

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN
VOLUME 18, SUPPLEMENT I

PROCEEDINGS
OF THE
INTERNATIONAL CONFERENCE
ON
CRYSTAL LATTICE DEFECTS

SYMPOSIUM, TOKYO

September 3-4, 1962

Published by
PHYSICAL SOCIETY OF JAPAN

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Etch Pit Studies of Dislocations in Copper Crystals Deformed by Bending: I Annealed Crystals; II Irradiated Crystals

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Annealed and irradiated copper crystals of low initial dislocation density were deformed by bending, and dislocation multiplication and motion were studied using an etch pit technique for observing the dislocations. For the annealed crystals there was dislocation motion and multiplication prior to macroscopic yielding, and the percentages of grown-in dislocations moved by the stress increased with the stress. The dislocations were hindered in the motion by sub-boundaries, and by interaction with other dislocations. Relaxation effects were observed and were much greater for stresses less than the yield stress than for higher stresses. For the neutron irradiated crystals there was no motion or multiplication of dislocations prior to yielding. The slip traces were long, with dislocations closely spaced in the trace. Although not conclusive, the evidence apparently was best interpreted in terms of source hardening. A cube-root dependence of the yield stress on neutron dose was observed.

The crystals (parallelepipeds $5 \times 6 \times 25$ mm with the 6×25 mm faces $(111)^n$), were prepared by acid sawing and polishing from 99.999% copper crystal rods, annealed at 1050°C for five days and, after annealing, the dislocation density was from 5×10^3 to $5 \times 10^4/\text{cm}^2$. The dislocation etch has been described¹⁾. The crystals were stressed at room temperature in a 4-point bending jig. Unless stated otherwise, the (111) faces were the tension and compression surfaces, and all stresses given are maximum resolved shear stresses. Some of the annealed crystals were irradiated at approximately room temperature with fast neutrons before deformation tests were made.

I. Annealed Crystals

A crystal with an initial dislocation density, N , of $10^4/\text{cm}^2$, and orientation 3° from $[\bar{1}01]$ was etched to locate the positions of the grown-in (old) dislocations, a stress of 100 g/mm^2 was applied, and the crystal re-etched. In the photomicrographs the large sharp-bottom pits indicate positions of old dislocations which did not move under the stress, the large flat-bottom pits to old dislocations which did move, and small pits to new dislocations or to new positions of old dislocations. Most of the old dislocations which were not in sub-boundaries were moved by the stress, Fig. 1.

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the United States Atomic Energy Commission.

The slip traces were long, and lay primarily in one slip plane, $(\bar{1}11)$, though the crystal was oriented for double slip, Fig. 2. There was some evidence of slip in both of the other slip planes, $(11\bar{1})$ and $(\bar{1}\bar{1}1)$, and there was evidence for dislocation interactions, since often a slip trace on $(\bar{1}11)$ ended at a short slip trace on either $(11\bar{1})$ or $(\bar{1}\bar{1}1)$, Fig. 3. The dislocations were piled-up by sub-boundaries, Fig. 1, but the dislocations in a "pile-up" were not all in a straight line, Fig. 4. The applied stress in this experiment exceeded the macroscopic yield stress, and the maximum plastic strain was $\sim 10^{-3}$.

Two crystals were tested with a series of stresses from 4 to 100 g/mm^2 . The percentage of old dislocations moved by the stress increased with the stress from about 1% at 4 g/mm^2 to about 75% at the yield stress. For stresses less than the macroscopic yield stress slip traces could be recognized only if the crystal was etched while the stress was applied. For stresses greater than the yield stress, the slip traces were similar to that described, Figs. 1-4.

The spacings of the dislocations were measured in a number of pile-ups, against sub-boundaries and out in the lattice, under stress and relaxed, and on pile-ups separated by distances large and small with respect to the pile-up length. In all cases the spacing of pits in a pile-up did not conform to that expected for a group of parallel dislocations

under a uniform external stress. The stress σ_p , on the i th dislocation in a pile-up of n dislocations can be described as $\sigma_p \propto \sum_{j=1}^n (x_i - x_j)^{-1}$, and a plot of the summation *vs.* x_i should be a straight line with zero slope. An example of such a plot is shown in Fig. 5. The shape of the curve was typical of that for all pile-ups measured.

From the simple model of pile-ups, it would be expected that the proper spacing of etch pits in a pile-up would be observed if the pits were formed 1) with the stress applied or 2) with the stress removed *and* there was a friction force on the dislocations which prevented them from relaxing completely. Evidently the dislocations saw barriers in the lattice which prevented their complete relaxation, but apparently these barriers were not uniformly dispersed on an atomic scale. A pile-up in the stress-relaxed condition is shown in Fig. 6, in which it is apparent that the

dislocations were closer together at each end than in the middle. Therefore, it is a reasonable postulate that an expanding dislocation loop would be hindered only at certain points. It follows that, in order for a pile-up of dislocations to be seen with the expected spacing while under stress, it would at least be necessary that the plane of examination contain the barrier. The chance of this condition being met is small. Thus, it is not surprising that a pile-up with the expected spacing was not observed, and this negative result cannot be used to alter the present theory relating to pile-ups.

