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INFLUENCE OF SURFACE ACTIVE AGENTS ON FRICTION, DEFORMATION, AND FRACTURE OF LITHIUM FLUORIDE

by Donald H. Buckley

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ABSTRACT

Sliding friction experiments were conducted with lithium fluoride crystals in various environments. These included air, water, hexadecane without and with various organic acids, and a paraffinic oil containing oleic acid. Sliding was on the (001) plane in the [100] direction at a speed of 0.005 millimeter per second and under loads of 5 to 200 grams on a millimeter-diameter sapphire rider which contacted the lithium fluoride flat. The results indicate that the presence of surfactants influences deformation and fracture in lithium fluoride. Crystals deform plastically more readily with an adsorbed organic acid than without it; this is the Rehbinder effect. Friction coefficient was influenced by the presence of the acid, its chain length, and its concentration.

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SUMMARY

An investigation was conducted to determine the influence of adsorbed surfactants on the deformation and friction coefficient of lithium fluoride single crystals in sliding friction experiments. The experiments were conducted on the (001) plane of lithium fluoride with sliding restricted to the [100] direction. A 1.6 millimeter-diameter sapphire ball slid on the crystal surface at a speed of 0.005 millimeter per second and under loads of 5 to 200 grams. The media in which friction experiments were conducted included air, water, water with myristic acid, hexadecane, hexadecane containing various organic acids, paraffinic oil containing oleic acid.

The results of the investigation indicated that plastic deformation is more readily achieved in the presence of surfactants such as the organic acids than in their absence; this is the Rehbinder effect. In the absence of organic acids, subsurface fracture cracks are observed in the zone of maximum subsurface shear stress; in their presence, plasticity is increased, thereby reducing the tendency for fracture. With increase in friction, fracture cracks are observed to move from subsurface (001) to surface (110) origin. These results are in agreement with theoretical shear stress considerations where the combined effects of compressive and tangential stresses are considered. Friction coefficient is influenced by the presence of an organic acid, its chain length, and its concentration.

INTRODUCTION

The concept of the inclusion of additives to lubricants to improve their lubricating ability dates back many years. Even to this day, however, the mechanisms associated with additive action are not completely understood in many areas. Much useful information might be gained from a more fundamental examination of the influence of additives on material behavior. It is well known, for example, that the deformation of solids influences adhesion, friction, and wear. Studies have also indicated that the deformation behavior of materials is markedly influenced by surface conditions, such as the presence of surface adsorbed species (refs. 1 to 3).

The first disclosure of this effect was reported in 1928, by Russian researchers (see summary of this work in ref. 1). While considerable information was generated in this area by Russian laboratories, particularly by the founder of the concept (Rehbinder and his associates), little support was given to the concept outside Russia because of the inability of Western researchers to reproduce what came to be known as the "Rehbinder effect." In recent years, however, the Rehbinder effect has been observed in studies outside Russia.

The Rehbinder effect has been shown in the deformation of ionic solids such as lithium fluoride and magnesium oxide (refs. 4 to 7). The increase in ductility or ability to deform plastically in the presence of adsorbed surface species has also been observed in metals, such as tin (ref. 1), zinc (ref. 8), cadmium (ref. 9) and aluminum (ref. 10). It also has been observed in germanium and metal carbides (ref. 5).

Reference 1 has shown that the addition of 0.2 percent oleic acid to a paraffin increased the ductility for tin. If the presence of surface active agents can have a marked effect on the deformation of solids, the concept is, then, of extreme importance to the field of lubrication and should be examined.

The objective of this investigation was to explore the influence of surface active agents on the friction, deformation, and fracture of lithium fluoride crystals in sliding friction studies. Lithium fluoride was selected as a material to examine for a number of reasons: (1) its slip and fracture behavior are very well understood, (2) the Rehbinder effect has been observed with it, (3) fresh, atomically clean surfaces can be prepared by cleavage, (4) cleavage can be used to study deformation and fracture modes, and (5) its surface is sensitive to small concentrations of surfactants.

Sliding friction experiments were conducted with a 1.6-millimeter diameter sapphire ball sliding on a (001) plane (cleavage plane) of lithium fluoride. Sliding was restricted to the [100] direction. The sliding speed employed to move the ball across the surface under various loads from 5 to 200 grams was 0.005 millimeter per second. Sliding surfaces were prepared by cleavage in the media in which the experiments were to be conducted. The media included air, water, water and myristic acid, hexadecane, hexadecane with various organic acids, as well as a paraffinic oil and the oil containing oleic acid.

REHBINDER CONCEPT

Rehbinder and coworkers have indicated that, in the presence of surface active agents, the stress necessary to produce a specific amount of plastic strain is reduced from that observed in the absence of the surfactant (ref. 1). The explanation given in reference 1 for this effect is that the surface energy of the interfaces newly formed at surface defects (ultramicrocracks) is decreased with adsorption. This concept should be distinguished from the Joffe effect, in which the solid surface defects are removed or reduced by dissolution of the solid surface, and the tensile strength is increased because of defect removal (ref. 11). Here the solid more nearly approaches theoretical strength. However, some more recent observations of the Joffe effect and their associated interpretations might indicate that the concept may be related to the Rehbinder concept. The presence of a solvent environment increases material ductility by reducing the ability of cracks to propagate (refs. 12 and 13).

Alternate, or more definitive, explanations have been put forth for the Rehbinder effect by others. Gilman, in an observation of the deformation behavior of lithium fluoride, had indicated that cross-gliding of screw dislocations is restricted normally by the frictional resistance of the lattice and the surface energy of the step created with motion of the screw dislocation. The adsorption of surface active species reduces this surface energy and thereby extends the mobility of the screw dislocations. Since cross-gliding can lead to dislocation multiplication during stressing, plastic deformation is therefore affected.

Westwood has suggested an alternate mechanism to explain the Rehbinder effect. The adsorption of polar molecules will occur at active or high energy surface sites such as those associated with the emergence of dislocations. The adsorbed polar molecule will then hinder dislocation motion by a pinning action. This restraining effect has been called "adsorption locking." With the Westwood theory, the presence of adsorbed molecules should result in an initial increase in yield stress because of the "locking" effect. This has been observed by Westwood (ref. 4). The initial increase is, however, usually followed by a decrease in stress for a given strain. The stress is then what is observed in agreement with the normal Rehbinder effect. None of the mechanisms proposed to explain the Rehbinder effect are completely satisfactory at this time.

MATERIALS

The only impurity detected spectrographically in the lithium fluoride crystals was a few parts per million of magnesium. The crystals contained subboundaries in which the average dislocation density was 5×10^4 per square centimeter.

The crystals were etched for dislocations with a solution of 1 part hydrofluoric acid (HF), 1 part acetic acid, and 10^{-5} part ferric chloride ($FeCl_3$). This etchant is the same as that used in the investigation of reference 12. The organic acids used were all reagent grade. The hexadecane was 99 + percent and was free of olefins. The oil was a straight additive free paraffinic oil.

EXPERIMENTAL PROCEDURE

All the crystals used in this investigation were examined in the as-cleaved condition. The crystals were cleaved at 20° C (after a 400° C furnace anneal) in an enveloping environment of the medium in which the crystal was to be investigated in sliding friction studies. The crystals were cleaved in the medium to provide a clean surface to which the surfactants could adsorb. When an ionic solid is cleaved, the fresh surface is covered with a series of positively and negatively charged sites even though the solid is on the whole electrically neutral. When wear tracks were examined normal to the sliding surface, the crystals were cleaved with a razor blade.

The sliding friction experiments were all made on the (001) plane with sliding in the [100] direction. Only a single pass was made over the crystal surface; that is, the wear tracks examined were the result of a single pass of the riders. During the experiments the crystal surface was always covered with a layer of fluid.

APPARATUS

The apparatus used in this investigation is shown schematically in figure 1. The apparatus consisted basically of a MicroBierbaum hardness tester to which a drive motor was attached in order to provide uniform motion at 0.005 millimeter per second of the crystal specimen under examination.

The rider specimen was a sapphire ball 1.6 millimeters in diameter which was locked in a holder. The arm containing the rider had a strain gage assembly for measuring frictional force. The sapphire ball was loaded against the crystal flat by the application of dead weights directly over the rider.

