The Internal Friction of Rock Salt Single Crystals*

D. R. Frankl†
Columbia University, New York, New York

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The internal friction of rock salt crystals is markedly decreased by mild x-irradiation. This is interpreted as the pinning of dislocations by cation vacancies liberated from vacancy pairs on the trapping of photoelectrons. Very small applied stresses are capable of breaking the pinning points. Under some conditions, such breakage under the vibrational stress of measurement may lead to a doubly valued dependence of internal friction on strain amplitude. A variety of other phenomena occur, most of them being qualitatively explainable on the basis of damping by moving dislocations.

I. INTRODUCTION

THIS paper presents some results of a survey of the amplitude-dependent internal friction of rock salt single crystals, carried out for the purpose of comparing the mechanical dissipation in this ionic solid with that in metallic crystals.

Read[1] first proposed, based on a study of zinc crystals, that the amplitude-dependent part of the internal friction of single crystals arises from the motion of dislocations in the lattice. Numerous investigations[2] on other metals have given strong support to this hypothesis, and Koehler[3] has presented a phenomenological theory which correctly predicts the usually observed form of amplitude dependence. However, the evidence is not entirely conclusive, since the existing theoretical calculations[4] of energy dissipation by moving dislocations fail to account for the magnitude of the observed damping. For this reason, it was felt that additional experimental results would be of interest.

Previous work on mechanical dissipation in ionic crystals includes the measurements by Chatelet and Cabarat[5] on rock salt crystals of various origins and the investigation by Breckenridge[6] of the temperature dependence of the anelastic relaxation. However, these authors give no results in the higher range of strain amplitudes, which is of principal interest in the present paper.

The plastic properties, on the other hand, have been extensively investigated, and a comprehensive review is given by Schmid and Boas.[7] Of particular interest in connection with the present work are the observations that the critical shear stress for slip is markedly increased by the introduction of F centers[8] or divalent substitutional foreign cations.[9]

II. EXPERIMENTAL METHODS

A. Specimens

The specimens used in this work were synthetic single crystals obtained from the Harshaw Chemical Company, Cleveland, Ohio. Checks of the lattice perfection by back-reflection Laue patterns disclosed no discernible asterism, mosaic structure, or lineage structure. However, spectrographic analyses of crystals from the same source, reported by Duerig and Markham,[10] indicate that they may contain as much as 0.2 percent of impurity, mainly Al and Fe.

The crystals were received in rough-cut form, and were reduced to appropriate size, *viz.*, about 3 cm in length and about 3 to 5 mm square in cross section, by cutting with a fine jewelers' saw and dry grinding on abrasive paper from No. 1 through 4-0 grit. Measurements were made on eight specimens, six of them cut from a single growth at a cylinder axis orientation of about 20, 76, 76 degrees, and the other two cut from a second growth at about 29, 65, 75 degrees.

In some cases, further reduction in cross section was accomplished by etching with water, usually while the crystal was cemented to a transducer, as described below, with its ends protected by a paraffin coating which was subsequently dissolved off with benzene. The paraffin and benzene were found to have no effect on the internal friction.

When not in use, the crystals were stored in the vacuum chamber of the measuring apparatus or in a desiccator over calcium chloride, calcium sulfate, or phosphorus pentoxide. No effects of adsorbed moisture were found.

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† Present address: Sylvania Electric Products, Inc., Physics Laboratories, Bayside, New York.

[1] T. A. Read, Phys. Rev. **58**, 371 (1940).

[2] T. A. Read, Trans. Am. Inst. Mining Met. Engrs. **143**, 30 (1941); T. A. Read and E. P. T. Tyndall, J. Appl. Phys. **17**, 713 (1946); I. H. Swift and J. E. Richardson, J. Appl. Phys. **18**, 417 (1947); C. A. Wert, J. Appl. Phys. **20**, 29 (1949); A. S. Nowick, Phys. Rev. **80**, 249 (1950); *Pittsburgh Symposium on Plastic Deformation of Crystalline Solids* (Mellon Institute, 1950); J. Marx and J. S. Koehler, *Pittsburgh Symposium.*

[3] J. S. Koehler, Chap. VII of *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952).

[4] G. Leibfried, Z. Physik **127**, 344 (1950); J. D. Eshelby, Proc. Roy. Soc. (London) **A197**, 396 (1950).

[5] J. Chatelet and R. Cabarat, Comp. rend. **23**, 2111 (1951).

[6] R. G. Breckenridge, Chap. VIII of reference 3.

[7] E. Schmid and W. Boas, *Plasticity of Crystals* (1935); (English translation published by F. A. Hughes and Company, Ltd., London, 1950).

[8] M. N. Podaschewsky, Phys. Z. Sowjetunion **8**, 81 (1935).