Summary of Results on Annealed Crystals

Including results from the previous studies¹¹ as well as the results presented here, a qualitative picture of the motion of grown-in dislocations in annealed copper crystals can be formulated. Dislocations first begin to move at a stress of about 4 g/mm², and



Fig. 1. 95×

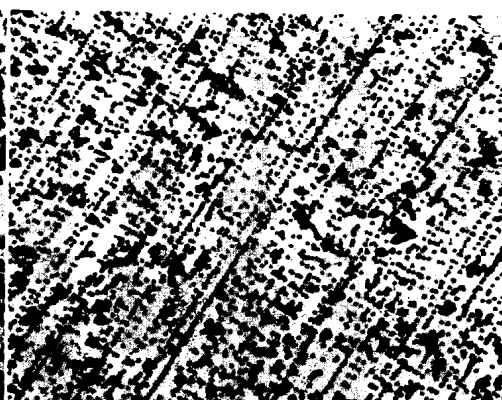


Fig. 2. 48×

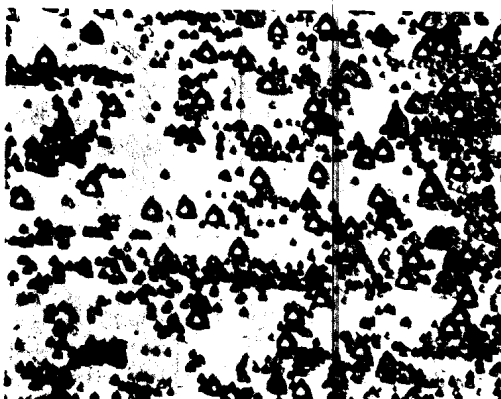


Fig. 3. 95×

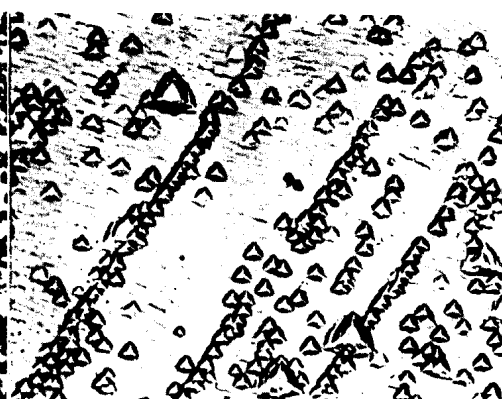


Fig. 4. 190×

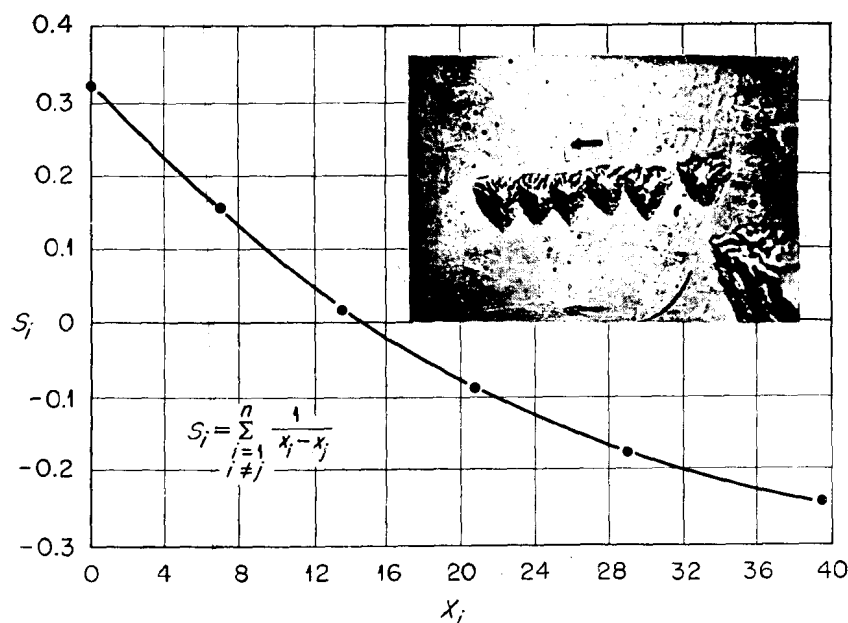


Fig. 5. A pile-up and an evaluation of the stresses on the dislocations in the pile-up. 500×

multiplication first begins at a stress of 15–20 g/mm². Macroscopic yielding occurs at a stress of 35–65 g/mm² (possibly depending on the impurity content of the crystal). The percentage of grown-in dislocations moved by the stress increases monotonically with the stress until approximately 75% are moved at the yield stress. The average distance of motion of the gliding dislocations is 1.4×10^{-1} cm after yielding (easy glide region), is probably 10^{-2} cm prior to yielding, and varies from 1 to 7.5×10^{-3} cm at 5 g/mm². The dislocations are hindered in their motion by sub-boundaries, interaction with other dislocations, and probably by impurity atoms. Pile-ups of dislocations formed under stresses less than the macroscopic yield stress relax completely when the stress is relieved. For stresses greater than the yield stress, the relaxation of the pile-ups is much less. Most of the slip occurs on one slip plane.

II. Irradiated Crystals

Crystals were irradiated with 10^{18} , 6×10^{16} , 4×10^{15} , and 1.3×10^{13} fast neutrons/cm².

10^{18} Neutrons

The initial N in this crystal was 10^4 /cm².

After a stress of 1.7 kg/mm² a few lines of pits corresponding to slip traces were seen through the central region of the compression and tension faces; one is shown in Fig. 7. This stress was defined as the yield stress. The dislocations were $\sim 1 \mu$ apart in the slip traces, and there were a few dislocations which were not quite in the same plane as the trace, and which were spaced irregularly along the trace. All of these traces ended at one end of the dislocation pattern around the contact points, and ran out of the crystal on the other end. The grown-in dislocations were not moved by this stress.

After application of a stress of 1.75 kg/mm² slip traces were observed over all the center portion. Apparently new slip traces were initiated from both the old slip traces (resulting from the stress of 1.7 kg/mm²) and new slip traces. There was never any visible evidence of a grown-in dislocation acting as a generator for the slip traces.

After application of a stress of 2.5 kg/mm² there was a high density of slip traces throughout the crystal, Fig. 8. There apparently was no tendency to form bands, in the sense as observed on LiF by Gilman and

Johnston². Even at this stress there was little tendency of the grown-in dislocations to move (the plastic strain was $\sim 4\%$).

Another crystal (10^{18} nvt) was placed in the bending jig so that the (111) faces were normal to the bend axis and was stressed just to the yield stress. It was etched before and after the stress application, and it was found that the slip traces from the tension and compression surfaces had passed each other in the vicinity of the neutral axis, Fig. 9.