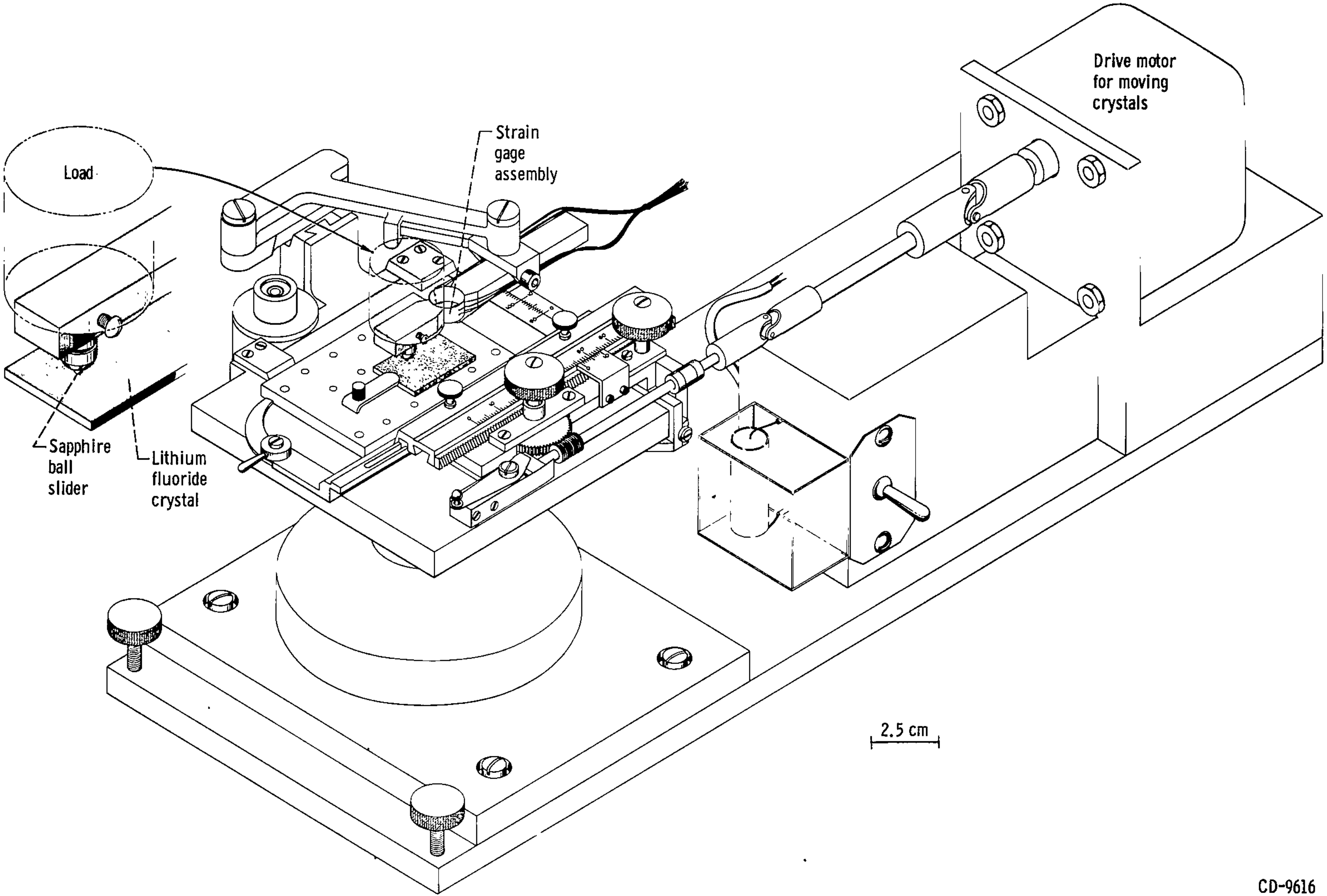


Figure 1. - Sliding friction apparatus.

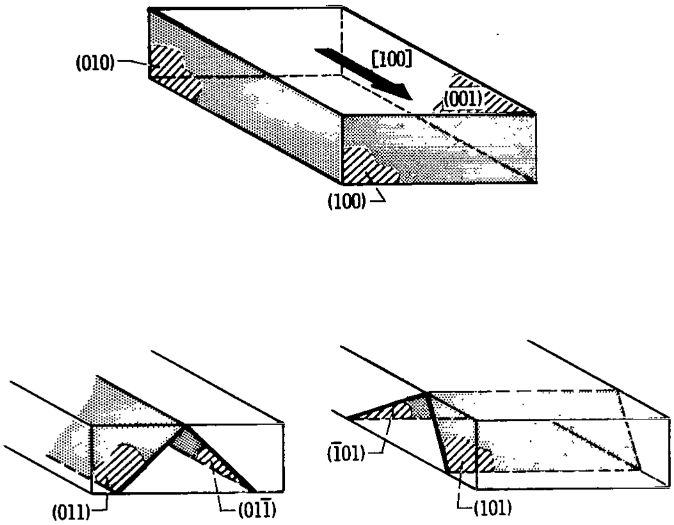


Figure 2. - Planes and directions in lithium fluoride.

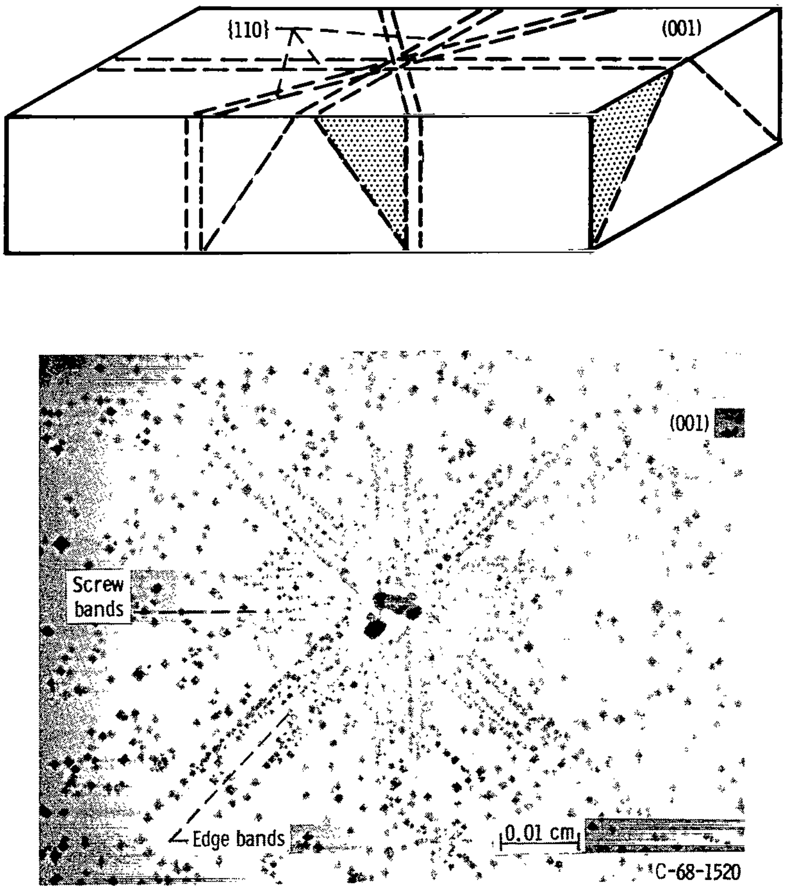


Figure 3. - Dislocation band developed by dropping a 1.6-millimeter sapphire ball on lithium fluoride (001).

RESULTS AND DISCUSSION

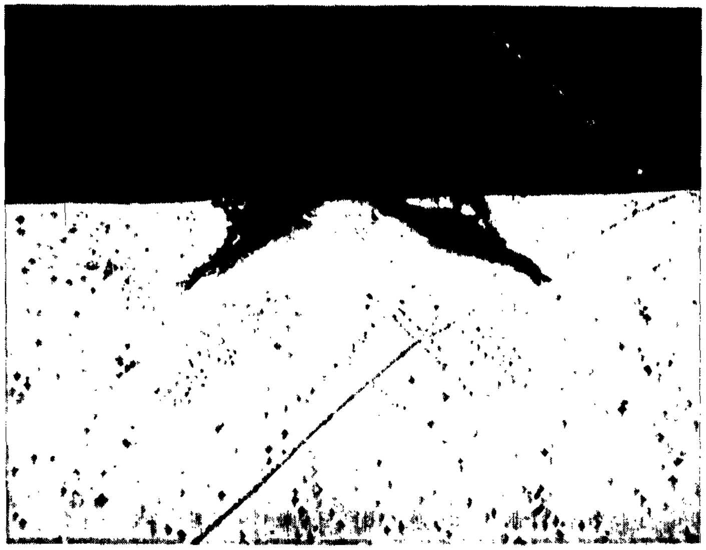
The sliding friction experiments of this investigation were all made on the (001) plane of a lithium fluoride crystal with sliding restricted to the [100] direction, as shown in figure 2. The lithium fluoride crystals were etch pitted with the etchant described in the MATERIALS section. If the sapphire ball used as a rider in these experiments was raised above the crystal surface, while in the retaining arm, and allowed to fall and strike the crystal surface, a pattern of etch pits, as shown in figure 3, was obtained. Edge dislocation bands develop on the surface along the ⟨110⟩ slip directions, while screw dislocation bands develop in the ⟨100⟩ directions. Similar observations of the development of "bands" on crystal surfaces are shown in reference 14.

