by the more conventional volumetric methods may be discovered in this way. Of course, it is not impossible that conversely two polymorphs with a large volume difference should be so nearly alike in shearing strength as to give no indication by the shearing method, but it happens that none such, or at most one such, has been found. A disadvantage of the method is that the results are not as accurate as by the volume method, for the reason that the stresses throughout the disk undergoing transition vary so much from point to point that the transition is spread over a range of mean stress rather than confined to a single stress of discontinuity. Also, to date, the shearing method has been applied only at room temperature, although there is no intrinsic reason why it should not be applied at other temperatures.

The quantitative use of the shearing method as a supplement of the volumetric method was checked at first on bismuth, which had already been found to have polymorphic transitions near 25,000 at room temperature. In Fig. 3 is shown the force required to produce rotation as a function of the mean normal pressure. The transitions known to occur in the neighborhood of 25,000 are accompanied by a drop in the shearing force; there are in reality two transitions here at not very different pressures, but the sensitiveness of the shearing method is not great enough to resolve them. In addition, Fig. 3 shows distinct breaks, both with increasing and decreasing pressure, in the neighborhood of 42,000, suggesting another transition at this point. Previous exploration by the volumetric method had failed to reveal any new transitions beyond 25,000, but reexamination of the data now showed that there had been a discontinuity of volume in the neighborhood of 42,000 which had been discarded as without significance because of its smallness. More careful repetition of the volumetric measurements verified the reality of this new transition, and a determination was successfully made of the approximate transition parameters as a function of temperature, which will be described in another paper.

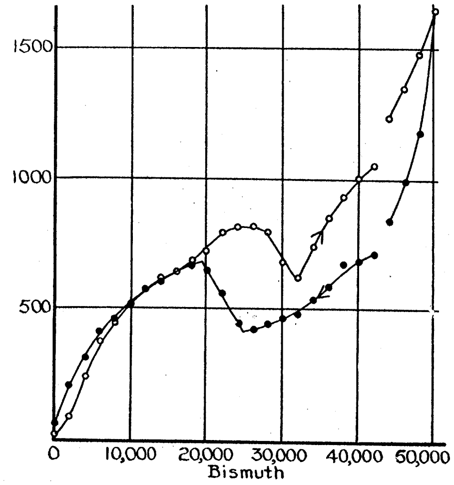

FIG. 3. The curve of shearing stress of bismuth in kg/cm^2 (ordinates) against mean hydrostatic pressure in kg/cm^2 (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure. The breaks in the curves indicate polymorphic transitions.

An additional advantage of the shearing method is that a transition is much less likely to be suppressed because of internal viscosity than when the stress is a hydrostatic pressure. An interesting example is antimony; this is similar chemically and in crystallographic properties to bismuth, so that high pressure polymorphism would be expected, but at higher pressures than

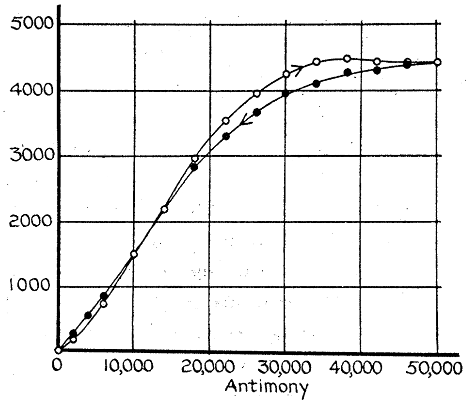

FIG. 4. The curve for antimony of shearing stress in kg/cm^2 (ordinates) against mean hydrostatic pressure in kg/cm^2 (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure. It is probable that the flat maximum with increasing pressure indicates the beginning of a transition analogous to the first transition of bismuth.

for bismuth because the melting point of antimony is so much higher than that of bismuth. Volumetric examination had failed to disclose any such transition up to 50,000. Shearing measurements, however, gave a curve which flattens off in the neighborhood of 50,000 exactly like the flattening off of the curve for bismuth in the neighborhood of 25,000, as shown in Fig. 4, and I believe that there is practically no doubt but that at 50,000 or higher antimony has transitions analogous to the transitions of bismuth near 25,000.

In interpreting the results of the shearing explorations for polymorphism, account must be taken of the effect of shearing stress as such on the transition temperature (or pressure). There is no general rule as there is for a melting temperature, the melting temperature of a sheared solid being always less than that of the unsheared solid, but depending on the relative elastic constants of the two solid phases the transition temperature at constant pressure of a sheared solid may be either raised or lowered. Judging, however, from the transitions studied thus far by both methods, the effect of shearing stress on transition temperature is not large in the majority of cases in actual practice, so that a rather close estimate of the pure hydrostatic pressure necessary to produce the transition at a given temperature can usually be made from the shearing measurements.

All the available elements, 57 in number, were systematically examined for polymorphism by the shearing method up to 50,000 kg/cm^2. The method is obviously not restricted to elements, and the next step on the program is to extend it to compounds.

The majority of the elements are not polymorphic at room temperature up to pressures of 50,000; nevertheless, even in these cases the information afforded by plotting rotating force as a function of pressure is of intrinsic interest, and we next consider what is the significance of these results.

As the normal pressure on the disk increases, three more or less distinct stages are to be recognized. First, at very low pressures, the material of the disk slips over the face of the steel pistons, as in conventional experiments made to determine the ordinary coefficient of solid friction. In this first stage the stresses are so low that there is no permanent or plastic deformation in either surface, and the friction may be thought of as arising from local elastic deformations as the unevennesses in one or the other surface force aside opposing projections of the other surface. With increasing normal pressure the second stage begins when the elastic limit is exceeded locally; there are now changes in the geometrical configuration of the surfaces, and the coefficient of friction departs from its initial constant value. The local plastic deformations which accompany slip often involve "seizing" or welding of one surface to the other. It seems to be usually the case that the beginning of seizing is accompanied by an increase in the coefficient of friction, but I believe that there is no intrinsic reason, particularly in the case of substances very much softer than steel, why the plastic flow which must accompany seizing should not sometimes result in a decrease of the effective coefficient. The second stage may be thought to end when the normal pressure has become so high that the whole surface has seized, or at any rate is involved in plastic flow, and from here on the material is in the third stage, where shear is brought about by plastic flow distributed more or less uniformly throughout the entire body of the material. Within the range of stress of ordinary engineering practice it seems to be the case, as already stated, that

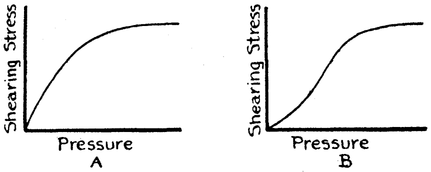

FIG. 5. Illustrates the two types of curve for shearing stress against pressure.

the shearing stress under these conditions of plastic flow is independent of the normal pressure, so that during the third stage the plot of rotating force against normal pressure would be a horizontal line parallel to the pressure axis. From a highly idealized point of view the complete curve of rotating force against normal pressure might be expected to have one of the forms indicated in Fig. 5, depending on whether the transition from the first to the second stage is accompanied by an increase or a decrease of the effective coefficient of friction. The actual curves often depart greatly from this shape, particularly with respect to the horizontal asymptote. Failure to approach a horizontal asymptote is a measure of the failure of shearing stress to be independent of normal pressure, and the very great departure of many of the elements from this behavior is one of the most significant of the results of these measurements.