10^{18} Neutrons

After applying a stress of 42 g/mm^2 there was some simple motion of the old dislocations. This motion appeared to be of the same type which occurs in annealed copper¹ except, of course, it occurred here at a stress ten times greater than for annealed copper. There were no slip traces in the crystal. After applying a stress of 51 g/mm^2 slip traces were observed across the central part of the crystal. The

dislocations in the traces were in distinct groups and there was no relaxation when the stress was relieved.

The results of the determination of the yield stress as a function of neutron dose are plotted in Fig. 10. The straight line in this plot has a slope of $1/3$ and is an extrapolation of the data of Blewitt *et al.*³. Thus, this experimental relationship of $\sigma_y \propto \phi^{1/3}$ has been established over seven decades of neutron dose.

Discussion of Irradiated Crystals

There was a striking difference in the behavior of dislocations under an applied stress in irradiated copper as against annealed copper. For annealed crystals the dislocations began to move at a low applied stress, and multiplication began at a slightly higher stress with the amount of motion and multiplication increasing with the stress. For irradiated crystals there was essentially no motion of

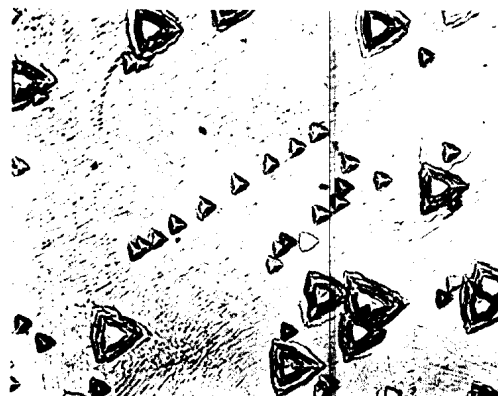


Fig. 6. Pile-up in stress-relaxed condition. $190\times$

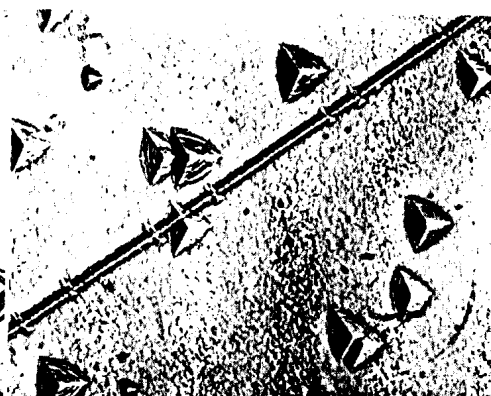


Fig. 7. $190\times$

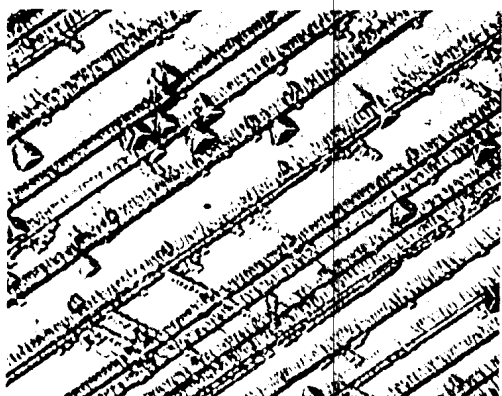


Fig. 8. Slip traces after a stress $\sigma = 2.5 \text{ kg/mm}^2$. $190\times$

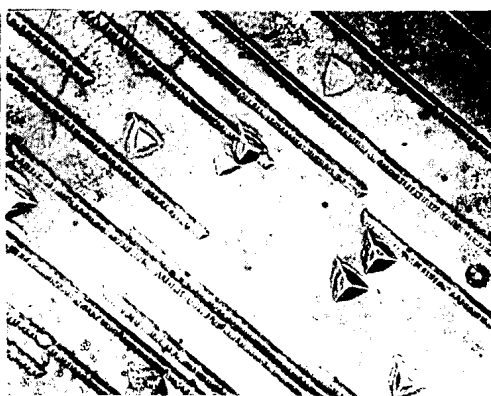


Fig. 9. Slip traces crossing at the neutral axis. $190\times$

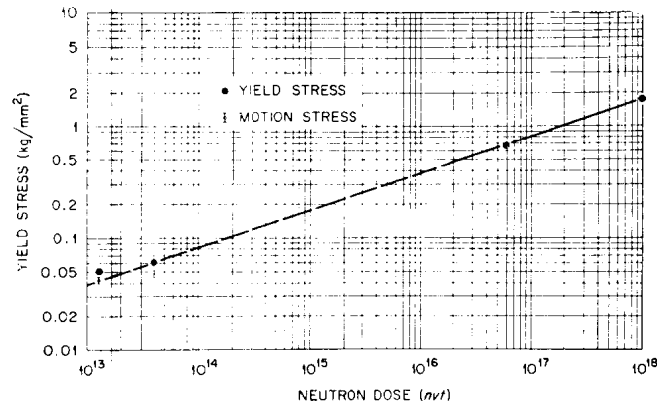


Fig. 10. Yield stress vs. fast neutron dose.

the old dislocations even at stresses greater than the yield stress. The slip traces were very long, the dislocations closely spaced in the traces, and the traces were relatively far apart. As the stress was increased past the yield stress the slip traces did not broaden into bands but simply increased in number. There was little evidence of hindrance of dislocation motion by sub-boundaries.

The most pertinent evidence for source hardening is as follows: (1) For the crystals irradiated with 6×10^{16} and 10^{18} neutrons there was essentially no motion of the old dislocations, even at stresses greater than the yield stress. If friction hardening were primary, most of the old dislocation should have moved some at such a stress. (2) The slip traces passed each other in the vicinity of the neutral axis just at yielding. It would be expected in a hard crystal that the slip traces would extend only a short way toward the neutral axis if a friction force were responsible for the hardening. (3) For the 10^{13} neutron irradiations some simple dislocation motion was observed prior to yielding, but at a stress ten times that necessary for simple motion in

annealed crystals.