FRICTION EXPERIMENTS IN AIR

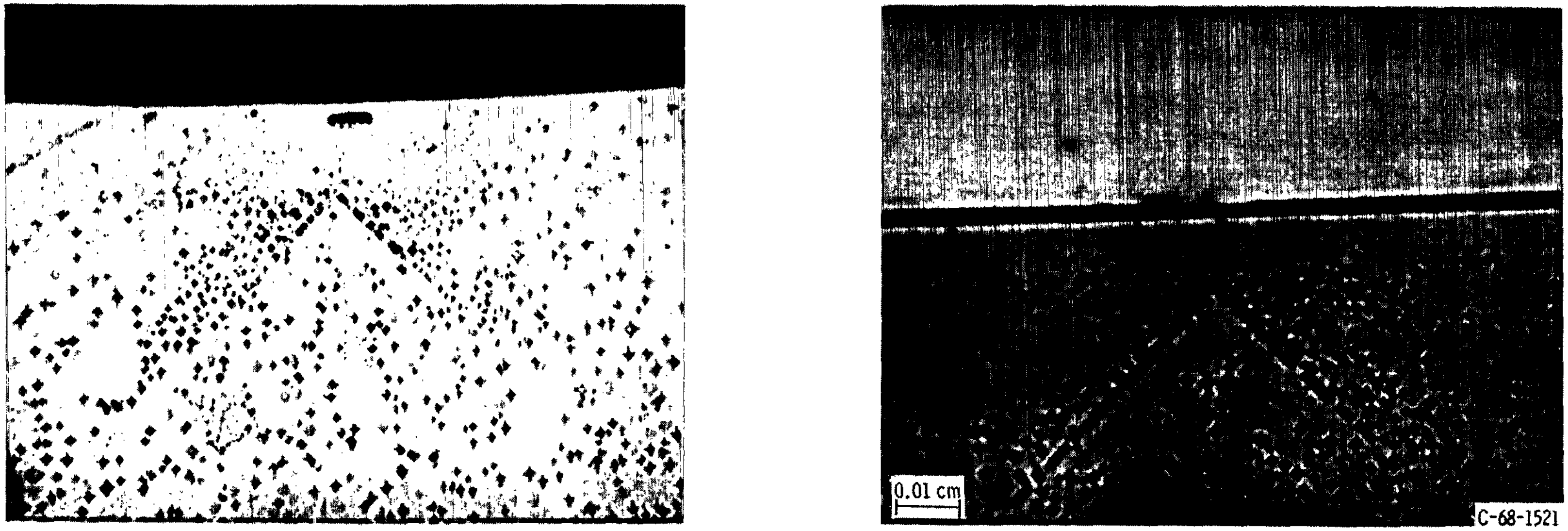
The sapphire ball was slid across a freshly cleaved lithium fluoride crystal in air. The specimen was then cleaved normal to the sliding track and subsequently etch pitted. The subsurface deformations and the development of cleavage cracks is shown in figure 4(a). Examination of figure 4(a) reveals that slip has taken place along the {011} and {101} sets of planes. Since these are the slip planes, plastic deformation might be expected to occur in such a fashion. In addition to the slip bands, cleavage cracks developed along the {011} slip bands and appear to have their origin at the crystal surface. Cracks can form the intersection of {110} slip planes according to the equation indicated in reference 15:

$$\frac{1}{2}a[011] + \frac{1}{2}a[101] = \frac{1}{2}a[110]$$

The cracks formed at or near the surface are discussed in greater detail with reference to experiments in oil. It is important to note at this point that the lithium fluoride will deform plastically as well as develop brittle cracks along the {110} slip bands. Similar cracks have been observed in references 16 and 17 in air sliding experiments.



(a) Dry air.



(b) Water.

(c) Water and 5.0×10^{-6} N myristic acid.

Figure 4. - Cross section of wear tracks on lithium fluoride in sliding friction experiments. Load, 200 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second; ball made a single pass across surface covered with three different media: air, water, and water with myristic acid.

FRICTION EXPERIMENTS IN WATER

Crystals of lithium fluoride were next cleaved in water, and friction experiments were conducted with water present on the crystal surface. The crystals were then cleaved normal to the wear track and etched. The track subsurface deformation is shown in figure 4(b). It is of interest to note that, while slip bands are evident from the dislocation etch pits along the (110) plane, a subsurface crack has formed in the crystal. This crack lies in a (001) plane. In air (fig. 4(a)), the cracks formed at the surface along (110) planes. Cleavage cracks of both types have been observed in lithium fluoride and magnesium oxide, another ionic solid with the sodium chloride structure. With plastic deformation of lithium fluoride, cracks can develop along a (100) plane with the intersection of {110} slip bands in accordance with the equation (from refs. 18 and 19)

$$\frac{1}{2}a[110] + \frac{1}{2}a[1\bar{1}0] \rightarrow a[100]$$

In compression loading, cracks were also observed (ref. 20) at the intersection of (110) slip planes, but the cracks were formed along (100) planes parallel to the compression axis rather than along cleavage planes normal to the compression axis, as shown in figure 4(b). The cracks shown in figure 4(b) were the result of both compressive and tangential force.

Figure 5(a) shows the development of a cleavage crack at the intersection of (110) slip bands with the formation of a crack at the point of pileup of dislocations. The glide dislocations then move to the crack and form cavity dislocations. The cavity or crack thus formed will grow along the cleavage plane.

Although lithium fluoride is a semibrittle ionic solid, it is of interest to examine the formation of a crack in a brittle material such as glass where the Griffith theory may be considered (ref. 21). The sketch of figure 5(b) shows a crack in a brittle material. For a brittle material, the crack and its relation to applied stress is expressed by a modified Griffith equation as

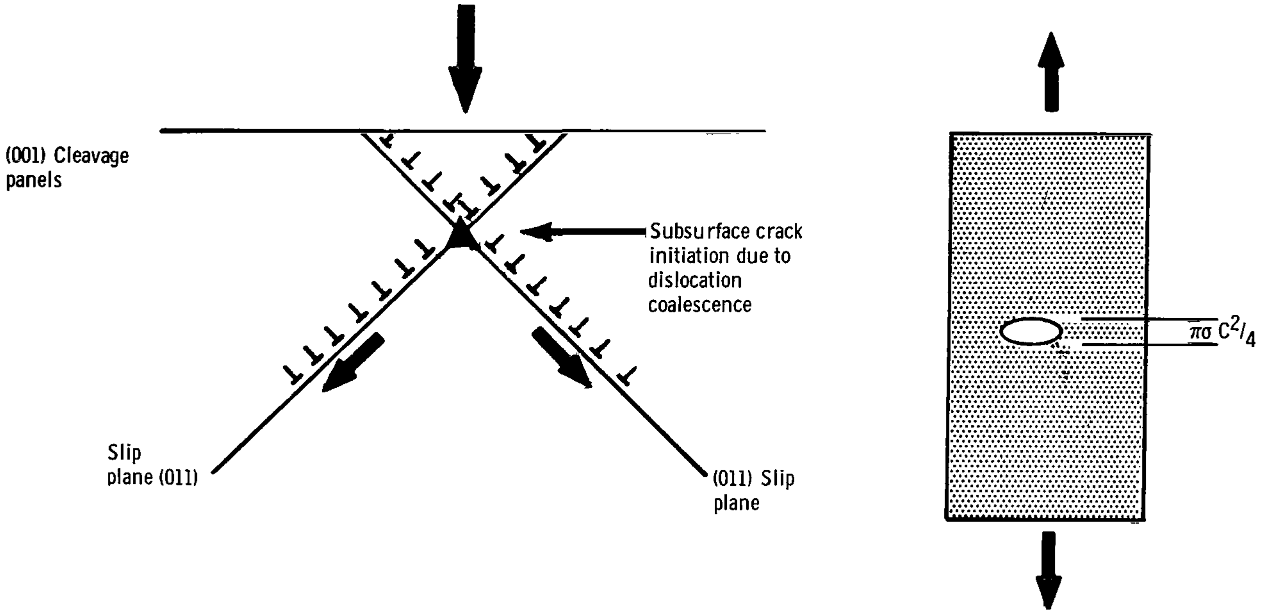
$$\sigma = \left(\frac{2E\gamma P}{\pi C}\right)^{1/2} \tag{1}$$

where

σ applied stress

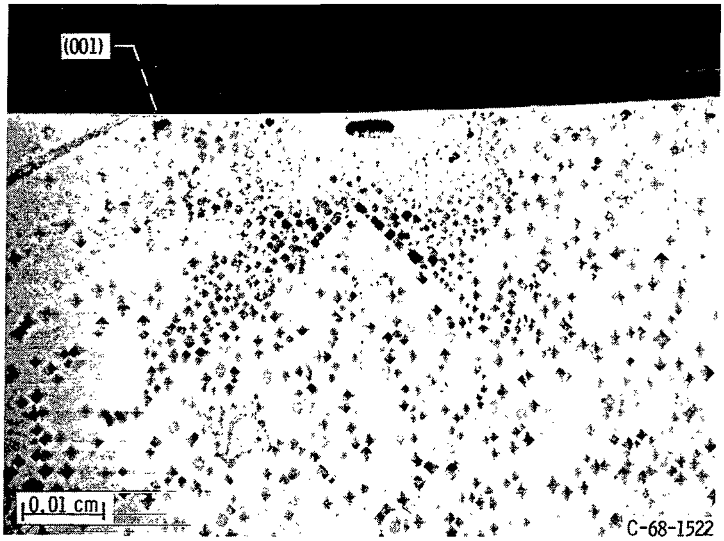
γ surface energy

C crack length



(a) Development of cleavage crack.

(b) Crack in brittle material.



(c) Subsurface cleavage crack in lithium fluoride.

Figure 5. - Development of subsurface cleavage crack in lithium fluoride during sliding friction experiments. Load, 200 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second; ball made a single pass; medium water.