A simple interpretation of the results is complicated by the deformation of the steel pistons, particularly in the case of the harder metals. With the softer metals the steel does not experience any permanent deformation, but its surface is left intact after the experiment. Some of the softer metals "seize" or weld to the steel almost perfectly, and have to be separated by cutting away with a razor blade; the union is as good as in a perfect soldered joint. For such substances the shearing force obviously gives a perfect measure of the shearing strength for uniform flow in the body of the metal. Even when the soft metal does not weld to the steel surface, slip must involve a large amount of plastic flow, so that the force to produce rotation must be a good indication of the resistance of the metal to shear in bulk. But in the case of the harder metals the interpretation of the results is not so simple. There is almost always a certain amount of welding, but it is confined to a small number of small spots; the disk can almost always be pried away from the anvil with a razor blade as a coherent whole. The surface of the steel is now almost always damaged; there may be microscopic pits or long circumferential scratches. This distortion of the steel is in itself instructive, for it means that the sheared metal has become harder than glass hard steel in some places. This local hardening doubtless involves a more or less complete destruction of the crystal structure. A striking example is afforded by graphite. In the ordinary massive form (Acheson graphite) it is soft enough to be whittled easily with a knife, but after its structure has been broken down by shearing under high pressure and while still under pressure it becomes a most effective abrasive. On one occasion a minute piece of graphite was subjected for 15 hours to a mean pressure of 100,000 kg/cm^2 by a special arrangement of the surrounding glass hard steel parts so as to afford the maximum of mutual support; the graphite was found partly embedded in the steel, as a diamond might have been forced in, but there was no permanent alteration in the graphite. A result of the ability of many of the harder and stronger materials to receive intense local hardening is that the total rotating force is not a measure of resistance to plastic flow homogeneously distributed throughout the mass, but is a measure of contributions made by only a part of the whole.

The strength of the *steel* is involved in the actual turning force in a complicated way depending on the distribution of the localities of permanent damage to the steel. One may be sure, however, that the shearing strength of the steel to a homogeneously distributed shear is at least as great as the highest shearing force observed for any of the materials. This maximum figure was 18,000 kg/cm^2, obtained with boron under a mean normal pressure of 50,000 kg/cm^2. In all other cases, it can be inferred that the shearing strength of the homogeneous metal is as great or greater than that given by the rotating force. The figure obtained in this way, although it is unsatisfactory because it is a lower limit, is, however, very informing in most cases because it is so much higher than the maximum shearing resistance to homogeneous flow at atmospheric pressure. The lower limit obtained in this way is probably not far from the value for homogeneously distributed flow in those cases where the curve is notably concave toward the pressure axis at the upper end, that is, in those cases where there is a strong tendency toward the expected horizontal asymptote.

The "self-welding" of most of the substances studied is much greater than their welding to the steel. Thus the original material may be in the form of a fine powder or it may be a coiled helix of wire; but the final form after exposure to pressure and shearing was almost always a coherent disk. A few substances, however, do not self-weld at all; these will be noted later. The fact that self-welding is so common suggests that the minimum value of the shearing force discussed in the last paragraph is probably not very far from the true value for homogeneously distributed flow.

The importance of the effect of "cold working" at high pressures may be estimated from the agreement of the curves of rotating force for increasing and decreasing pressure. If an important amount of work hardening is produced by pressures between 30,000 and 50,000 in addition to that produced by the initial pressure of 30,000, then the curve with decreasing pressure will lie above that with increasing pressure, and if such an effect is not important, then the two curves will coincide. In the case of many of the harder metals the work hardening in this range appears to be unimportant.

It is perhaps not surprising that the shearing force at plastic yield is in many cases a strong function of normal pressure when it is considered that the viscosity of liquids has been found to vary more with pressure than any other physical property, and that the nature of plastic yield of a solid as completely disorganized as these solids must be under such extreme stresses must have points in common with viscous slip in a liquid. The effect of pressure on the viscosity of liquids varies enormously with the complication of the molecule, being comparatively small for monatomic mercury, and becoming very large for complicated organic compounds. Similarly, one might anticipate that for monatomic elements the shearing force for plastic flow might not vary greatly with normal pressure, but that in complicated organic compounds the variation might be very large. This idea was tested by measuring the rotating force for ordinary solid paraffin as a function of normal pressure; the results are shown in Fig. 6. The shearing strength of paraffin is so low that all observable points on the curve must refer to the third stage of the process described above, that is, the stage of plastic flow throughout the interior of the paraffin. If the shearing stress for plastic flow were independent of normal pressure, then the curve should be a horizontal straight line not higher than the lowest observed point. As a matter of experiment, the highest observed force was 900 times as great as the lowest, so that the shearing force at plastic flow fails to be independent of normal pressure by at least 900-fold. Furthermore, the rate of increase of plastic shearing stress with normal pressure itself increases with pressure, the slope of the curve at the maximum pressure being approximately seven times as great as initially.

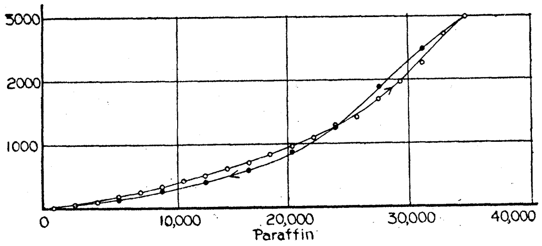

FIG. 6. The curve for paraffin of shearing stress in kg/cm² (ordinates) at plastic flow against mean hydrostatic pressure in kg/cm² (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure.

In addition to the broad features of the phenomenon just discussed, a number of other considerations are necessary before the complete significance of the results can be estimated. These other features are perhaps best suggested by a description in detail of the experimental procedure. The specimen as originally placed in the apparatus was usually, in the case of the metals, in the form of a disk of approximately the diameter of the piston and of convenient thickness, usually somewhere between 0.010 and 0.030 inch. For nonmetallic elements, a disk was also used when possible, made by compressing the powdered material into a proper form. In some cases the powdered material was placed directly on the piston, and kept in place by a narrow paper collar. The first stage in the experiment consisted of an initial application of pressure, usually somewhere between 10,000 and 30,000 kg/cm^2, depending on the nature of the material. The anvil was then rotated back and forth until a steady value of the rotating force was reached; this steady value was always reached from below, the force rising toward an asymptotic value, and the variation during the attainment of the steady value might be as much as 100 percent. The rotation was back and forth through an angle of about 35°, and sometimes a dozen alternations were necessary before the steady value was reached. Pressure was then released to zero, and regular readings were begun. Each point, plotted as in Figs. 3, 4, and 6, is the mean of readings for the two directions of rotation. There usually were consistent differences in the readings for the two directions, the magnitude of which depended on the nature of the material; the softer metals gave very consistent readings in the two directions, whereas with the harder nonmetals, such as graphite, the difference might be as much as 30 percent, or occasionally even more. The reading for one direction of rotation was itself a complicated thing, the turning force passing through a regular pattern of variation. The force to start rotation was usually not the same as the final force; during perhaps the first 10° of the rotation the force would rise from below or fall from above to an asymptotic value which persisted rather closely during the last 25°. It is the mean of the asymptotic values which is plotted in the figures. Sometimes the pattern of variation was more complicated, such as rising to a maximum, falling to a minimum, and then rising to a steady value. In the case of most metals the total range of variation was of the order of 10 percent, but the variation might be much larger for brittle nonmetallic elements.

The initial variations on reversing direction of rotation are doubtless connected with the setting up in the disk of some sort of structure depending on the direction of rotation. The amount of distortion required to reach the steady condition is very considerable, corresponding to a lateral displacement by shear of one face of a cube with respect to the opposite face by an amount of the order of 20 times the side of the cube, the displacement corresponding to the full rotation of 35° being of the order of 60 times the cube side. What the structure is under such extreme conditions it is not easy to say; that there must be more left of the undistorted crystal structure than one might be at first inclined to admit is shown by the fact that the material is capable of exhibiting the same polymorphic transitions that it does under hydrostatic pressure. Doubtless while the rotating force is attaining its steady value there is a reorientation of the planes of slip within the crystal. Recrystallization does not take place in such a direction, however, as to give slip planes in such locations as to reduce the rotating force to a minimum. This was strikingly shown by several experiments in which the disk was initially a piece of single crystal with the slip planes parallel to the face of the pistons; such experiments were made with bismuth, antimony, zinc, and Ceylon graphite. The seasoning effects in these cases are abnormally high, that is, rotation is exceedingly easy as long as slip may take place on planes parallel to the face, but this initial structure is speedily broken up, and the rotating force rapidly rises. This effect was especially marked with single crystal Ceylon graphite, for which the rotating force rose 15-fold during break-up of the regular laminated structure.