The facts that slip traces did end in the crystal, and that there was no relaxation indicate that there was some friction force introduced by the irradiation. This friction was probably related to the interaction of gliding dislocations with the vacancy and interstitial loops which result from the irradiation⁽⁴⁾. Therefore, the conclusion is drawn that, although a friction force was present the hardest force to overcome was a pinning force, and that the yield stress was determined by source hardening. Probably the friction force played a role in determining the details of the deformation process after yielding.

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- 3 T. H. Blewitt, R. R. Coltman, R. E. Jamison and J. K. Redman: J. Nuclear Materials **2** (1960) 277.
- 4 J. Silcox and P. B. Hirsch: Phil. Mag. **4** (1959) 1356.

DISCUSSION

Suzuki, T.: 1) Have you tried to apply the Read's theory to your bend test to get some knowledge about the frictional stress in irradiated copper crystals? 2) Did you avoid a local yielding in the vicinity of the root of knife edges to observe the motion of dislocations?

Young, F. W., Jr.: 1) No. 2) There was local yielding in the vicinity of the contact points of the bending jig. As pointed out, the slip traces appeared to be related to this local deformation. However, experiments were performed in which the bending

was done with my fingers in such a way that there was no apparent local deformation. The arrangement of the slip traces was the same as that described. Also, the old dislocations did not move.

Roberts, J. M.: You pointed out that the passage of dislocations from the surface into the crystal, overshooting the neutral axis in irradiated crystals, suggested that the flow stress in this case was governed by source hardening not friction hardening. Do you observe the same phenomena in annealed crystals and do you come to the same conclusion for annealed crystals?

Young, F. W., Jr.: In annealed crystals the flow stress is believed to be determined by impurities as based upon my previous publications. At stresses above the yield stress in annealed crystals dislocation motion into the vicinity of neutral axis occurs.

Fujita, F. E.: On the side surfaces, it may be possible to observe the difference between the distribution of dislocations on the surface and that in the deep interior of the crystal. Did you observe this effect?

Young, F. W., Jr.: In annealed crystals the dislocations travel only short distances from the tension and compression surfaces when small stresses are applied. Since the edges of the crystal are rounded because of electropolishing, this rounded area is not of (111) orientation so that no information can be obtained. At higher stresses slip traces are found extending away from the tension and compression surfaces. No systematic study has been made of the arrangements of the dislocations on these surfaces.

The Hardening of Alkali-Halide Crystals by Point Defects*

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The hardening of alkali-halide crystals by divalent impurities and by radiation-produced defects has been studied in the temperature range of 20.5°K to 300°K. The amount of hardening produced by small concentrations of divalent metal impurities, and the temperature dependence of the hardening depend sensitively on the state of dispersion of the impurities. At 20.5°K the greatest hardening was produced by divalent ion-vacancy pairs. At 300°K the greatest hardening was produced by impurity clusters in extremely slowly cooled crystals.

From mechanical tests and optical studies of irradiated crystals it is deduced that the severe hardening produced at room temperature by x-rays and γ -rays is due to the interstitial halogen ions that are formed when F -center vacancies are created. The V_K -center (self-trapped hole) that is produced during irradiation at 77°K is also very effective in hardening LiF. The behavior of alkali halide crystals is compared with that of other materials in which severe hardening is produced by small concentrations of defects. The principal correlation is that all defects which produce severe hardening have non-symmetrical strain fields associated with them. The manner in which the non-symmetrical, or tetragonal strain can produce the great hardening is discussed.

I. Introduction

It has long been known that alkali halide crystals can be hardened appreciably by point defects present in small concentrations. Over thirty years ago Smekal and co-workers⁽¹⁻⁴⁾ showed that divalent metal impurities that are soluble in NaCl will produce severe hardening, whereas monovalent metal impurities cause relatively little hardening. Recent work on hardening by radiation-produced defects⁽⁵⁻⁷⁾ has shown that severe hardening is observed after irradiations that produce low concentrations ($<10^{-5}$) of point defects. In this latter work the hardening has been attributed to clusters of defects, rather than to individual point defects.

In the present paper we will report additional experimental evidence regarding the impurity hardening and irradiation hardening of several alkali halide crystals, although most of the data will refer to LiF. It will become apparent that the hardening by small concentrations of divalent impurities depends sensitively on the state of dispersion of the impurities, and that some of the simple point defects produced during irradiation can produce pronounced hardening.

The role of dislocations in the deformation of alkali halide crystals is well understood, and it is known that the flow stress is determined by the resistance to motion of the many fresh dislocations that are produced during deformation⁽⁸⁾. Although there are indeed pinning effects due to impurities and radiation-produced defects, which are of interest in themselves, the values of critical resolved shear stress or flow stress that are reported in this work are not determined by the state of dislocation pinning.⁽⁹⁾ The role of point defects in determining the flow stress must be understood in terms of how these defects impede the motion of fresh dislocations.

II. Hardening of LiF by Divalent Impurities

The behavior of LiF single crystals containing ~75 ppm of Mg has been compared with that of relatively pure crystals⁽⁹⁾. Both crystals were obtained from the Harshaw Chemical Company, and were of comparable structural perfection. The critical resolved shear stress of the crystals was measured in compression. It was found that the hardness of the impure crystal depended on prior heat treatment, in particular on the rate of cooling from about 200°C or 300°C down to room temperature, whereas the purer crystals were in-

* This research was sponsored in part by the Aeronautical Research Laboratory, Office of Aerospace Research, United States Air Force.

sensitive to heat treatment. This behavior is shown in Fig. 1. (The rise in hardness of

following two different heat treatment is shown in Fig. 2. The flow stress of the