E modulus of elasticity

P Poisson's ratio

When a material has some ductility, the elastic energy may be absorbed in plastic deformation near the crack tip and the equation becomes

$$\sigma_p = \left[2E\left(\frac{\gamma + p}{\pi C}\right)\right]^{1/2}$$

where

p energy absorbed in plastic deformation

σ_p stress necessary for crack formation in the presence of plastic deformation

When p is very large in relation to γ, this equation may be reduced to

$$\sigma_p = \left(\frac{2Ep}{\pi C}\right)^{1/2}$$

Thus, the greater the amount of energy absorbed by plastic deformation, the higher is the stress normally required to develop crack growth. If the appropriate values for lithium fluoride are substituted in equation (1), the actual crack length in figure 5(c) is 1/40 of the crack length predicted from equation (1). The energy which might otherwise be absorbed in crack growth is absorbed by plastic deformation of the lithium fluoride (fig. 5(c)). The crack of figure 5(c) is near the point of maximum subsurface shear stress which can be calculated from the equation for such stress.

In regard to the possible operation of cross slip in lithium fluoride, it was shown (ref. 20) that cross slip in lithium fluoride is extremely difficult. The screw dislocations of (110) planes must glide onto (100) planes. It is very difficult for screw dislocations to move on the (100) planes. Reference 22 indicates that the flow stress is 15 times higher for the {100} planes than for the {110} planes. Thus, cross slip could not be expected to occur on {100} planes until this flow stress ratio of 15 is exceeded. In general, the cleavage or fracture stress is reached before extensive cross slip can become operable, and the consequence is shown in figure 5(c).

A 5.0×10^{-6} N (normal) solution of myristic acid was used in a sliding friction experiment. Examination of figure 4(c) indicates that, in the presence of the acid, there was no evidence of a subsurface crack, as shown in figure 4(b). Note, however, in figure 4(c) that the depth to which the (011) slip bands extend subsurface is appreciably greater. Thus, a greater degree of plasticity appears to exist in the presence of the myristic acid. The energy associated with the sliding process appears to have been absorbed completely in plastic behavior. In air and water, however, under the same stress, fracture occurs in addition to plastic behavior.

The presence of water as a solvent can have an effect on the surface behavior of myristic acid. For example, growth of dislocation tracks has been observed with myristic acid in water (ref. 4). When, however, that same acid was in hexadecane, no increase in track length was observed.

FRICTION EXPERIMENTS IN HEXADECANE WITH ACIDS

In the examination of the influence of surface active media on the deformation behavior of materials, two of the acids used by Rehbinder and his coworkers were stearic and oleic in straight chain hydrocarbon solvents. Some sliding friction experiments were therefore conducted with these same two acids in hexadecane. The widths of the surface wear tracks, as determined by dislocation etch pittings, are plotted in figure 6 for light loads. The track was wider in the presence of the acids.

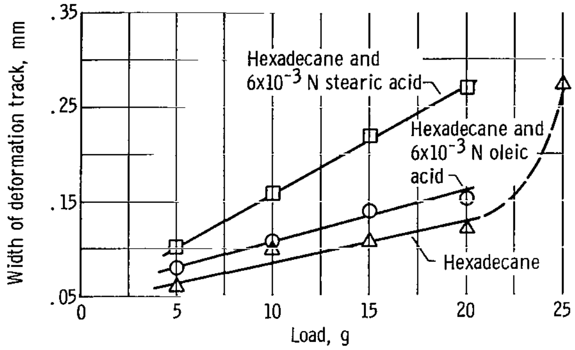
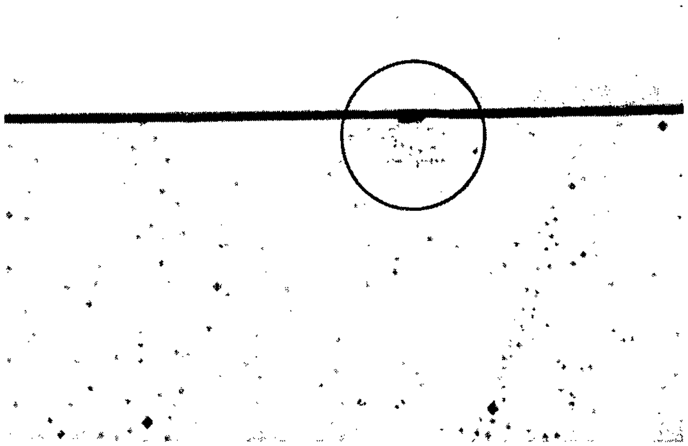
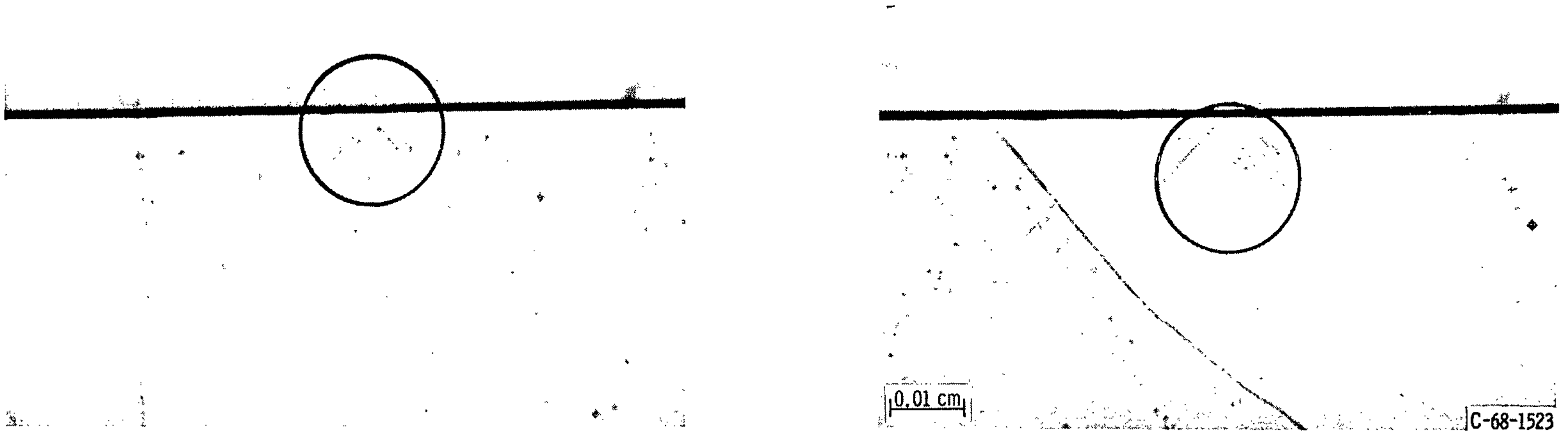


Figure 6. - Plastic deformation of lithium fluoride in sliding friction experiments with presence of various fluids at surface. Rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second.

Section of track normal to the sliding surface at loads of 5, 10, and 15 grams are shown in figure 7. At a load of 5 grams, a row of etch pits appears subsurface and parallel to the surface itself. These etch pits are from (10$\bar{1}$) slip planes. At 10 and 15 grams, the etch pits are most visible along the (011) slip planes. The (011) slip appeared the most visible at loads from 10 to 150 grams. At 200 grams, (101) slip bands were again visible.



(a) Load, 5 grams.



(b) Load, 10 grams.

(c) Load, 15 grams.

Figure 7. - Photomicrographs of surficial plastic deformation in lithium fluoride from friction experiments in hexadecane. Rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second. Areas under study are encircled. Lithium fluoride crystals cleaved before experiments in hexadecane.

Sliding experiments with various acids (including stearic) in hexadecane showed the same track widths as experiments with hexadecane only (fig. 8). The friction coefficient showed a marked difference, however, between hexadecane and hexadecane with stearic acid (fig. 8). This deviation from Amonton's law has been discussed in reference to dry sliding studies with lithium fluoride (ref. 16). The coefficient of friction in the presence of stearic acid is, however, relatively constant over the entire range of loads examined. The friction coefficient is very good evidence, then, for the adsorption of stearic acid from the solvent hexadecane onto the lithium fluoride surface. With metals, metallic soaps are usually formed in combination with the acid. With lithium fluoride, this is not possible.

The depth of the subsurface deformation at loads from 25 to 200 grams was greater in the presence of stearic acid than in its absence even though the track width in figure 8 was essentially the same. Furthermore, at 200 grams, surface cracks developed in hexadecane but such cracks did not appear in the presence of stearic acid.