The speed of rotation was usually of the order of 10° per second, but no important variation of the force was observed within rather wide limits of variation about this value. In this respect there is a complete contrast with the viscous distortion of a liquid, showing that plastic flow in a solid is a different kind of phenomenon. The fact that the force is independent of the speed is, as already mentioned, a strong argument for believing that the rise of temperature at the surfaces of slip is not an important factor.

There was the greatest difference conceivable between the behavior of an ordinary metal and many of the brittle nonmetals. Rotation in the case of the metals was almost always accomplished quietly and smoothly, but the nonmetals usually emitted grinding and snapping noises, and the rotating force was often very jerky; it might hang at an approximately constant level, but with more or less periodic drops to a smaller value, rapidly climbing back, or it might periodically jump to a higher value, and almost at once snap back.

In recording the readings the pattern of variation of the rotating force as well as the final asymptotic value was almost always noted, recording the turning points before the steady value was reached. Similar readings were made at regular pressure intervals up to the maximum, and back to zero again. There were almost always differences between the curves with increasing and decreasing pressure. This is to be expected under the conditions; during increasing pressure the disk is being squeezed out laterally from between the pistons and this is being resisted by radial friction. This frictional effect, of course, does not reverse on decrease of pressure; the disk does not suck back into itself material from beyond the pistons, but on the contrary contracts more or less elastically. The elastic deformations in some of the materials under 50,000 must be rather high, and it was in fact not uncommon to find radial cracks in the disk after release of pressure. Further, the pistons almost always suffer some permanent damage from the maximum pressure. In view of these important elements of irreversibility, the degree of accord between increasing and decreasing runs was in general better than I would have expected, and gives evidence that the curves give information about some intrinsic property of the material.

After return to zero pressure the apparatus was dismounted, the thickness of the disks measured, and notes made about the general appearance of the disk and the nature of the permanent damage to pistons and anvil. All in all, it will be seen that the complete record of a single run, although it might occupy less than one hour, embraces many complicated factors, and an exhaustive study of all the significant results which might be extracted from the experiments would be very time consuming. In the following an attempt is made to touch on only the most striking features; critical points in the curves and the increase of shearing stress for plastic flow with normal pressure. In general the materials which are weak and soft under ordinary conditions offer the least resisting force to rotation, and are squeezed out to the thinnest disks.

Measurements were made altogether on 57 elements. About 40 of these were measured with two different pieces of apparatus. The first apparatus differed in details that need not be discussed from the final apparatus shown in Fig. 2; the construction was such that sometimes at the higher pressures part of the force to produce rotation was used in overcoming friction in the apparatus itself. When the importance of this was realized, all the measurements were repeated with the final apparatus, the construction of which allows no friction except between the anvil and disks. The measurements with the first apparatus were not entirely valueless by any means, but afforded welcome confirmation of the main features of the results obtained with the final apparatus.

Extreme purity in the material appears not to be an important factor. This was checked by measurements on copper of commercial and of 99.999 percent purity. This is what might be expected in view of the probable high degree of disorganization of the material while flowing. This is to be contrasted with the fact that the initial yield in a single crystal is highly sensitive to slight impurities.

A relatively large number of the curves show more or less sharp breaks in direction. The interpretation of these breaks requires discussion. In a number of cases I have verified by independent volumetric analysis that these breaks correspond to ordinary polymorphic transitions which occur under pure hydrostatic pressure at a pressure not far from the mean pressure in the shearing experiments. The interpretation of the break in these cases is thus obvious; furthermore the conclusion can be drawn that the transition parameters are not greatly affected by the shearing force. In a number of cases, however, there are breaks in the curves which have not been checked by volumetric analysis. Some of these I hope to examine later by the volumetric method. If the result is negative, it is still possible that there is a polymorphic transition with change of volume too small to detect; many cases of this character should be amenable to an examination by the method of discontinuity of electrical resistance. Until this exami-

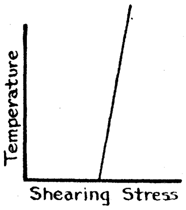

FIG. 7. A possible relation between transition temperature and shearing stress. If curves of this type exist, then there may be transitions produced by shearing stress which cannot be produced by hydrostatic pressure alone.

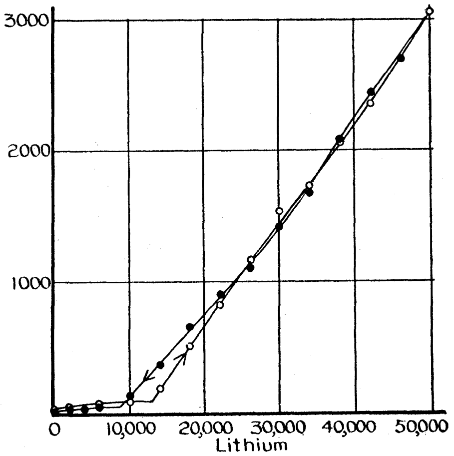

FIG. 8. The curve for lithium of shearing stress in kg/cm^2 (ordinates) against mean hydrostatic pressure in kg/cm^2 (abscissae). Open circles obtained with increasing pressure, solid circles with decreasing pressure.

nation has been made, the correct explanation of these breaks must remain in abeyance. Several possibilities in addition to polymorphism must be recognized. In the first place it is barely possible that a break may arise from a sudden change in the mechanism of slip; a corresponding phenomenon is known in single crystals of iron, for example, where beyond a certain stress, slip begins on a new set of planes. The break in all cases of this sort must be a break with decreasing slope of the rotating-force *vs.* pressure curve. There are a few such breaks, but there are also breaks with increasing slope, to which this suggestion cannot apply. It does not seem to me very probable, however, that crystallographic slip planes can play a very important part when the material is so thoroughly disorganized as here, and in any event I should expect the corners of the break to be rounded. A second possibility which I think must be recognized is that the break may mean a new kind of transition, produced by shear only. It is true that all ordinary transitions are affected by shearing stress; if the shearing stress acting on such systems is varied continually to the vanishing point, the transition temperature at a constant hydrostatic pressure varies continuously toward a limiting value. But it need not follow conversely that all transitions which take place under a definite shearing stress at a definite temperature permit a continuous variation of shearing stress to zero; it is conceivable that the relation between shearing stress and temperature might be like that indicated in Fig. 7. This would mean that under shearing stress a type of transition could be brought about not realizable by ordinary methods. Such a possibility does not seem to have been hitherto discussed; it would obviously be difficult to establish under ordinary conditions. But I believe that the possibility must be kept in mind; a case in point is lithium, the curve for which is given in Fig. 8. There is a break in the curve at a mean normal pressure of about 12,000 kg/cm^2. But both the volume and the electrical resistance of lithium have been measured up to hydrostatic pressures of 20,000 and no ordinary transition has been found. It may be that there is an ordinary polymorphic transition at pressures higher than 20,000 at room temperature, and that this pressure is displaced by an unusually large amount by shearing stress, or it may be that there is an ordinary transition not far from 12,000 and that it is suppressed under ordinary conditions by internal viscosity, or finally I believe that the possibility must be kept in mind that we have here a new kind of transition, produced by shear only.