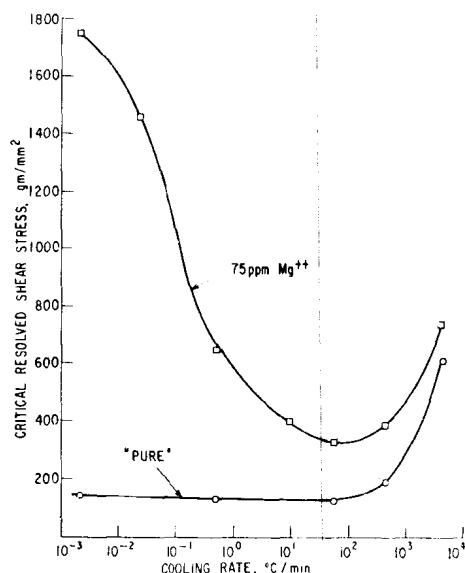


Fig. 1. Effect of cooling rate from 400°C on the room temperature critical resolved shear stress of relatively pure LiF crystals and crystals containing 75 ppm of Mg.

both crystals at the faster cooling rates is due to quenching strains, and is not of interest to us here.) The greatest hardening of the impure crystals was achieved by cooling extremely slowly ($\sim 3^\circ\text{C}/\text{day}$), and the least hardening was obtained by air-cooling to room temperature.

Resonance studies¹⁰⁻¹³) and ionic conductivity measurements¹⁴) on analogous alkali halide-impurity systems have shown that after air-cooling to room temperature the divalent impurity ions are present as impurity ion-vacancy pairs. Prolonged annealing near room temperature or very slow cooling rates from higher temperatures tend to produce clusters of impurities. It, therefore, appears that the pronounced room temperature hardness of the slowly cooled crystals is due to a precipitation hardening effect. There were no visible precipitates in the slowly cooled crystals in the present experiments, but the early work on NaCl has shown that visible precipitates produce no hardening²⁻⁴), presumably because they are indicative of over-aging.

The temperature dependence of the flow stress of pure and impure crystals of LiF

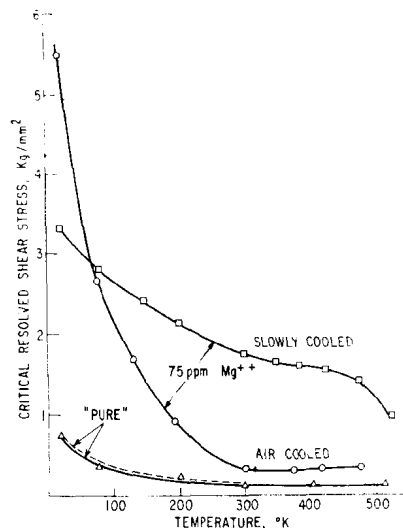


Fig. 2. Temperature dependence of critical resolved shear stress. The solid curve for the pure crystals corresponds to slowly cooled specimens, and the dashed line is for air-cooled specimens. The two cooling rates were $\sim 0.002^\circ\text{C}/\text{min}$ and $\sim 50^\circ\text{C}/\text{min}$.

purcrystals is relatively insensitive to test temperature, regardless of prior heat treatment. The slowly cooled, or precipitation hardened, impure crystals, which were very hard at room temperature, became somewhat harder as the test temperature was lowered. On the other hand the rapidly cooled, or solution treated, impure crystals which were soft at room temperature, became much harder at low temperatures, and were even harder than the precipitation hardened crystals at the lowest test temperature.

It is apparent that the hardening produced by divalent metal impurities depends sensitively on the state of dispersion of the impurities, and there are two problems one may consider. The first concerns the precipitation hardening of the slowly cooled crystals, in which we will have no further interest. The second problem concerns the extreme hardening produced by divalent ion-vacancy pairs at very low temperature, and the temperature dependence of that hardening. It will be of interest to compare the behavior of these impurity-vacancy pairs with the behavior of other simple lattice defects.

The dependence of hardening due to impurities on prior heat treatment has been observed also in impure NaF and NaCl crystals¹⁵, and the behavior is qualitatively similar to that described above for LiF. It has been reported that impure MgO also responds to heat treatment in a manner similar to that described above for LiF¹⁶.

III. Hardening by Radiation-Induced Defects

A. Experimental

Pure alkali halide crystals, obtained from the Harshaw Chemical Company, were irradiated with 70 kV x-rays and gamma-rays from a cobalt-60 source, at room temperature and liquid nitrogen temperature¹⁷. The crystals were very soft as-received from Harshaw, which indicates that they were relatively free of divalent metal impurities⁹.

The effect of radiation-induced defects on the mechanical properties was determined by measuring the critical resolved shear stress in compression tests at temperatures ranging from 20.5°K to 300°K.

The types of defects produced by irradiation were determined by optical absorption measurements. The nature of the stable defects that resulted from irradiation depended upon the temperature of irradiation, and to some extent on the particular alkali halide. After room temperature irradiation of LiF with either x-rays or γ -rays, only *F*-centers and *M*-centers appeared in the absorption spectrum. After irradiation at 77°K, only *F*-centers and *V*-centers were observed. In LiF crystals that were irradiated at 77°K and warmed to room temperature, only *F*-centers were retained in sufficient numbers to produce measurable optical absorption. NaCl and KCl crystals irradiated at room temperature contained *F*-centers, *M*-centers, and a relatively small concentration of *V*₃-centers.

B. Hardening Due to Defects That are Stable at Room Temperature

The increase in room temperature critical resolved shear stress correlated very well with the *F*-center concentration of irradiated crystals as shown in Fig. 3. In that figure are shown data for LiF crystals at various stages of build-up of *F*-center concentration during room temperature irradiation, data for crystals at various stages of annealing, and data for crystals that were irradiated at 77°K

and warmed to room temperature. It is apparent that the hardness increase is closely related to the concentration of radiation-produced *F*-centers, regardless of how the concentration of *F*-centers is attained. On the other hand, no correlation was found between hardness increase and concentration of *M*-centers, which were the only other color centers present in significant numbers at room temperature in LiF. Therefore, the *M*-centers is not an important source of hardening at the radiation dosages employed in the present experiments.