[9] W. Metag, Z. Physik **78**, 363 (1932).

[10] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

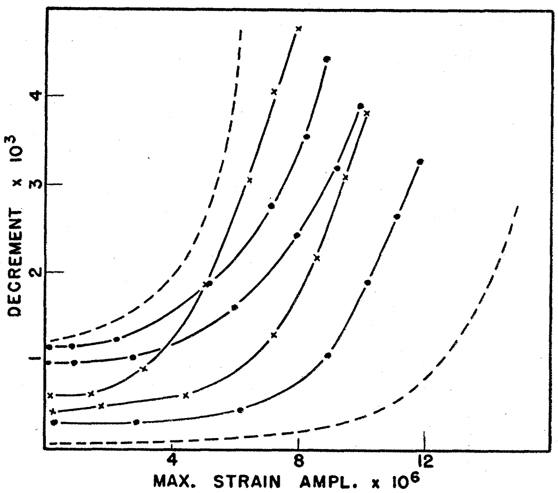

FIG. 1. Normal internal friction curves, showing the usually observed dependence of Δ on U. The solid lines are typical runs on one specimen, and the broken lines give roughly the range covered by seventy-eight runs on the eight specimens.

B. Measurements

The internal friction measurements were made by the composite piezoelectric oscillator method,[1] the transducer being a Straubel-cut quartz rod having contacting electrodes. The specimen and transducer were cemented together under light finger pressure with either phenyl salicylate ("salol") or a beeswax-rosin mixture. Despite all precautions, the cementing operation was found to produce an appreciable increase in the internal friction. The salol bond tended to be less objectionable in this respect but had the disadvantage of relatively high volatility, so that it could not be used for assemblies which were to be left undisturbed for more than a few days.

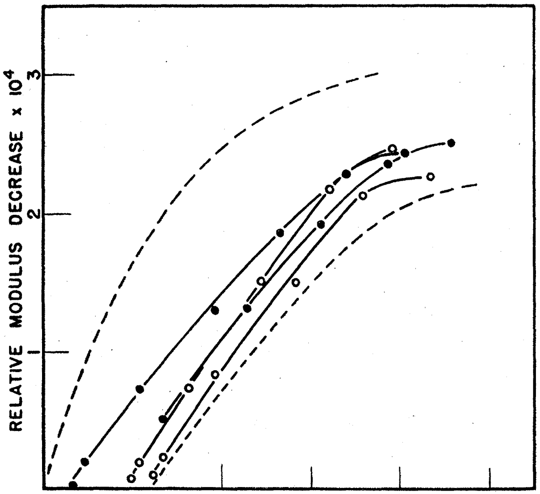

FIG. 2. Decrease in Young's modulus with increasing amplitude, plotted as function of the decrement. The solid lines are some of the runs shown in Fig. 1, and the broken lines give roughly the range covered by all runs.

Each specimen was adjusted in length to have, within a few tenths of a percent in most cases, the same resonant frequency as its transducer. These frequencies, about 70 kc/sec, agreed within a few tenths of one percent with the values calculated from the elastic constants of rocksalt given by Durand.[11]

The measure of internal friction used throughout the present paper is the *decrement* Δ, defined as the ratio of the energy dissipated per half-cycle to the vibrational energy in the specimen. This quantity corresponds to the logarithmic decrement of amplitude in the case of small linear damping. The measure of the amplitude of vibration is the *maximum strain amplitude* U in the specimen. Under the present conditions of good frequency matching and small damping, the local strain amplitude is very nearly $U\sin(\pi x/L)$, where x is the position along the specimen rod, measured from either end, and L is the length of the rod.

C. Coloration

Introduction of F centers was accomplished by placing the specimen directly before the 0.0005-in. mica[12] window of an x-ray tube operating at 40 kv and about 20 ma for a few minutes at each of a number of spots covering one entire longitudinal face. At room temperature this dosage was sufficient to impart an amber coloration throughout the volume of the crystal, with some decrease of intensity in the direction of incidence. For low-temperature coloration, the specimen was held in a groove in a copper block which formed one face of a liquid nitrogen reservoir, the temperature being measured by a thermocouple embedded in a dummy crystal, and moisture being excluded by a cellophane tape window. The resulting coloration was considerably less intense than that at room temperature.

III. RESULTS

A. Amplitude Dependence

As would be expected for a structure sensitive property, the internal friction of rock salt crystals was found to be extremely sensitive to all details of their previous history. Consequently, conclusions can be based only upon fairly broad patterns of behavior, and small differences must be ignored.

Under most conditions of previous history, Δ is a monotonically increasing function of U as shown in Fig. 1; curves having about this shape and magnitude will henceforth be designated as "normal."