There follows now a brief summary of the results for 57 elements; those showing breaks are given first. The order of presentation appears unsystematic; it was mostly determined by similarities in the nature of the shearing curves, which are not immediately related to more familiar properties. A number of the elements have been found by ordinary volumetric methods to have polymorphic transitions; the detailed discussion of the thermodynamic parameters of these transitions will be given in another paper.

A. Elements showing breaks

Lithium. The curve has already been given in Fig. 8. The experiment was repeated with 3/8-inch pistons, giving a break of the same character and at nearly the same location, and with the same value for the shearing strength, 850 kg/cm^2, at the maximum pressure reached with the 3/8-inch pistons, which was 22,000 kg/cm^2. The shearing strength at 50,000 was 3050 kg cm^2. The almost linear increase of rotating force with normal pressure beyond the break is a notable feature; in so soft a material as lithium the flow must be homogeneously distributed throughout the entire mass, so that this means an almost linear increase with pressure of shearing stress at plastic flow.

Strontium. There are two distinct breaks in direction, both with increasing and decreasing pressure, the interpretation of which probably is a polymorphic transition at a mean pressure in the neighborhood of 25,000 kg/cm^2. The existence of this transition was not checked by volumetric analysis. Beyond the transition, shearing force against pressure is concave upwards, reaching a maximum value of 2500 kg/cm^2 at 50,000. This means an enormous increase over the value at atmospheric pressure, since strontium is a relatively soft metal.

Calcium. There appear to be two slight breaks in direction, both with increasing and decreasing pressure. The breaks are so slight that probably no significance would have been attached to them if they had not been qualitatively similar to the much more pronounced breaks in the chemically similar strontium. There is probably a transition at a mean pressure of 30,000 kg/cm^2; the volume change at the transition must be small because it was not found by volumetric analysis at $-80°$. At room temperature the volumetric exploration was not complete. The shearing strength at 50,000 was 1800 kg/cm^2.

Barium. The relations are very much like those for calcium; there are two slight breaks both with increasing and decreasing pressure, which probably mean a transition near 30,000. Again the transition was not found by volumetric analysis either at $-80°$ or at $+150°$, so that if the transition exists its volume change must be small, or else the pressure displacement by shearing stress must be abnormally large. The shearing strength at 50,000 was 1200 kg/cm^2.

Cadmium. This metal I have already found to be polymorphic with two transitions at room temperature near 3000 and 6000 kg/cm^2. The transitions are unusual in that they could be detected only in single crystals of pure metal; volumetric analysis even with the extremely sensitive apparatus for measuring linear compressibility gave negative results on polycrystalline material. It is therefore very gratifying that with the shearing apparatus, by using 0.5-inch pistons to a maximum pressure of 17,000 kg/cm^2, very definite breaks were found at a mean pressure of 4300 kg/cm^2, corresponding closely enough to the mean of the two pressures above. The method does not have a high enough resolving power to split the two transitions. The experiment was repeated with essentially the same results. It is probable that there are no other breaks up to 50,000, but this is not certain because the measurements to 50,000 with 0.25-inch pistons were made only with the first form of apparatus which is somewhat uncertain because of friction.

Zinc. Because of the chemical and crystallographic similarity of zinc to cadmium similar transitions would be expected, but none have hitherto been found. The shearing experiments, however, showed very marked anomalies at the high pressure end of the range, indicating a probable transition in the neighborhood of 40,000. The experiment was repeated with essentially the same results. The shearing strength at 50,000 was 1800 kg/cm^2 for the first set-up, and 2200 on repetition, enormously higher than the upper limit for severely worked zinc crystals under ordinary conditions. At the low pressure end of the range the curve is concave toward the pressure axis with a rather unusually sharp knee in the neighborhood of 10,000, probably marking the beginning of flow throughout the body of the metal, with a closer approach to constant shearing force beyond this point than shown by most metals.

Vanadium. This material had about 5 percent impurity, and was from the same batch as the former compressibility specimens.[2] Vanadium begins to verge on the nonmetallic in its shearing

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[2] P. W. Bridgman, Proc. Am. Acad. **62**, 219 (1927).

properties; rotation did not always take place smoothly, and there were occasional snapping noises. The steel pistons were more scarred than usual, with distinct welding on limited areas. There were very definite breaks in direction both with increasing and decreasing pressure, meaning probably a transition at a mean pressure of 37,000 kg/cm^2 and a mean shearing stress of 7800 kg/cm^2. The shearing strength at 50,000 was 13,000 kg/cm^2, well toward the top of the materials measured. No volumetric analysis was attempted.

Manganese. This is the same material as that whose compressibility and electrical resistance under pressure have already been measured.[3] It was in the form of rods about 0.020 inch in diameter, which were laid together in the form of a grid compactly covering the pistons. There was little or no self-welding or welding to the steel. The rotation was almost perfectly smooth, being thus more metallic in this respect than vanadium. There were very definite breaks in direction (increase of slope) both with increasing and decreasing pressure at a mean hydrostatic pressure of 20,000 kg/cm^2 and mean shearing stress of 3300 kg/cm^2. Beyond the break the shearing force increases nearly linearly with pressure, with only slight concavity toward the pressure axis, to a maximum of 4500 at 50,000. This is probably still far below the point of homogeneous distribution of shearing stress.

Antimony. This has already been mentioned; the shearing force passes through a flat maximum at 40,000 with a decline of a few percent at 50,000. The highly probable interpretation is a transition in the neighborhood of 50,000 analogous to the known transition of bismuth. There was practically no welding to the steel. The shearing strength at 50,000 was 4400 kg/cm^2.

Tellurium. This shows the phenomenon of polymorphism very strongly developed—a strong maximum, decrease, and then a strong rise again, indicating probably two transitions at a mean hydrostatic pressure of 39,000 kg/cm^2 and mean shearing stress of 3000 kg/cm^2. The high pressure modification therefore has a lower shearing strength than the low pressure modification. A more detailed discussion will be found in the paper on volumetric analysis. This is a good example of the value of the shearing method to supplement the volumetric analysis; a preliminary volumetric analysis did not disclose anything definitely at room temperature, the volume change being beyond the end of the range at this temperature, but after the very striking evidence given by the shearing measurements the volumetric measurements were repeated and the effect easily found at higher temperatures.

Iodine. The results with this were doubtful. Near 50,000 the curve with increasing pressure rapidly becomes flat, and there is almost a maximum at 50,000. Because of the extreme softness of iodine the shearing stress must have become homogeneously distributed long below 50,000, and the interpretation of a transition seemed plausible. But this interpretation was made doubtful because the curve with decreasing pressure did not reproduce the effect, but was approximately linear with pressure over the entire range. This was not by any means a conclusive consideration because it has been my experience that characteristic features have a tendency to become smeared out with decreasing pressure. The interpretation of a transition was made certain by the volumetric analysis, which showed a small volume discontinuity. This is one of the few examples where the shearing method has given less definite indications than the volume method; as already remarked there is no reason why the shearing method should not sometimes fail altogether.

Lanthanum. The original material was massive metal, obtained from Mackay, and said to be of about 98 percent purity. This shows distinct breaks with an increase of slope of between two- and threefold, both with increasing and decreasing pressure, at a mean hydrostatic pressure of 12,000 and a mean shearing stress of 700 kg/cm^2. It is therefore probable that there is a transition near this point. Measurements had been previously made to 12,000 both of compressibility and of electrical resistance without disclosing any transition. Not enough material was available for a volumetric analysis to high pressures. Beyond the transition, the curve of shearing force is concave toward the pressure axis, reaching 3100 kg/cm^2 at a hydrostatic pressure of 50,000.

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[3] P. W. Bridgman, Proc. Am. Acad. **64**, 62 (1929).