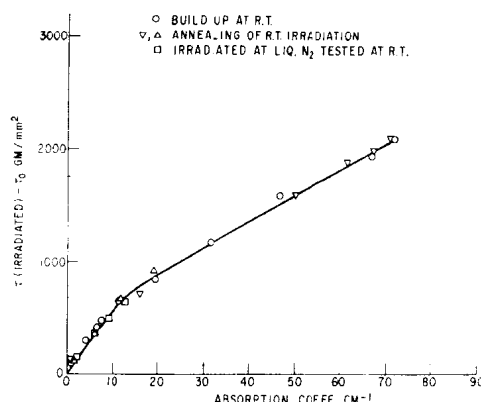


Fig. 3. Increase in room temperature flow stress vs. absorption coefficient in the *F*-band. (The *F*-center concentration is $\sim 0.2 \alpha_F$ ppm).

The correlation between *F*-center concentration and hardness increase shown in Fig. 3 seems to imply that the *F*-centers are responsible for the severe hardening. This possibility is ruled out by the experiments of Suzuki and Doyama¹⁸, who produced *F*-centers in KCl by additive coloration and found only moderate hardening. The *F*-centers produced by additive coloration are optically the same as those produced by irradiation, yet it is seen in Fig. 4 that there is relatively little hardening due to additively produced *F*-centers as compared to the hardening in irradiated crystals.

We must conclude that the room temperature hardening of irradiated alkali halides is not due to the *F*-centers *per se*, but that it is due to a specific defect that is formed at the same rate as *F*-centers, and disappears at the same rate as *F*-centers during annealing. Further, this defect is not present in comparable numbers in additively colored crystals.

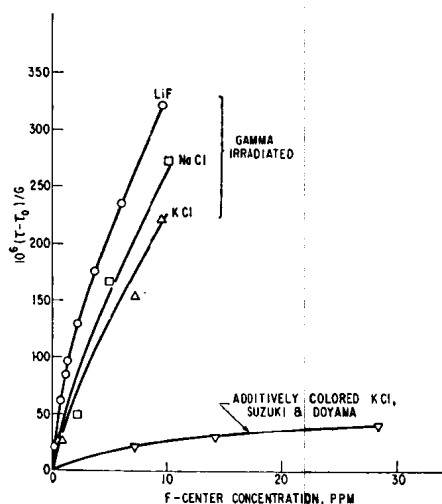


Fig. 4. Increase in flow stress *vs.* *F*-center concentration in radiation-colored and additively-colored alkali halides. The flow stresses were normalized by the shear modulus, $G = [C_{44}(C_{11} - C_{12})/2]^{1/2}$.

That it is a specific point defect, and not a cluster or colloid, is apparent because the relation between hardening and *F*-center concentration is independent of irradiation temperature or annealing treatments which should severely affect the state of clustering. The defect responsible for the hardening is very stable at room temperature in LiF; there was no observable decrease in hardness in a crystal that had been stored for over a year at room temperature following irradiation.

We suggest that the defect responsible for the room temperature hardening is the interstitial halogen ion or atom that is formed when the *F*-center vacancy is created, and which recombines with the vacancy during annealing. In the discussion below it will be argued that for such an interstitial ion to cause severe hardening is consistent with the severe hardening effect of particular types of defects in other systems.

The temperature dependence of the hardening due to defects produced by room temperature irradiation is shown in Fig. 5 and is compared with the temperature dependence of the hardening due to impurity-vacancy pairs. The hardening due to impurity-vacancy pairs is far more temperature-sensitive. If the hardening is due merely to an elastic interaction between a dislocation and a *fixed*

point defect of constant size, it is difficult to understand why the two types of defects should give such different temperature dependences for the hardening.

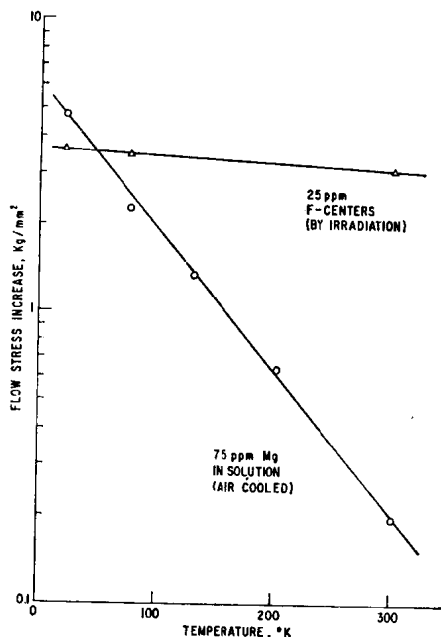


Fig. 5. Temperature dependence of hardness increase due to impurity-vacancy pairs, and due to interstitial halogen ions in LiF.

C. Hardening Due to V_K -Centers

V_K -centers, or "self-trapped holes"¹⁹, that are produced by irradiation at 77°K are also effective in hardening LiF. After irradiation at 77°K, optical absorption measurements made at the same temperature revealed the presence of *F*-centers and V_K -centers. The hardness increase at 77°K after irradiation was greater than the *F*-centers alone would have produced. The excess hardness disappeared when the crystal was heated to the temperature ($\sim 120^\circ\text{K}$) at which the V_K -center disappeared from the paramagnetic resonance spectrum in the experiments of Kanzig²⁰, and from the optical absorption spectrum in the experiments of Wiegand and Smoluchowski²¹.

The behavior after irradiation at 77°K is shown in Fig. 6, where the hardness is plotted against *F*-center concentration. Data are presented during build-up of the radiation damage at 77°K, and after annealing at successively higher temperatures above 120°K. It is seen that after annealing at 120°K the

relation between F -center concentration and hardness increase is the same as in a crystal that had been irradiated at room temperature.