In order to determine the extent of the effect observed with the organic acids, similar deformation experiments at loads from 25 to 200 grams were conducted in the pres-

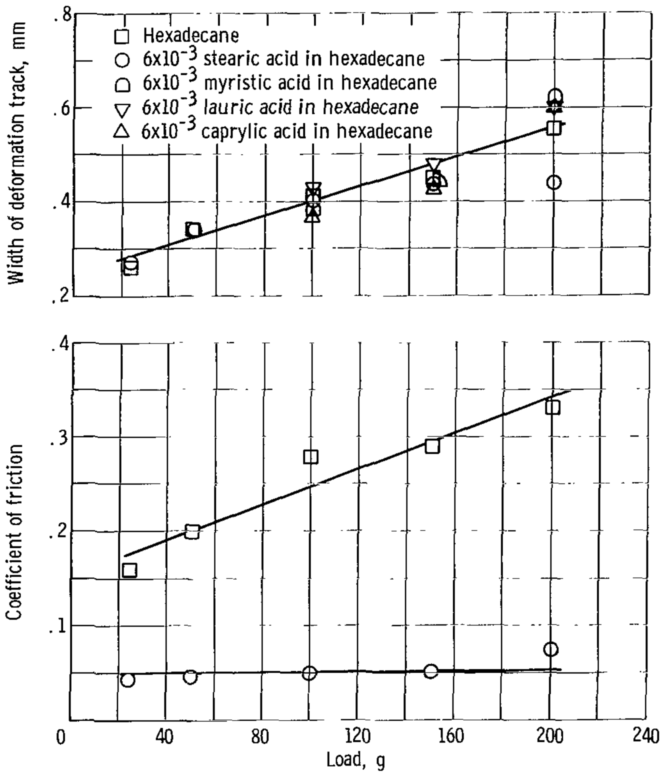


Figure 8. - Effect of load on coefficient of friction and deformation of lithium fluoride crystals in various fluids during sliding friction experiments.

ence of myristic, lauric, and caprylic acids in the same concentration as used in the stearic acid experiments. The results obtained are also shown in figure 8. Again, for these acids, the track width did not deviate from that observed in hexadecane alone. The track depth subsurface was greater in the presence of each acid than it was in pure hexadecane. With none of the acids was there evidence of surface or subsurface cracks at a 200-gram load.

With deformation of a surface, dislocation loops grow on (101) planes, and etch pitting will reveal the terminal points of the dislocations. The presence of dislocation loops along the wear track at 25 grams is evident in the photograph of the etch-pitted surface in figure 9. The surface was covered with a film of stearic acid in hexadecane.

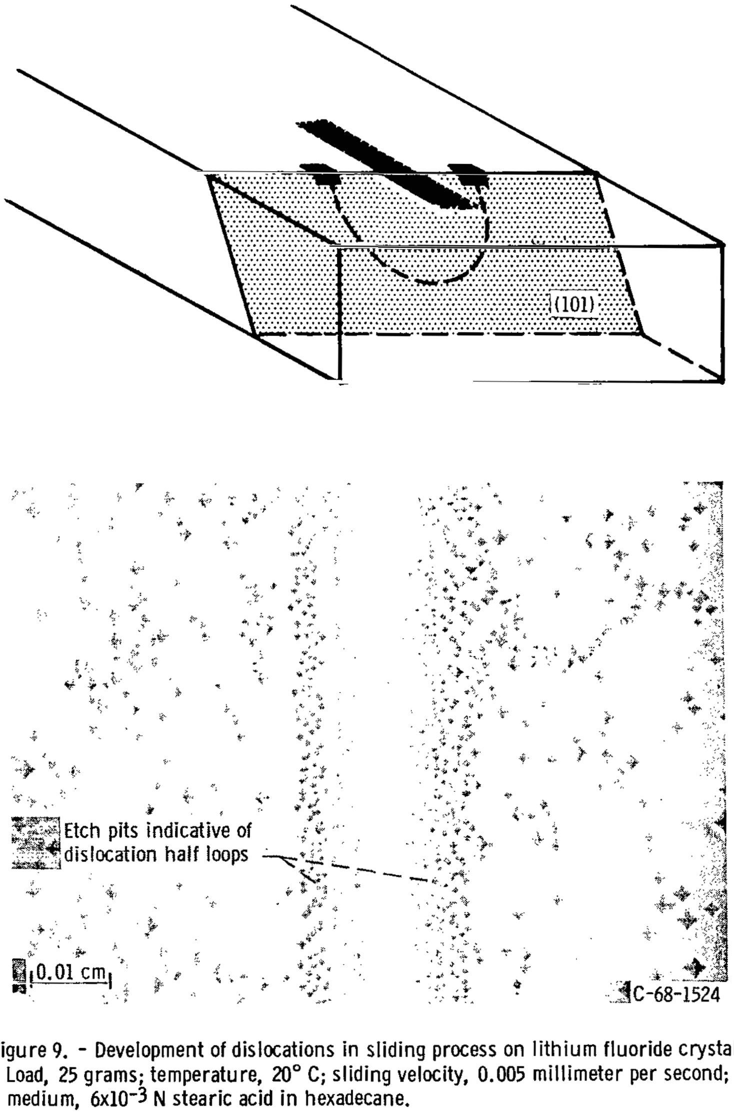


Figure 9. - Development of dislocations in sliding process on lithium fluoride crystals. Load, 25 grams; temperature, 20° C; sliding velocity, 0.005 millimeter per second; medium, 6×10^{-3} N stearic acid in hexadecane.

The mechanism of the dislocation motion with applied stresses for lithium fluoride is discussed in detail in reference 14.

With stearic acid in hexadecane at a load of 200 grams, (1$\bar{1}$0) slip bands were observed in the wear path of the lithium fluoride crystal. These bands were observed at a stearic acid concentration of 6×10^{-3} N. Close inspection of the wear tracks will also reveal the presence of (10$\bar{1}$) slip lines in the track proper.

The development of orthogonal slip bands has been observed in the plastic deformation of lithium fluoride. Orthogonal slip bands were observed in the course of the sliding friction experiments of this investigation. In figure 10, these slip bands are present in the wear track developed in sliding under a 200-gram load in an environment of 6×10^{-3} N

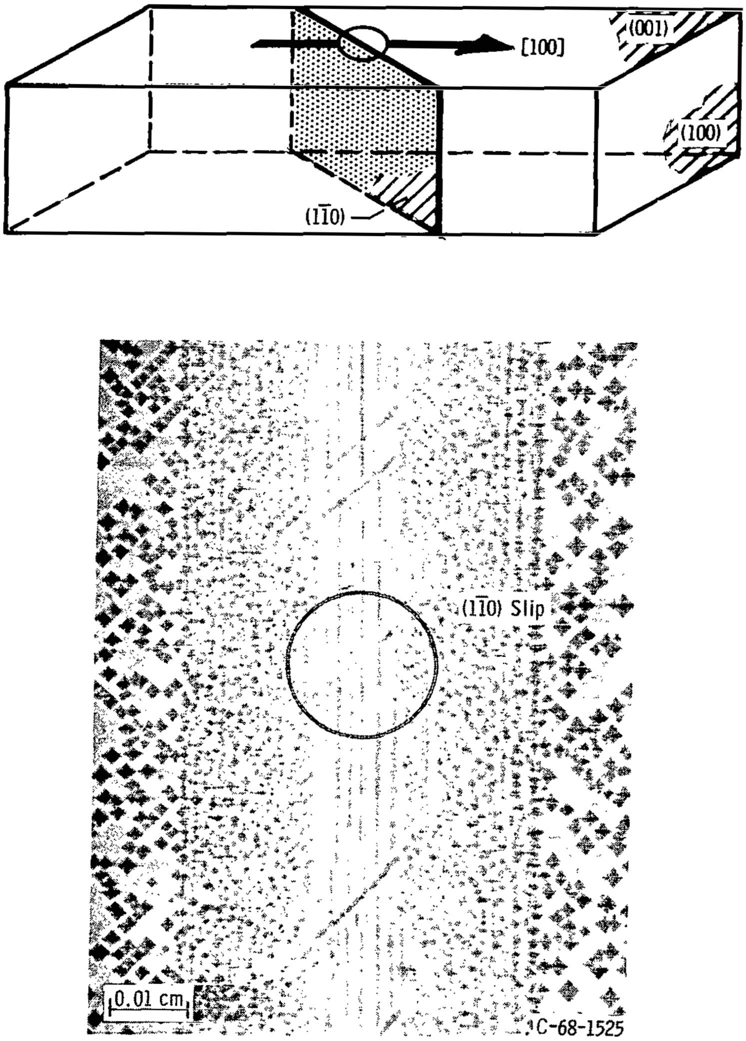


Figure 10. - Development of orthogonal slip bands in sliding process on lithium fluoride crystals. Load, 200 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second; medium, 6×10^{-3} N stearic acid in hexadecane.

stearic acid in hexadecane. The slip plane involved in the development of these loads is shown schematically in figure 10 above the photomicrograph of the wear track after etch pitting.

It has been shown that the effect of surface active agents on the deformation process is markedly influenced by the concentration of surfactant (refs. 1 to 4). For example, with tin crystals, it was shown (ref. 1) that the maximum increase in plasticity for oleic acid in octane occurred at a concentration of 1×10^{-2} N; minor deviations from this concentration in either direction resulted in a marked decreased in plastic behavior.

The effect of the concentration of stearic acid in hexadecane was, therefore, examined in sliding friction experiments with lithium fluoride. The influence of stearic acid concentration is shown in figure 11. Decreases in stearic acid concentration below 5.0×10^{-3} N resulted in a marked increase in friction coefficient. At acid concentrations below 10^{-5}, the friction coefficient was characteristic of that obtained in pure hexadecane.