Cerium. This has already been found to be polymorphic, the transition pressure at room temperature being about 7500 kg/cm². The shearing measurements showed a very sharp break, with decrease of slope practically to zero, at a mean hydrostatic pressure of 13,000 and a mean shearing stress of 2300 kg/cm². I think there can be no doubt that the transition is the same as found before; the rather unusual feature is the large effect of the shearing stress on the mean hydrostatic pressure of transition. The high pressure modification has, at the transition point, a lower shearing strength than the low pressure modification. Beyond the transition, the shearing strength rises, at first convex toward the pressure axis, then a point of inflection and reversal of curvature, reaching a maximum shearing strength of 3800 kg/cm² at 50,000.

Erbium. The original material was the powdered metal, obtained from Mackay, and must have contained a fairly large quantity of the oxide. There was much self-welding of the powder after the run; this method may perhaps make it possible to get the massive metal from the powders of some of the other rare earths. There was a comparatively small break in the curve of shearing force, with decreasing slope, at a mean hydrostatic pressure of 10,000 kg/cm² and a mean shearing stress of 900 kg/cm². It is perhaps possible, although I do not think it highly probable, that this break may mean a transition.

To a not bad first approximation, the shearing force is linear against pressure over the entire range, rising to 6400 kg/cm² at the maximum pressure of 50,000.

Thallium. There are two distinct breaks, both with increasing and decreasing pressure. The transition will be discussed in much greater detail in the volumetric paper. It is unusual that the pressure of transition is here markedly depressed by shearing stress, instead of being raised, as in the case of cerium, for example. The mean shearing strength at the transition was only 350 kg/cm², thallium being a very soft metal. The curve of shearing strength rises more rapidly beyond the transition, the high pressure form having the higher shearing strength, and at 50,000 reaches 1100 kg/cm².

Bismuth. Results for this have already been shown in Fig. 3 and details will be given in the volumetric paper. Modification III has a much lower shearing strength than I, whereas the high pressure modification IV has a considerably higher strength than III. The shearing strength of IV at 50,000 is 1660 kg/cm².

Thorium. The material was obtained from massive 4-mm rods of high purity from the Westinghouse Lamp Works. Four sets of experiments were made; the first three with the original apparatus gave definite evidence of breaks, but the sharpness of the results was obscured by friction in the apparatus, and there was also trouble from breaking of the pistons. The last experiment with the final frictionless apparatus confirmed the provisional results. There are two distinct breaks, both with decrease of slope, so that the high pressure modification must have a lower shearing strength than the low pressure modification. The breaks occur at a mean pressure of 12,000 kg/cm² and a mean shearing strength of 2500 kg/cm². Previous measurements of compressibility and electrical resistance under pure hydrostatic pressure had shown no transition to 12,000. The exploration under pure hydrostatic pressure has not been extended further. Beyond the transition point the shearing stress increases nearly linearly with pressure, reaching 5500 kg/cm² at 50,000.

Tin. This is one of the very soft metals; the shearing was throughout surprisingly easy and also perfectly smooth. There should be some commercial use in bearings subject to very high pressures. There is a distinct break in the curve of rotating force, with decrease of slope, at the same normal pressure, 10,000 kg/cm², both with increasing and decreasing pressure. The shearing force is 230 kg/cm² at the break. Previous measurements of compressibility and electrical resistance have shown no polymorphic transitions up to 12,000, and volumetric analysis by the new method showed nothing up to 50,000. It may be, therefore, that this is not an ordinary sort of transition. The change of slope is such that a possible explanation would be slippage on a new set of planes. Beyond the break the curve is slightly S shaped, with a maximum hysteresis between ascending and descending branches of about 6 percent. The shearing strength at 50,000 was 770 kg/cm^2.

Yttrium. The shearing curves show a break which possibly may mean a transition. This is doubtful however, so that I have preferred to give it in the next section, where fuller details will be found.

Praseodymium. This was material of high purity for which I am much indebted to Dr. H. C. Kremers. Initially the shearing curve rises steeply, as would be expected of one of the harder metals. Near 10,000 kg/cm^2, however, where the shearing force is 750 kg/cm^2, there is a rapid decrease of slope, and the curve runs nearly horizontally up to nearly 30,000, where it turns again and rises rapidly to a shearing force of 2240 kg/cm^2 at 50,000. The same essential features are retraced with decreasing pressure, but with considerable hysteresis and rounding of the corners. This is one of the more striking of the transitions found, with a very drastic change of properties from a comparatively hard metal at low pressures to a modification stable at high pressures which is among the softest of those found.

B. Elements without breaks

We turn now to those elements which show no breaks and hence probably have no polymorphic transitions. The arrangement here is in order of atomic weight.

Beryllium. The rotation was perfectly smooth. The curve of shearing force against pressure was slightly S shaped, that is, at first convex toward the pressure axis, then a point of inflection and finally concavity, with very little hysteresis. The shearing strength at 50,000 was 7400 kg/cm^2.

Boron. The original material was amorphous powder, which experienced no appreciable self-welding. This was the hardest and most brittle of all the elements tried; rotation was accompanied by much jumping and loud snapping. In order to save the steel anvil, only a few readings were made with increasing pressure. Rotating force against pressure is convex toward the pressure axis for the entire range. The shearing force at a pressure of 50,000 kg/cm^2 was 18,000 kg/cm^2. As already remarked, the figure 18,000 thus sets a lower limit for the shearing strength of the hardened steel pistons.

Carbon. A rather large number of experiments were made with graphite. A number of these experiments were made with preliminary forms of apparatus before the evolution of the final form. Always I had a hope that the permanent change to diamond might be induced, but such never occurred. In the final measurements both single crystal graphite, with the cleavage planes parallel to the faces of the piston, and ordinary massive Acheson graphite were used. As already remarked, rotation of the single crystal was at first surprisingly easy, until the crystal structure was broken up. Then it settles down into a final behavior like the ordinary massive graphite. Up to a certain pressure, in the neighborhood of 12,000 kg/cm^2, rotation is smooth and metallic; at this point there is a break in the curve with the beginning of snapping and jumping, which gets steadily more violent, until at the maximum pressure the jumps are 50 percent of the average reading. The graphite acts like an abrasive on the steel. The graphite itself emerges as a fine powder with no self-welding. The curve of rotating force against pressure is nearly linear, slightly S shaped in the normal direction, with a maximum width of the hysteresis loop averaging about 5 percent of the maximum. The shearing strength at the maximum pressure of 50,000 is 10,000 kg/cm^2. Explorations were also made by the volumetric method, but no discontinuities were found up to 50,000.

Sodium. The curve of rotating force for sodium is highly remarkable. At the lowest pressures, rotation was so easy as to be almost below the limits of measurement with the particular dimensions of apparatus; this is as is to be expected because of the great softness of sodium. But the curve rapidly rises at an accelerated pace, and is convex toward the pressure axis over its entire extent. This must mean a very unusually great increase of shearing strength with pressure. With decreasing pressure there is unusually large hysteresis, the maximum width of the loop being nearly 20 percent of the maximum effect. This perhaps is not surprising because the irreversible geometrical phenomena must be unusually prominent with so soft a material. The general aspect of the curve is much like that already found for lithium, with the difference that the sharp break in direction of lithium is here smeared out into a region of unusually great curvature. The maximum shearing strength at 50,000 was 5200 kg/cm^2, against 3000 for lithium, and this in spite of the fact that initially sodium is much softer than lithium. Behavior under shearing stress therefore appears to be another phenomenon in which the relative position of the alkali metals becomes reversed at high pressures; I have already found that the order of the melting points and of the thermal expansions reverses at high pressures.