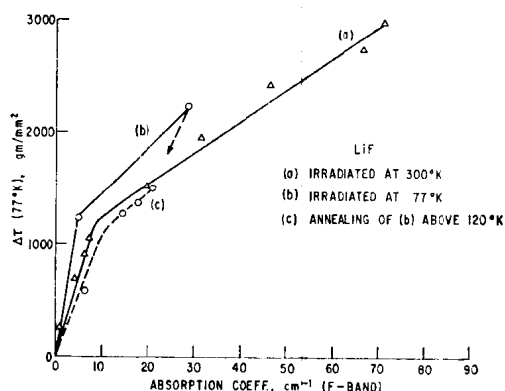


Fig. 6. Flow stress increase vs. absorption in F -band, both measured at 77°K. Curve (a)—Measurements at 77°K following room temperature irradiation with gamma rays. Curve (b)—Measurements following irradiations at 77°K, without warm-up. Curve (c)—Measurements at 77°K and annealed for 30 min at successively higher temperatures above 120°K.

The concentration of V_K -centers was calculated from the absorption peak, assuming the oscillator strength to be the same as for the F -center, ($f=0.5$). This assumption was made because the oscillator strength of the V_K -center is not known and it allows the hardening per defect to be calculated. It was found that the hardening attributed to V_K -centers was approximately the same *per defect*, as the hardening produced by F -centers.

IV. Discussion

A. Relative Hardening Produced by Various Defects

On the basis of existing experimental information, it appears that defects in alkali halides can be divided into two classes with regard to how effectively they harden a crystal. Monovalent impurity ions and F -centers have relatively little hardening effect, whereas pronounced hardening is produced by clusters of divalent ions and by interstitial halogen ions at room temperature, and by V_K -centers and divalent ion-impurity pairs at low temperature. This large difference between the hardening produced by different defects is not unique to the alkali halides, but may be

observed in many different types of crystals²³.

The existence of two classes of defects may be demonstrated by taking as a measure of the hardening the increase in flow stress per unit concentration, $\Delta\tau/\Delta c$. In order to facilitate comparison of data for different crystals, the stress increase is given in terms of the shear modulus, G . Table I shows the observed hardening by defects in various crystals, including the alkali halides. There are several cases in which two different types of defects produce very different rates of hardening in the same matrix crystal. The distinction between the two types of hardeners is *not* that of interstitial *vs.* substitutional, since both classes of defects include both substitutional and interstitial types of defects, *e.g.*, low hardening is produced by interstitial carbon in nickel and high hardening is produced by divalent substitutional ions in alkali halides.

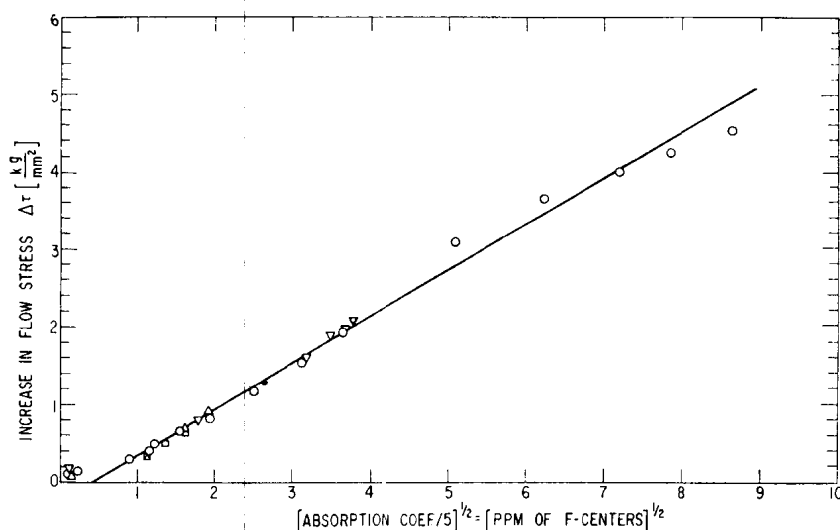
The distinction is, rather, between symmetrical defects that have at least cubic symmetry and asymmetrical defects that have large tetragonality in their strain fields. All the defects in the lower part of the table, whose concentration dependence of hardening is high ("rapid" hardeners), have an axis of large displacement: $\langle 100 \rangle$ for interstitials in copper, iron, and niobium; $\langle 110 \rangle$ for interstitials and divalent ion-vacancy pairs in alkali halides; and $\langle 111 \rangle$ (or $\langle 110 \rangle$) for vacancy disks in aluminum. The defects in the upper half of the table ("gradual" hardeners), all tend to produce symmetrical strains in the lattice.

Table I somewhat exaggerates the difference between the hardening from the two classes of defects, because, at least for the more dilute cases, the hardening is not linear, but is proportional to the square root of the concentration. The result is that $\Delta\tau/\Delta c$ will be larger at low c . Fig. 7 shows that the data presented above for the hardening of lithium fluoride during room temperature irradiation fits the relation $\Delta\tau \propto c^{1/2}$. Even if it is assumed that all defects exhibit this concentration dependence of hardening, it can still be concluded that the hardening per defect is typically at least ten times larger for the rapid hardening class of defects than for the gradual hardeners.

Table I. Effects of different defects in hardening crystals: $\Delta\tau/\Delta c$ is given in terms of the shear modulus G . Typical values are shown.

Material	Defect	Conc.	Typical Hardening $\Delta\tau/\Delta c$
Al	Substitutional atoms ²³⁾	10^{-2}	$G/10$
Cu	Substitutional atoms ²⁴⁾	10^{-2}	$G/20$
Fe	Substitutional atoms ²⁵⁾	10^{-2}	$G/16$
Ni	Interstitial carbon ²⁶⁾ , (77°K)	5×10^{-3}	$G/7$
Nb	Substitutional atoms ²⁷⁾	10^{-2}	$G/10$
NaCl	Monovalent substitutional impurities ²⁾	10^{-4}	$< G/30$
KCl	F -centers, additive coloring ¹⁸⁾	10^{-5}	$1.5G^*$
Al (quenched)	Vacancy disks ²⁸⁾	10^{-4}	$2G$
Cu (irrad.)	Interstitial atoms ²⁹⁾ (inferred in Ref. 22)	10^{-4}	$9G$
Fe	Interstitial carbon ²⁵⁾	10^{-4}	$3G$
Nb	Interstitial nitrogen ³⁰⁾	10^{-4}	$2G$
NaCl	Substitutional divalent ions ²⁾ - ⁴⁾	10^{-4}	$2G$
KCl (irrad.)	Interstitial chlorine(?) F -center conc.	10^{-5}	$18G^*$
LiF	Divalent impurity clusters	10^{-4}	$6G$
LiF	Divalent impurity-vacancy pairs (77°K)	10^{-4}	$10G$
LiF (irrad.)	V_K -centers (77°K)	2×10^{-6}	$25G^*$
LiF (irrad.)	Interstitial fluorine(?) F -center conc.	10^{-4}	$5G$

* These values of $\Delta\tau/\Delta c$ are particularly high because they were taken at very low concentrations. The measurements were at room temperature unless otherwise noted.