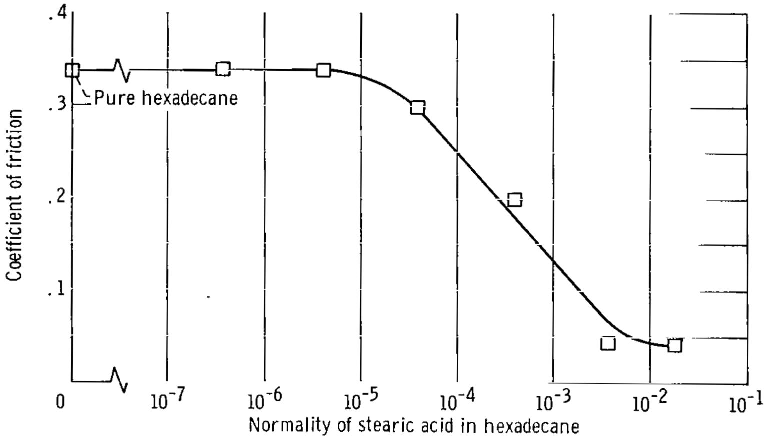
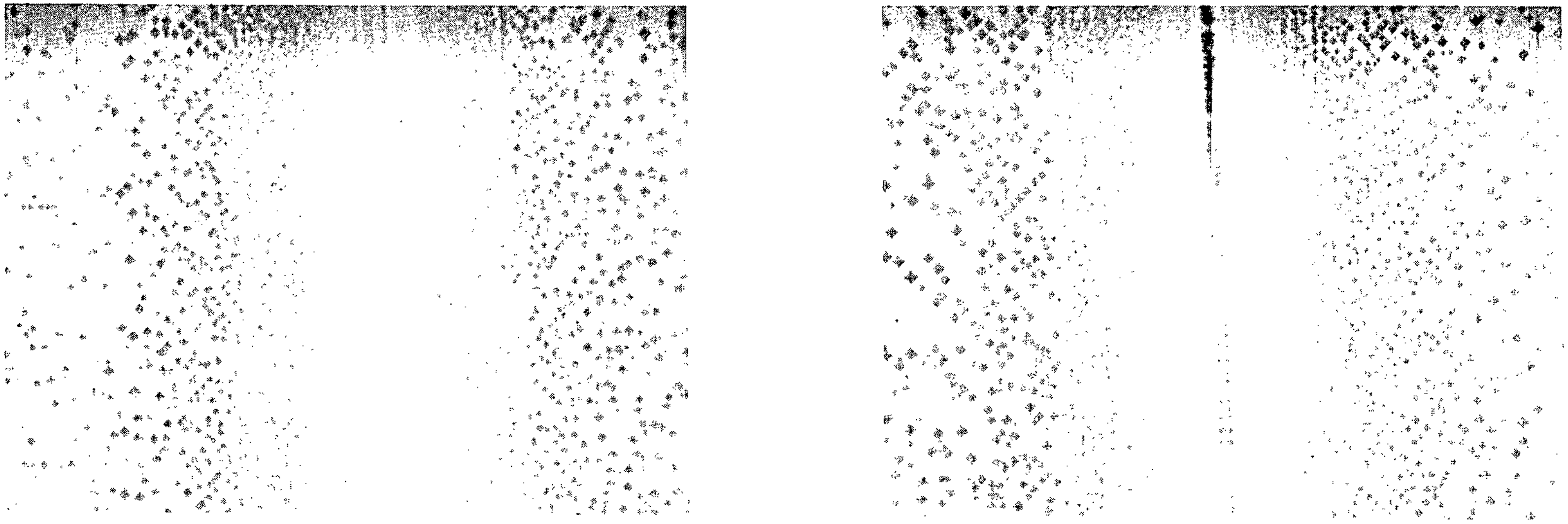


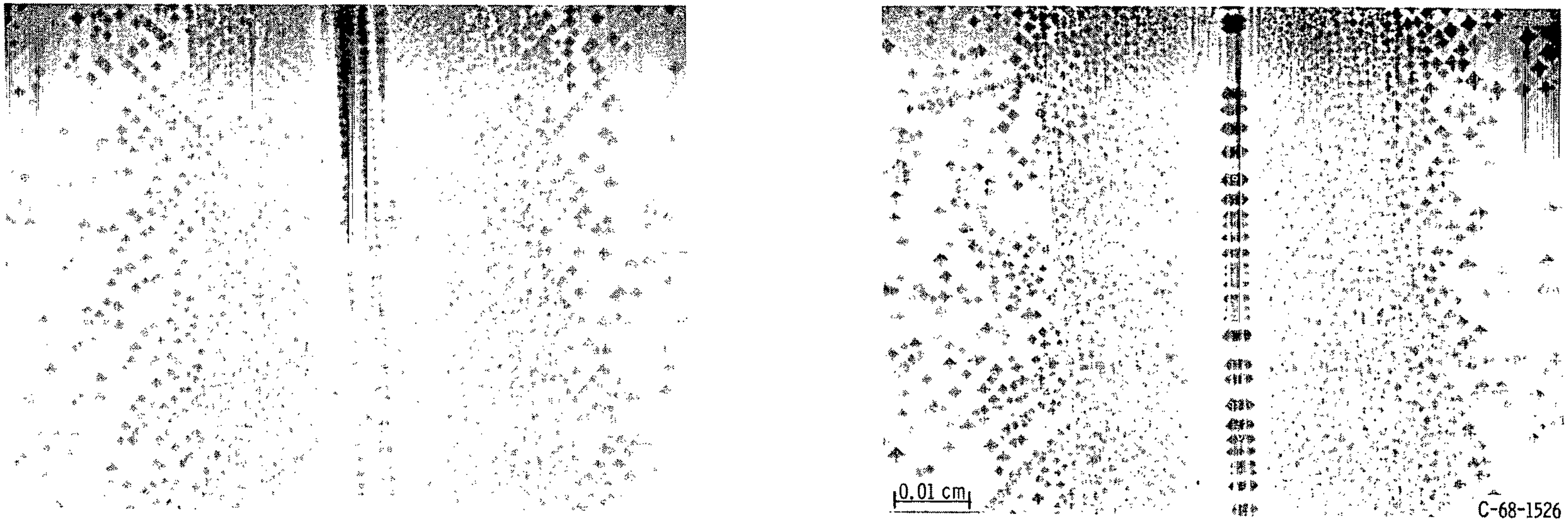
Figure 11. - Effect of normality of stearic acid in hexadecane on coefficient of friction of lithium fluoride during sliding friction experiments. Load, 200 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second.

The width of the deformation track with decreasing acid concentration was not markedly affected. With a decrease in acid concentration, however, surface changes did take place and cleavage or fracture cracks began to develop in the wear track proper. This effect is shown in figure 12. At an acid normality of 6×10^{-2} N, the deformation was completely plastic with no evidence of fracture cracks in the track (fig. 12(a)). No subsurface cracks were visible when the specimen was examined normal to the track (i.e., on the (100) surface). This complete plastic behavior was also observed at a stearic acid concentration of 6×10^{-3} N.



(a) Stearic acid concentration in hexadecane, 6×10^{-2} N.

(b) Stearic acid concentration in hexadecane, 6×10^{-4} N.



(c) Stearic acid concentration in hexadecane, 6×10^{-6} N.

(d) Hexadecane.

Figure 12. - Photomicrographs showing development of cleavage cracks on surface of lithium fluoride with reduction of surface active agent during sliding process. Load, 200 grams; temperature, 20° C; sliding velocity, 0.005 millimeter per second.

When the stearic acid concentration was reduced to 6×10^{-4} N, cracks began to appear in the center of the wear track (fig. 12(b)). Thus, insufficient stearic acid was present to prevent fracture. The stress applied could no longer be accommodated by plastic deformation, and fracture cracks developed. A further reduction in acid to 6×10^{-6} N resulted in a greater concentration of the surface cracks (fig. 12(c)). In pure hexadecane, the results shown in figure 12(d) were obtained. The hexadecane shows the same type of cracks developing but of a larger size. Examination of these tracks in cross section, that is, on the (100) plane, revealed (011) cracks subsurface.

It might be hypothesized that the decrease in acid concentration has nothing to do with plasticity of the lithium fluoride but is related simply to adhesion of the lithium fluoride to the aluminum oxide (sapphire ball). While this hypothesis might hold for aluminum oxide in contact with metals because of oxygen-metal interaction (ref. 23), chemical interaction of aluminum oxide with lithium fluoride is unlikely. An examination of the chemistry involved would seem to preclude any chemical interaction of these two materials. Furthermore, even if surface adhesion were the case, it could not account for subsurface cracks observed to a depth of 0.20 millimeter along (011) slip bands.

Many years ago it was shown that increasing the number of carbon atoms in an aliphatic acid reduced the friction coefficient of steels (ref. 24). Similar experiments were conducted with lithium fluoride in this study, and the results obtained are presented in figure 13. Again, as was observed with steels in reference 24, friction is influenced by acid chain length. Herein, however, the effect is seen with an ionic solid where soap formation may not be the explanation.

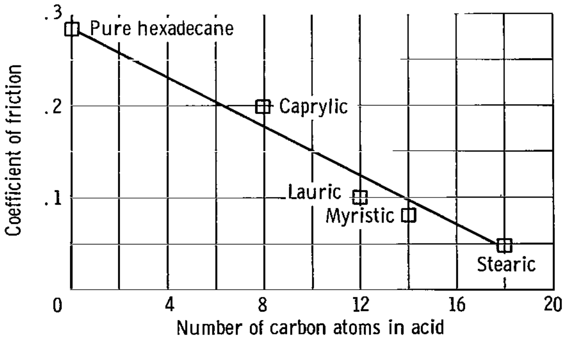


Figure 13. - Effect of number of carbon atoms in surface active agent on coefficient of friction for lithium fluoride. Load, 100 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second; acid concentration, 6×10^{-3} N.