Magnesium. This metal behaves more like what our preliminary discussion suggested we might naturally expect than nearly any other substance. Shearing is perfectly smooth, with very little difference between maximum and minimum rotating force at any fixed pressure; furthermore there was very little hysteresis between increasing and decreasing pressure. In the very early stages the curve of rotating force is slightly convex toward the pressure axis, then there is an inflection at about 2000 kg/cm^2 normal pressure, and from here on concavity, with a closer approach to a horizontal asymptote than usual. Thus at 12,000 kg/cm^2 pressure the shearing strength was 840 kg/cm^2, and at 24,000, 980. In the final measurements, the 0.5-inch pistons were used and pressure was not carried higher than 24,000, but in a couple of preliminary experiments it was found that there is probably no transition up to 50,000.

Aluminum. This gives perfectly smooth rotation, with little variation of force and little hysteresis. There was some welding of the aluminum to the steel. The curve of rotating force is composed approximately of two linear parts, joined by a region concave toward the pressure axis. At 12,000 pressure the shearing strength was 1100 kg/cm^2, and at 50,000, 3200.

Silicon. The initial material was massive silicon of high purity which I obtained 10 years ago from the National Physical Laboratory at Teddington. Rotation was accompanied by grinding noises and by jumping, from the lowest pressures over the entire range. There was no self-welding, but the silicon was compressed into an apparently coherent cake, which fell apart on the slightest handling. There was much abrasive action on the steel. Rotating force against pressure is gently concave upwards over the entire range, with a shearing strength of 9000 kg/cm^2 at 50,000. The measurements were repeated with essentially the same results.

Phosphorus. In the qualitative part I have already described how violet phosphorus is transformed by shearing into the denser variety of black phosphorus; this is the only method yet found for changing violet to black. Measurements on black phosphorus disclosed no further transitions up to 50,000. Black phosphorus under atmospheric conditions is a greasy feeling substance, much like graphite, but even softer. The rotation was not quiet, but from almost the lowest pressure there was continuous snapping, and there was distinct abrasive action on the steel pistons. At any fixed pressure, the steady readings corresponded to the maximum rotating force, with momentary jumps to lower values. With increasing pressure the curve of rotating force is gently concave upward; the decreasing curve shows much hysteresis, and is of the conventional S shape. The shearing strength at 50,000 was 8300 kg/cm^2.

Sulfur. A great many measurements were made on sulfur, both with the volumetric and the shearing apparatus, because it was my strong conviction that there must be a metallic form of sulfur analogous to black phosphorus; this, however, was never found. Both ordinary crystalline sulfur and the amorphous modification obtained by quenching hot liquid sulfur into water were investigated. There are still some unsettled questions as to what happens. On one occasion, starting with amorphous sulfur as the initial material, there was quite a violent detonation on rotating at 50,000. On another occasion, starting with crystalline sulfur, there was a mild detonation at 25,000 on the seasoning application of pressure, but from here on everything went smoothly. On another occasion with crystalline sulfur as the initial material, the entire shearing program was carried through with no detonation. I am inclined to think that the detonations are due to the presence of a greater or smaller amount of oxygen adsorbed onto the sulfur, since the qualitative experiments showed an unusual instability of the oxides. At any rate, I think there can be no doubt, from the appearance of the end product, that the original crystalline material is converted by shearing force into the rubber-like, sticky, amorphous variety. The volumetric experiments with nearly pure hydrostatic pressure showed no such transformation.

Shearing of sulfur was not smooth throughout, but beyond 25,000 was accompanied by scraping noises and slight chattering. The final curve is an unusually close approach to a straight line, with very gentle concavity toward the pressure axis, and a hysteresis loop with a maximum width of not more than 5 percent of the maximum effect. The shearing strength at 50,000 was 7000 kg/cm^2, enormously higher than the shearing strength under normal conditions.

Titanium. The original material, for which I am indebted to the Research Laboratory of the Westinghouse Electric Company, was said to contain about 5 percent impurity; it was very brittle, with a glass-like fracture, which reminded one more of the intermetallic compounds than of a metal. In spite of this, it permitted shearing much more quietly than anticipated, there being only very little snapping or jumping. There was distinct abrasive action on the steel parts. The curve of rotating force is convex toward the pressure axis over the entire extent, both with increasing and decreasing pressure, with a maximum width of the hysteresis loop of 10 percent of the maximum effect. The shearing strength at 50,000 was 13,000 kg/cm^2, which is thus among the highest.

Chromium. The material was from Kahlbaum, made by the Goldschmidt process, from the Laboratory stock, and was evidently made a number of years ago. In spite of its brittleness, shearing was perfectly smooth and quiet, with little variation of force, and slight width of the hysteresis loop. There was, however, marked abrasive action on the steel. The curve of rotating force is gently concave toward the pressure axis, with a slight initial hook. The shearing strength under 50,000 was 12,300 kg/cm^2.

Iron. This material was the purest Armco iron. It rotated perfectly smoothly. Up to a pressure of 25,000 the curve of rotating force against pressure was much more markedly S shaped with increasing than with decreasing pressure; above 25,000, the curve is nearly linear and without hysteresis. The shearing strength at 42,000 (the maximum in this experiment) was 10,600 kg/cm^2; in view of the softness of the original material it was a surprise that this figure was so high.

Nickel. This sheared perfectly smoothly. The curve with increasing pressure was much more notably S shaped than with decreasing pressure, with a point of inflection near 30,000. Above 30,000 there is marked concavity toward the pressure axis. The shearing strength at 50,000 was 8700 kg/cm^2.

Cobalt. This sheared perfectly smoothly. The curve of rotating force in broad outline is gently S shaped with little hysteresis. Near 40,000 there appears to be a slight break in direction, with decrease of slope. This was found both with increasing and decreasing pressure, and I suspect that it might have been better to list this substance in the first group, among those with polymorphic transitions, but marked doubtful. The shearing strength at 50,000 was 6300 kg/cm^2. Notice the decrease in shearing strength in the series Fe, Ni, Co, or for that matter in the series Ti, V, Cr, Mn, Fe, Ni, Co.

Copper. Measurements were made both with commercial copper and with 99.999 percent electrolytic copper, with no essential difference. Shearing is perfectly smooth; the hysteresis is rather larger than usual, and rather less with electrolytic than with commercial copper. The curve of rotating force is convex toward the pressure axis over nearly its entire extent, with a slight hook near the origin. The shearing strength is 4700 kg/cm^2 at 50,000.

Germanium. The material was highly purified, for which I am indebted to Professor Dennis of Cornell. Shearing was not smooth, and there was so much fluctuation in the force that it was difficult to estimate what the best mean value was, but paradoxically there was no noise. The steel pistons were hardly touched, and the general behavior was surprising in view of the pronounced glass-like nonmetallic character of the original material. The curve of rotating force is gently concave toward the pressure axis over the entire extent. The shearing strength at 50,000 was 5700 kg/cm^2.

Arsenic. This material was originally from Kahlbaum. The first set-up was with powdered material that had been exposed to the air for several days. This detonated at 20,000 on the first application of pressure, doubtless due to the oxide. The next set-up was with freshly cleaved flakes from a single crystal that I had left from previous work. Even with this there was a very slight detonation at 30,000. This probably had the effect of eliminating the slight amount of oxygen; the measurements were continued with regular results, and at the conclusion a residue of metallic arsenic was found as expected. Shearing was not smooth, but there was snapping and jumping, continually getting more violent beyond 5000. There was no abrasive action on the pistons, which were practically untouched. The curve of rotating force is gently S shaped, with the point of inflection at 5000, and little hysteresis. The shearing strength at 50,000 was 11,200 kg/cm^2. With so high a figure as this one might expect more action on the steel.

Previous work with single crystal arsenic[4] had shown some anomalous effects associated with one of the directions of the crystal. One might have expected some reflection of this in the shearing experiments, but none was found. One might also have expected high pressure polymorphism, analogous to the polymorphism of bismuth and the probable polymorphism of antimony.