Fig. 7. Hardness increase in irradiated LiF plotted against the square root of the F -center concentration.

B. Possible Reasons for the Difference between the Hardening Produced by the Two Classes of Defects

The ratio of a factor of ten of the two strengthening effects is consistent with the magnitudes of the relative elastic interactions with dislocations that have been calculated for the two types of defects. This ratio is larger for the case of screw dislocations, because they have only second order interactions with symmetrical defects, but direct, considerably greater interaction with tetragonal distortions. The interaction energy, E_A , for a screw dislocation interacting with a tetragonal distortion, and the analogous energy, E_S , for interaction with a symmetrical defect have been calculated^{(22), (31)}. When the defect is about one atom spacing from the dislocation, the ratio between these two interaction energies, E_A/E_S , is about ten. At larger distances from the dislocation the ratio of the two energies is even larger. These elastic considerations appear to be capable of explaining the observed difference of a factor of ten in hardening effects, at least qualitatively.

For a more specific description of the hardening mechanism, two possibilities have been suggested. As a dislocation approaches a defect it may either: 1) avoid the defect by cross glide, or 2) pass close by the defect and interact strongly with it.

(1) *Hardening by jogs*—In the first case, if the dislocation avoids a high stress region by cross glide, jogs will form which will tend to produce point defects or dislocation dipoles in the wake of a screw dislocation. As the jogs are dragged along, leaving behind trails of defects, there will be a dragging force exerted on the dislocation. In lithium fluoride crystals the number of such defect trails has been measured, and it appears that they provide a significant contribution to the resistance to dislocation motion⁽³²⁾. It has been suggested that a possible effect of defects is to cause more dislocation cross glide, thereby increasing the steady-state number of jogs, and hence the dragging force on the dislocation⁽⁹⁾. As yet, however, a realistic, quantitative theory of such hardening is not available.

(2) *Hardening by local stress fields*—If the dislocation does not avoid the obstacles on the glide plane by cross gliding, it will feel

some maximum force from each defect as it encounters the defect at close range. The magnitude of this force may be estimated for the two types of defects by taking the derivatives of the energies E_A and E_S with respect to position of the dislocation along the glide plane. The maximum value of the forces may then be obtained, and the ratio F_A^{\max}/F_S^{\max} thus derived is about the same as the ratio of the energies, E_A/E_S , which is numerically consistent (within the accuracy of the calculations) with the observed hardening by the two classes of defects.

It should be recalled, however, that if the defect remains stationary while it interacts elastically with a dislocation, and if its strain field does not vary strongly with temperature, it is difficult to rationalize the great difference in temperature dependence of the hardening produced by divalent impurity-vacancy pairs and radiation-produced interstitials in lithium fluoride.

The suggestion that has been made, that the pronounced room temperature hardening produced by irradiation of alkali halides is due to the interstitial ions formed when F -centers are created, is consistent with the correlation that it is only defects with tetragonal strain fields that produce such "rapid" hardening. In the absence of other known defects of a tetragonal nature that are created and destroyed at the same rate as F -centers, the interstitial ion appears to be the most likely cause of the room temperature hardening.

C. Some Proposed Experiments

If the tetragonality of a defect is of major importance in the amount of hardening it produces, we should expect the hardening of a single defect to be anisotropic. If most, or all, of the defects could be aligned along a single direction in a crystal, it should be possible to observe gross anisotropies in the plastic deformation behavior of the crystal. The possibility of aligning the asymmetrical defects has been demonstrated for at least two of the defects in alkali halide crystals. Dreyfus⁽³³⁾ has shown that the divalent impurity-vacancy pairs in an alkali halide can be oriented with an electric field, while Delbecq, Smaller, and Yuster⁽³⁴⁾ have shown that the V_K -center can be oriented with polarized light.

A second type of experiment involves separating the divalent ion-vacancy pair, so that instead of one tetragonal defect there will be two symmetrical ones. Hayes¹³ has reported that in NaF it is possible to separate the associated divalent impurities and vacancies by irradiation with ultraviolet light at room temperature. If the hardening depends on the symmetry of the defect, the impure NaF crystal should be softer at low temperatures after a room temperature irradiation with ultraviolet light, and the hardening should return during room temperature aging as the impurities and vacancies again become associated¹⁸. Dreyfus and Nowick¹⁴ have shown that divalent impurities and vacancies can be kept from associating in NaCl crystals by cooling moderately rapidly to below room temperature. It is not clear, however, that a sufficiently large fraction of the impurities can be kept from associating to produce a measurable difference in the hardness.

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DISCUSSION

Seeger, A.: What is the detailed meaning of some of the entries in Table I? For example, does the interstitial hardening of irradiated copper refer to electron or neutron-bombardment? Electron bombardment hardening may be due to interstitial atoms. However, the hardening by electron irradiation is much less than neutron hardening. It appears that much more severe defects than interstitials are required to explain the experimental facts on neutron hardening.

Johnston, W. G.: It should be emphasized that the table is meant to show qualitatively that there are two classes of defects with regard to how severely they harden a crystal when present in small concentrations. The particular entry that has been questioned by Prof. Seeger refers to an interpretation of radiation damage in copper²²