PARAFFINIC OIL AND ACID

In lubrication systems, active agents are most frequently present in an oil rather than in hexadecane. Some sliding friction experiments were therefore conducted with a paraffinic oil and with the oil containing oleic acid as the surface active agent. The data obtained in the two media are presented in figure 14. With increases in load, an increase in friction was observed. It is of interest to note that the friction coefficient is the same in the presence or absence of the surfactant. Oleic acid has a melting point of 19° C. With stearic acid in hexadecane (fig. 8), a marked decrease in friction was obtained. Stearic acid has a melting point of 69° C. It has been established that, where friction measurements are made above the melting point of organic acids in oils, the organic acid is not better as a boundary lubricant than the pure paraffinic oil (ref. 25, pp. 200-201). The friction experiments of both figures 8 and 14 were performed at 20° C.

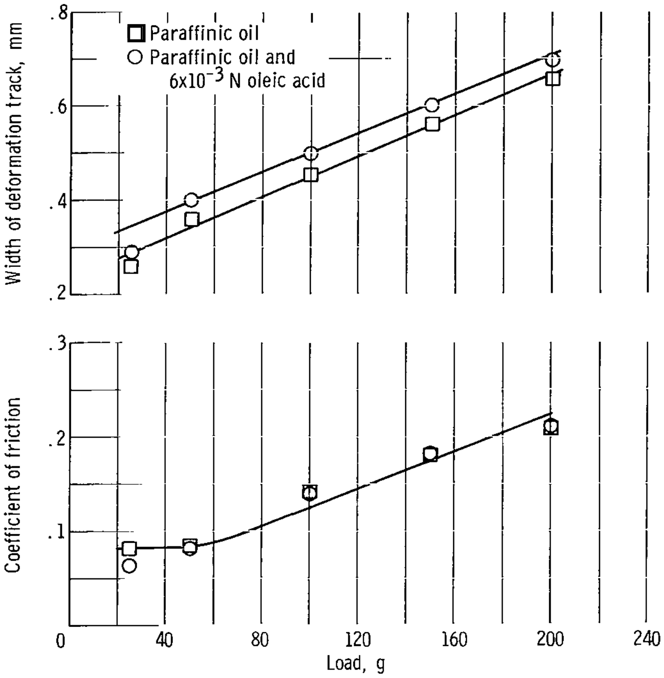
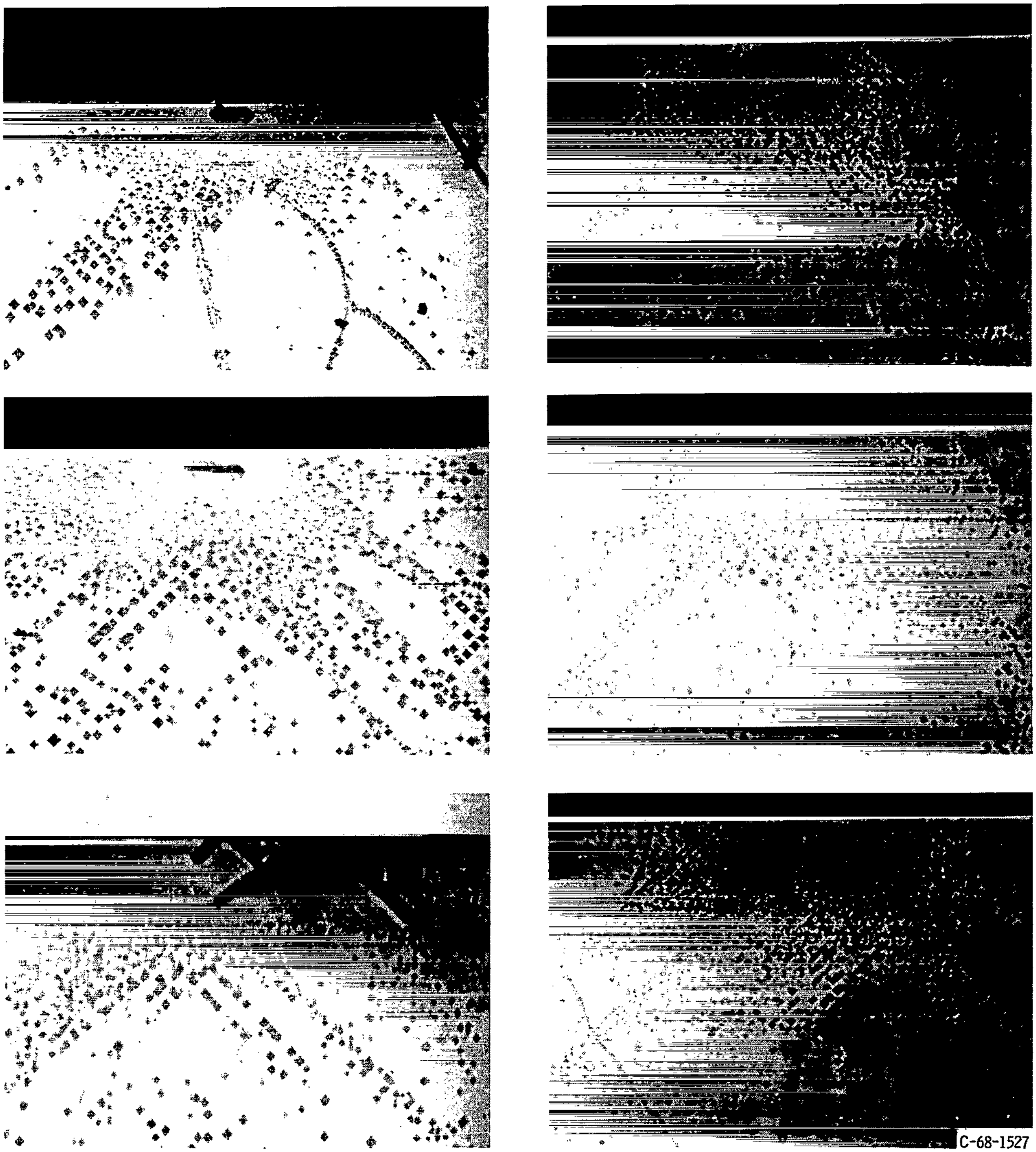


Figure 14. - Effect of oleic acid in paraffinic oil on friction and deformation of lithium fluoride. Rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second.

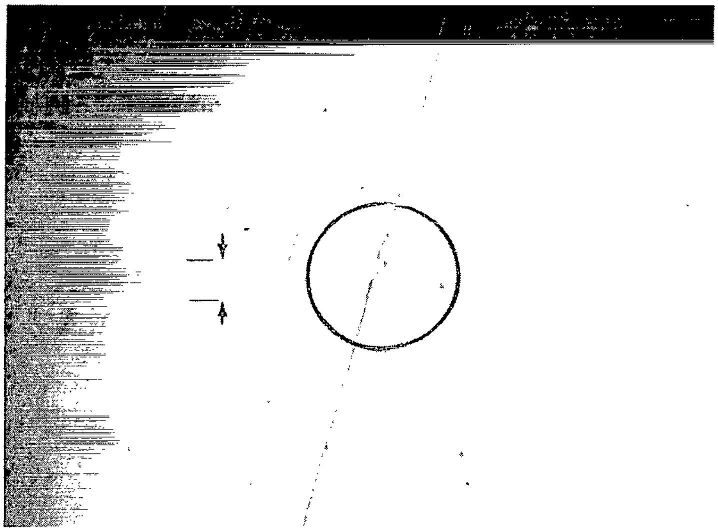
The photographs of figure 15 indicate the marked difference in deformation behavior in the presence and absence of the oleic acid. The wear tracks of three loads, 100, 150,



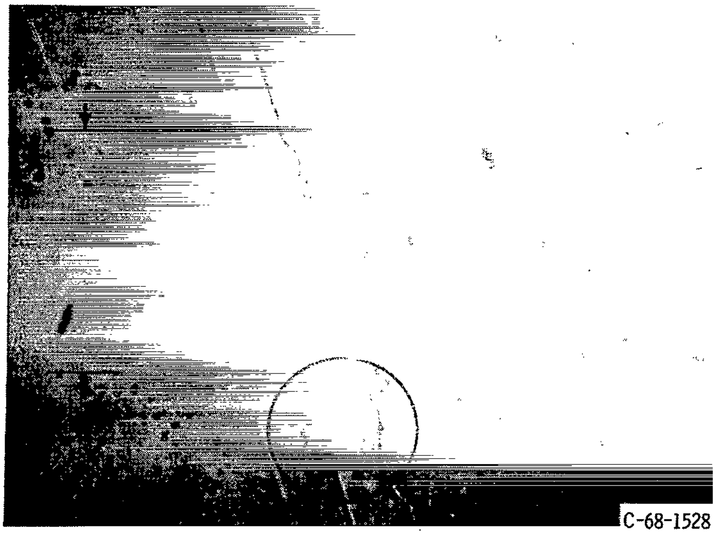
(a) Paraffinic oil.

(b) Oil and acid.

Figure 15. - Photomicrogaphs showing development of (a) surface and subsurface fracture cracks in lithium fluoride in absence of surface active agent at various loads; (b) absence of cracks in presence of surfactants. Temperature, 20° C; sliding velocity, 0.005 millimeter per second; medium, paraffinic oil and oil containing 6×10^{-3} N oleic acid.