Selenium. A number of different measurements were made on this; it is an interesting substance both because of the possibility of an irreversible transition like black phosphorus, and also because it normally exists in two forms, an amorphous and a metallic form with large difference of density. The amorphous material used in these experiments was amorphous material from Kahlbaum; the metallic was material purified in this laboratory several years ago by Dr. W. E. Danforth, Jr., by very slow distillation over a period of several weeks. No appreciable difference could be found in these experiments between the two modifications. In both cases shearing is smooth over almost the entire range, there being slight squeaks of protest only occasionally. The curves are gently concave toward the pressure axis, with only a slight hook at the origin, and with very small hysteresis. The shearing strength at 50,000 was found to be 5500 kg/cm^2 for the metallic and 5600 for the amorphous variety, essentially the same. Dr. Jacobs was kind enough to make an x-ray examination of the various products. The metallic showed at the conclusion of the experiments the same lines and of very nearly the same sharpness as the initial material. This result is of itself of much interest as showing that the grain size even under such extremely drastic conditions is not reduced below the value necessary to give fairly well-defined x-ray pictures. The amorphous material, on the other hand, showed a distinct alteration after the shear, there now appeared the lines of the metallic selenium, but less sharp. It would appear, then, that amorphous selenium is converted into metallic by shearing. This conversion must take place at a very low shearing force, because in the endeavor to locate this transition, which of course was expected, I made the measurements on amorphous selenium with no initial seasoning, and in spite of this found no evidence of change at the lowest measured point, where the hydrostatic pressure was 4000 and the shearing force 400 kg/cm^2. On the other hand, the volumetric exploration showed no transition of amorphous to metallic selenium up to 50,000.

Yttrium. The material was finely powdered metal from Mackay. Shearing was quiet up to 35,000, from here on there was slight noise and jumping. The powder was self-welded by the shearing into a coherent disk. To a first approximation the curve of shearing strength against pressure is linear, slightly concave toward the pressure axis over the entire range, and with hysteresis rising at the maximum to 10 percent of the maximum effect. The shearing strength at 50,000 was 4300 kg/cm^2. Superposed on this there is a small but definite break, both with increasing and decreasing pressure, at a mean pressure of 16,000 kg/cm^2 and a mean shearing stress of 1600 kg/cm^2. It is not unlikely that the breaks mean a transition.

Zirconium. This material was originally from Eindhoven, left from previous measurements of compressibility and resistance.[5] It sheared perfectly smoothly. The curve of rotating force with increasing pressure was markedly S shaped; the curve was also S shaped with decreasing pressure, but not to so great an extent, with a maximum width of the hysteresis loop of 15 percent of the

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[4] P. W. Bridgman, Proc. Am. Acad. **68**, 39 (1933); **68**, 109 (1933).

[5] P. W. Bridgman, Proc. Am. Acad. **63**, 347 (1928).

maximum effect. The shearing strength at 50,000 kg/cm^2 was 4400 kg/cm^2. This is perhaps not as great as might be expected in view of the initial hardness. The curvature is greater than usual, with a closer approach than usual to the ideal conditions of shearing strength independent of pressure.

Columbium. Shearing was perfectly smooth. The curve of rotating force with increasing pressure was markedly convex toward the pressure axis over the entire range; the curve with decreasing pressure was slightly S shaped, with a maximum width of the hysteresis loop of 20 percent of the maximum effect. The mean curve for both increasing and decreasing pressure is also markedly convex toward the pressure axis over the entire range. The shearing strength at 50,000 was 9000 kg/cm^2.

Molybdenum. Shearing was perfectly smooth. Both increasing and decreasing curves were convex toward the pressure axis over the entire range, with a maximum hysteresis of 10 percent of the maximum effect. The shearing force at 50,000 was 12,100 kg/cm^2, one of the highest, as might be expected.

Ruthenium. Shearing was perfectly smooth; the pistons were burnished after the run, but there was no abrasive action. The curve of rotating force was slightly S shaped both with increasing and decreasing pressure, with a hysteresis amounting to 7 percent at the maximum. The shearing force at 50,000 was 9600 kg/cm^2.

Rhodium. Shearing was perfectly smooth; the pistons were burnished with some welding of the rhodium to them. The curve of rotating force was nearly linear over its entire extent, with a slight hook at the origin, and maximum hysteresis of 9 percent. There were various slight irregularities in the curve, which probably were of no significance. The shearing force at 50,000 was 8900 kg/cm^2.

Palladium. Shearing was perfectly smooth, with nearly constant readings at any one pressure. The curve of rotating force was markedly concave toward the pressure axis over the entire range, with a maximum difference between increasing and decreasing readings of 4 percent. The shearing strength at 50,000 was 5600 kg/cm^2 and at 25,000, 4100. Notice the same decrease of shearing strength in the series Ru, Rh, Pd as in Fe, Ni, Co.

Silver. Shearing was perfectly smooth, but with more variation of the force than usual during the process of attaining a steady value. The curve of rotating force with increasing pressure was slightly concave toward the pressure axis with a slight hook at the origin. The decreasing curve showed a rather large drop on starting back, which probably is of no significance because it was not found with the first apparatus. The shearing strength at 50,000 was 4700 kg/cm^2.

Indium. This is one of the very soft metals, and the rotating force was throughout very small. The increasing and decreasing curves differed only slightly in absolute terms, but cross a couple of times. The crossing is probably without significance, because with the first apparatus crossing was also found, but in the reverse order. Both pieces of apparatus gave mean curves gently convex toward the pressure axis over their entire extent. The shearing strength at 50,000 was 750 kg/cm^2.

Tantalum. Shearing was perfectly smooth. There was distinct welding to the steel pistons and tearing of the steel surfaces. The curve of rotating force is very markedly S shaped with increasing pressure, with the region of pronounced and maximum curvature near 20,000. The S shape was not so prominent with decreasing pressure. The maximum width of the hysteresis loop was 8.5 percent of the maximum effect. The shearing strength at 25,000 was 7700 kg/cm^2 and at 50,000, 11,500.

Tungsten. Shearing was perfectly smooth. There was considerable scratching of the pistons, and the tungsten lost its original coherent form and was broken up into small flakes, showing little if any self-welding under these conditions. This is not surprising in view of the high melting point. The curve of rotating force was markedly convex toward the pressure axis over the entire extent with increasing pressure, but had a slight S shape with decreasing pressure, and a maximum hysteresis of 18 percent. The shearing stress at 50,000 was 12,700 kg/cm^2, one of the highest, as was to be expected.

Rhenium. The material was finely powdered metal from Mackay, of unknown purity. Shearing was quiet, with much variation of force. Self-welding takes place to a very appreciable extent, the end-product consisting of flakes of coherent metal. The curve of shearing force is gently convex toward the pressure axis over the entire length, with a maximum difference between ascending and descending branches of 3 percent. The shearing strength at 50,000 was 7500 kg/cm^2.

Osmium. The original material was some electric lamp filaments, 0.020 inch in diameter, obtained a number of years ago from the General Electric Company, a product of the early extensive experimentation to find the best material for filaments. These filaments were highly crystalline and very brittle; they were broken into appropriate lengths and laid closely side by side on the pistons. Rotation was never smooth, but was only accomplished with noisy protest, and there were violent fluctuations in the rotating force. The pistons were deeply abraded. The curve of rotating force was almost linear against pressure, with slight convexity toward the pressure axis, and with inappreciable hysteresis. The shearing force at 50,000 was 17,400 kg/cm^2, nearly as high as for boron.

Iridium. The material was lengths of wire 0.030 inch in diameter, which had been previously used in compressibility and resistance measurements, laid side by side underneath the pistons. Rotation was perfectly smooth. There was no self-welding of the pieces of wire, and the pistons were burnished rather than scratched. The curve of rotating force is almost exactly linear, with very slight concavity toward the pressure axis, and a slight hook near the origin. Except at the very lowest pressure, readings with increasing and decreasing pressure were indistinguishable. The shearing stress at 50,000 was 8400 kg/cm^2; one might expect a figure near the top because of the proverbial hardness of iridium.

Platinum. Shearing was perfectly smooth, with little variation of force. The curve of rotating force was markedly concave toward the pressure axis with a slight hook at the origin. Beyond 15,000 the readings with increasing and decreasing pressure were indistinguishable; the greatest difference was at 6000, where the hysteresis amounted to about 8 percent of the maximum effect. The shearing stress at 50,000 was 5800 and at 25,000, 4100 kg/cm^2. Notice again the striking decrease in the series Os, Ir, Pt, and also the progression in curvature.

Gold. Shearing was perfectly smooth with little variation of force. The curve was markedly S shaped with increasing pressure, but much less pronounced with decreasing pressure, in fact the two curves cross, with a maximum difference between increasing and decreasing readings of 13 percent of the maximum effect. The mean curve is gently concave toward the pressure axis over its entire length. The shearing stress at 50,000 was 4500 kg/cm^2. The shearing strength of Cu, Ag, and Au at 50,000 are almost identical; the rather large initial differences, shown most strikingly by the great malleability of gold, thus are wiped out at high pressures.

Lead. This is one of the weakest and softest of the metals and gave low shearing forces as would be expected. Shearing was throughout perfectly smooth; the force rises approximately linearly with pressure, reaching 710 kg/cm^2 at 50,000 pressure. The existence of no polymorphic transition was checked by a volumetric exploration.

Uranium. This was massive material, obtained through Mackay, originally prepared by the late Professor James of New Hampshire State College, and said to be of high purity. It was not perfectly homogeneous in appearance, however, but seemed to contain some sort of inclusion. Two runs were made, the first sample appearing to be more homogeneous than the second. The shearing of the first was perfectly smooth, but the second showed a little jumping. The shearing strengths at 50,000 were, respectively, 8900 and 10,200, the difference being in the direction to be expected. In both cases the curves of rotating force were slightly S shaped, with little difference between increasing and decreasing readings.

DISCUSSION

It is interesting to summarize the results with respect to the ease with which shearing takes place. It is almost always the case that a typical metallic structure, face-centered cubic, body-centered cubic, or hexagonal close packed, permits plastic flow quietly. Apparent exceptions were osmium and vanadium, but it is highly questionable in view of the very brittle character of the original material whether these were sufficiently pure. Other apparent exceptions are Li, Sr, Ce, and Er, but all these have been shown probably to have transitions at high pressure, and shearing loses its smoothness only at high pressures in these cases. It is therefore probable that in these cases the change in the character of the shearing is to be attributed to the transition, and in fact this change in character affords additional presumptive evidence of the reality of the transition. We may draw the further conclusion that the high pressure forms are probably of lower symmetry than the low pressure forms. Lithium is particularly interesting because of its extreme softness. Yttrium does not shear smoothly; its crystal structure appears not to be known. The substances which make the greatest fuss on being sheared are the typical nonmetallic elements B, C, Si, black P, Ge, and As. On the other hand, S, a thorough nonmetal, shears quietly, but we have seen that S probably changes to the amorphous rubber-like variety on shearing. The crystal structure is not completely determinative in this regard, because Bi and Sb both have As structure and shear quietly; but the properties of these are more metallic than of As.

There is no close correlation between smoothness of shearing and the numerical value of the resistance to shear.

In Table II are collected the values of one-half the tensile strength, taken from the last edition of Landolt and Börnstein, and also the shearing stress supported at the maximum pressures reached in the experiments of this paper.

TABLE II. *Comparison of shearing strength at 50,000 kg/cm² and one-half tensile strength at atmospheric pressure.*

SUBSTANCE	SHEARING STRENGTH AT 50,000 (kg/cm²)	½ TENSILE STRENGTH AT ATMOS. PRESS. (kg/cm²)	SUBSTANCE	SHEARING STRENGTH AT 50,000 (kg/cm²)	½ TENSILE STRENGTH AT ATMOS. PRESS. (kg/cm²)
Al	3,200	300	Mo	12,100	3,500
Pb	650[1]	90	Ni	8,700	2,500
Cd	860[2]	325	Pd	5,600	1,050
Ca	1,800	250	Pt	5,800	950
Co	6,300	1,250	Ag	4,700	650
Fe	10,600	1,250	Tl	11,000	45
Au	4,500	700	W	12,700	7,500
Cu	4,900[3]	1,100	Zn	2,000	750–1,000
Mg	980[4]	1,000	Sn	770	125

[1] At 23,000; [2] at 10,000, [3] at 40,000; [4] at 23,000.

Except in the case of Mg, where I believe that there must be a misprint in the tabulated value, the shearing stresses withstood here are higher by a factor of several-fold than one-half the tensile strength, showing how profound an effect high pressure may have on shearing strength.

High shearing stress means high shearing strain. A pure shear is accompanied by an elongation in one direction equal numerically to one-half the shearing strain, and a compression of equal numerical magnitude at right angles. It follows that the actual separation of atoms or molecules under these conditions is much greater than the maximum attainable under ordinary tensile test conditions, where the limit is set by rupture. If the elongation is great enough, one might expect the molecules to be actually torn apart, and to regroup themselves in configurations of greater stability. It may well be that something of this sort plays a part in some of the cases of chemical instability described in the first part. One might perhaps be disposed to expect the effect to be particularly important among the organic compounds, the elastic constants of which are usually low, which means in general a large deformation. Or particular classes of compound may be particularly sensitive to distortion; one suspects that the oxides may be such a class.

There are doubtless other important factors which enter into the chemical effects. Under the disorganized plastic flow which accompanies shear in these experiments every sort of conceivable regrouping must be taking place, thus allowing a chance for any phenomenon to take place which is thermodynamically possible. One would expect phenomena of inhibition, such as subcooling, or the failure under ordinary conditions of reactions like $2H_2+O_2=2H_2O$, to be entirely suppressed. An example of this sort taken from the polymorphic transitions described above is that of tellurium; this transition takes place at room temperature under shearing stress, but volumetric analysis discloses it only at higher temperatures, although an extrapolation of the results indicates that it should be found at room temperature if it were not for viscous resistance. Allied with this effect is the fact that under the grinding action incident to plastic flow the reactants are brought into such intimate contact that reactions otherwise suppressed take place. The reaction between SiO_2 and Al must have a large element of this effect in it. Finally, there may be the simple displacement by shearing stress of the temperature and pressure at which the thermodynamic potential of the two reactants are equal, thus allowing the possibility of bringing a reaction or transition into the attainable range which ordinarily would be outside it. There are a couple of examples above where the displacement seems to be as much as 10,000 kg/cm^2.

Results of much geophysical interest may be anticipated from a study of more complicated systems than those examined above. Polymorphism may be expected to be a common phenomenon under the high pressures in the interior of the earth. The volume changes associated with polymorphic transitions combined with the greatly enhanced shearing strength under pressure of practically every substance must afford opportunity, at least locally and temporarily, for the development of high shearing stresses in the interior of the earth, under the action of which novel chemical reactions may well occur.

Note added October 30. Additional experiments to elucidate the reason for the detonations described in the qualitative section make it appear that in at least some cases the primary cause of the detonation is mechanical. Apparently certain substances have such a relation between coefficient of friction, plastic flow stress, normal pressure, and film thickness that when the pressure reaches a critical value the film may become mechanically unstable and be violently expelled, having as a secondary effect local, very considerable increases of temperature. The subject is evidently complex and a single type of explanation will probably not apply in all cases.