(a) Wear track crossing cleavage step.



(b) Generation of ductile wear particle.

Figure 16. - Wear tracks on lithium fluoride crystals indicating plasticity in wear track under paraffinic oil with 5.63×10^{-3} oleic acid. Load, 100 grams; rider, 1.6-millimeter-diameter sapphire ball; temperature, 20° C; sliding velocity, 0.005 millimeter per second; ball made a single pass.

and 200 grams, are shown in the presence and absence of the oleic acid. In the paraffinic oil at 100 and 150 grams, subsurface cracks were observed in the zone of maximum subsurface stress. The crack length at 150 grams was larger than at 100 grams, which is in agreement with the equations as discussed relative to the water experiments. With an increase in stress, an increase in crack length is to be anticipated. In both experiments, the presence of the acid increased plasticity with no evidence of crack formation.

At a load of 200 grams, with the crystal in the paraffinic oil, the cracks were no longer subsurface but of surface origin. Furthermore, rather than showing crack formation along the (001) plane, the cracks developed along the (011) planes. Close examination of the wear track subsurface in figure 16 revealed the presence of both (101) and (011) slip bands as was observed in air (fig. 4).

An analytical study (ref. 26) considered the zone of maximum subsurface stress in compression when there is also a tangential stress applied, such as that encountered in rolling or sliding. As the tangential stress is increased, the zone or point of maximum subsurface shear stress moves toward the surface. The zone of maximum shear stress will occur at the surface when some friction coefficient is exceeded, according to the analysis of reference 26. At 100 and 150 grams, as shown in figure 14, the maximum stress is still subsurface. When the load reached 200 grams, the maximum stress was on the surface. The coefficient of friction at this load was 0.20, and at 150 grams load it was 0.18. The photomicrographs of figure 15 would indicate that between 0.18 and 0.20 the tangential force is sufficient for lithium fluoride to move the cracks from subsurface to surface origin.

The degree of plasticity of lithium fluoride observed in sliding friction experiments is shown in figure 16. In figure 16(a) the wear track passed over a cleavage step. Interference measurements of such steps indicate that they averaged about 1000 angstroms ($\times 10^{-7}$ m) in height. Plastic flow is evident in the figure by the projection of material extending beyond the step line. In figure 16(b), examination of a double cleavage step reveals the generation of what could, with repeated passes over the surface, become a shearing fracture and the generation of a wear particle due to plastic flow of the lithium fluoride. The particle forming in figure 16(b) was formed with a single pass of the sapphire rider over the surface.

SUMMARY OF RESULTS

Based on the results obtained with lithium fluoride crystals in sliding friction experiments, the following summary remarks are made:

1. The presence of organic acids influences the plastic deformation and formation of fracture cracks in lithium fluoride at light loads. In general, fracture does not occur as

readily in the presence of organic acids, because of increased plasticity, as it does in their absence.

2. Subsurface cleavage cracks develop in lithium fluoride in the region of maximum subsurface stress and the site of interaction of {110} slip bands.

3. Surface cleavage cracks in lithium fluoride develop along the {110} slip planes.

4. With a paraffinic oil, increase in load results in an increase in friction coefficient, and with sliding, a movement of fracture cracks from subsurface to surface origin. This observation is in accord with shear stress theory which indicates that the zone of maximum stress moves from subsurface to the surface with increases in surface tangential stresses due to friction.

5. The concentration of organic acid in hexadecane influences friction, deformation, and fracture behavior. In the experiments reported herein, concentrations of less than 6×10^{-3} N influenced friction coefficient.

6. As observed with metals by other investigators, the number of carbon atoms in the organic acid influences friction. The greater the number of atoms the lower the friction; this effect was examined at carbon chain lengths up to that for stearic acid.

7. When deformation occurs during sliding, subsurface slip is first observed along the $(\bar{1}01)$ slip bands.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 24, 1968,
129-03-13-02-22.

REFERENCES

1. Rehbinder, P.; and Lichtman, V.: Effect of Surface Active Media on Strains and Rupture in Solids. Proceedings of the Second International Congress of Surface Activity. J. H. Schulman, ed. Academic Press, 1957, pp. 563-582.
2. Westwood, A. R. C.: Sensitive Mechanical Properties. Chemistry and Physics of Interfaces. Am. Chem. Soc. Publications, 1965, pp. 161-171.
3. Gilman, J. J.: The Mechanism of Surface Effects in Crystal Plasticity. Phil. Mag., vol. 6, no. 61, Jan. 1961, pp. 159-161.
4. Westwood, A. R. C.: The Rebinder Effect and the Adsorption-Locking of Dislocations in Lithium Fluoride. Phil. Mag., vol. 7, no. 76, Apr. 1962, pp. 633-649.
5. Westbrook, J. H.; and Jorgensen, P. J.: Indentation Creep of Solids. Trans. AIME, vol. 233, no. 2, Feb. 1965, pp. 425-428.

6. Walker, W. W.; and Demer, L. J.: Effect of Loading Duration on Indentation Hardness. Trans. AIME, vol. 230, no. 3, Apr. 1964, pp. 613-614.

7. Westwood, A. R. C.; Goldheim, D. L.; and Lye, R. G.: Rebinder Effects in MgO. Phil. Mag., vol. 16, no. 141, Sept. 1967, pp. 505-519.

8. Harper, S.; and Cottrell, A. H.: Surface Effects and the Plasticity of Zinc Crystals. Proc. Phys. Soc. London, Ser. B, vol. 63, pt. 5, May 1950, pp. 331-338.

9. Andrade, E. N. da C.; and Randall, R. F. Y.: The Thermal Etching of Single Crystals of Cadmium. Proc. Phys. Soc. London, Ser. B, vol. 63, pt. 3, Mar. 1950, pp. 198-208.

10. Kramer, I. R.: The Effect of Surface-Active Agents on the Mechanical Behavior of Aluminum Single Crystals. Trans. AIME, vol. 221, no. 5, Oct. 1961, pp. 989-993.

11. Joffe, Abram F.: The Physics of Crystals. McGraw-Hill Book Co., Inc., 1928.

12. Gurney, C.: Delayed Fracture in Glass. Proc. Phys. Soc. London, vol. 59, pt. 2, Mar. 1947, pp. 169-185.

13. Pulliam, George R.: Precipitation in Microscopic Cracks. J. Am. Ceramic Soc., vol. 42, no. 10, Oct. 1959, pp. 477-482.

14. Gilman, J. J.; and Johnston, W. G.: The Origin and Growth of Glide Bands in Lithium Fluoride Crystals. Dislocations and Mechanical Properties of Crystals. J. C. Fisher, W. G. Johnston, R. Thomson, and T. Vreeland, Jr., eds., John Wiley & Sons, Inc., 1957, pp. 116-163.

15. Keh, A. S.; Li, J. C. M.; and Chou, Y. T.: Cracks Due to the Piling-Up of Dislocations on Two Intersecting Slip Planes in MgO Crystals. Acta Met., vol. 7, no. 10, Oct. 1959, pp. 694-696.

16. Steijn, R. P.: Sliding and Wear in Ionic Crystals. J. Appl. Phys., vol. 34, no. 2, Feb. 1963, pp. 419-428.

17. Steijn, R. P.: Friction and Wear of Single Crystals. Mechanisms of Solid Friction. P. J. Bryant, M. Lavik, and G. Salomon, eds., Elsevier Publ. Co., 1964. pp. 48-66.

18. Stokes, R. J.; Johnston, T. L.; and Li, C. H.: The Relationship Between Plastic Flow and the Fracture Mechanism in Magnesium Oxide Single Crystals. Phil. Mag., vol. 4, no. 44, Aug. 1959, pp. 920-932.

19. Washburn, J.; Gorum, A. E.; and Parker, E. R.: Cause of Cleavage Fractures in Ductile Materials. Trans. AIME, vol. 215, no. 2, Apr. 1959, pp. 230-237.

20. Whapham, A. D.; and Makin, M. J.: The Hardening of Lithium Fluoride by Electron Irradiation. Phil. Mag., vol. 5, no. 51, Mar. 1960, pp. 237-250.

21. Griffith, A. A.: The Phenomena of Rupture and Flow in Solids. Phil. Trans. Roy. Soc., vol. 221 A, 1921, pp. 163-198.

22. Gilman, J. J.: Plastic Anisotropy of LiF and Other Rocksalt-Type Crystals. Acta Met., vol. 7, no. 9, Sept. 1959, pp. 608-613.

23. Buckley, Donald H.: Friction Characteristics in Vacuum of Single and Polycrystalline Alluminum Oxide in Contact with Themselves and With Various Metals. ASLE Trans., vol. 10, no. 2, Apr. 1967, pp. 134-145.

24. Hardy, Willian B.: Collected Scientific Papers. Cambridge Univ. Press, 1936.

25. Bowden, F. P.; and Tabor, D.: The Friction and Lubrication of Solids. Clarendon Press, Oxford, 1950.

26. Smith, J. O.; and Liu, Chang Keng: Stresses Due to Tangential and Normal Loads on an Elastic Solid with Application to Some Contact Stress Problems. J. Appl. Mech., vol. 20, no. 2, June 1953, pp. 157-166.

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