Along with the increase of Δ corresponding to an increase of U, there is a decrease in the Young's modulus

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[11] M. A. Durand, Phys. Rev. **50**, 449 (1936).

[12] D. R. Frankl and T. A. Read, Phys. Rev. **89**, 663 (1953). In this note it was erroneously stated that the x-ray tube had a beryllium window. However, the manufacturer's literature indicates that the transmission spectra of these two windows are essentially identical.

E of the specimen, detected as a small but measurable shift in the resonant frequency of the composite oscillator. The fractional decrease $-\delta E/E$ in the modulus is shown as a function of Δ in Fig. 2. When plotted in this manner the $\delta E/E$ curves observed under a wide variety of conditions all tend to cluster together in a fairly narrow band, even when Δ is far outside the normal range. Thus, $\delta E/E$ is, roughly, a function of Δ alone, suggesting that the modulus shift and the damping arise through the same mechanism.

In contrast to the normal internal friction, several other forms of dependence of Δ on U were observed. For example, five of the specimens behaved, at times, in the manner shown in Fig. 3, i.e., at the higher values of driving voltage applied to the transducer, an increase in voltage brought about such a large increase in damping that the amplitude of vibration was reduced. Under such conditions, Δ is a doubly valued function of U. Unfortunately, all attempts to determine the conditions under which a specimen would display this behavior failed. Indeed, all specimens in which it was observed at any time subsequently reverted to normal behavior. It seemed, however, that cold-working was part of the required treatment.

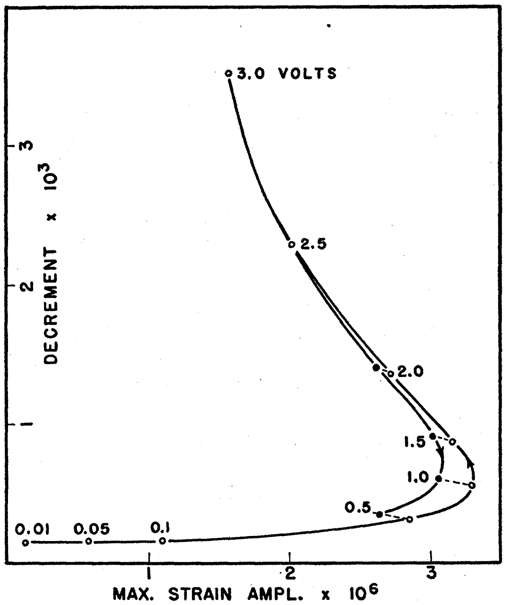

FIG. 3. Example of doubly-valued dependence of Δ on U.

Still another type of amplitude dependence observed is a nearly discontinuous increase in Δ with increasing driving voltage, as shown in Fig. 4. At intermediate voltages in the discontinuity region, Δ changed with time so rapidly that measurements were impossible. However, with decreasing voltage, the corresponding decrease in Δ was continuous and reproducible. This behavior was displayed by one specimen after x-irradiation; other x-irradiated specimens sometimes behaved similarly, but with a more gradual increase in Δ.

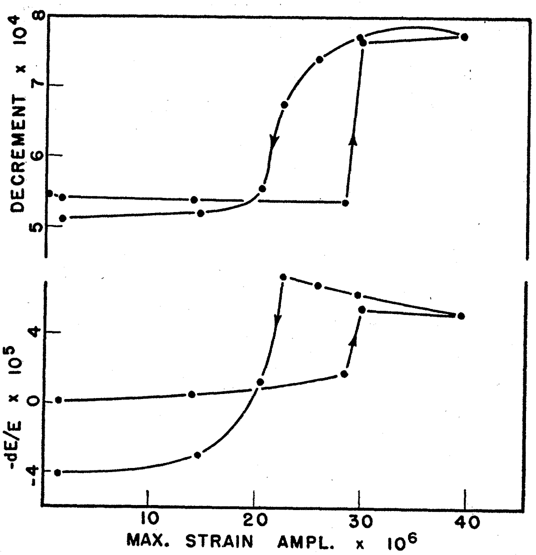

FIG. 4. Example of discontinuous dependence of Δ and $\delta E/E$ on U.

B. Effects of Photochemical Coloration

The effects of introduction and subsequent removal of F centers were briefly described in reference 12. The salient observations, here presented in Figs. 5 and 6, are as follows. (a) On mild coloration by x-rays at room temperature, the internal friction is drastically reduced. Concurrently, E increases by about 0.1 percent. (b) On subsequent bleaching with visible and infrared radiation, Δ *remains small.* (c) On mild annealing, *viz.*, 30 min at 200°C in the case shown and somewhat longer at this temperature in other cases, Δ is increased considerably toward its initial magnitude. (d) On coloration at liquid nitrogen temperature, there is no reduction of internal friction if the crystal is subsequently bleached while still cold; however, if the

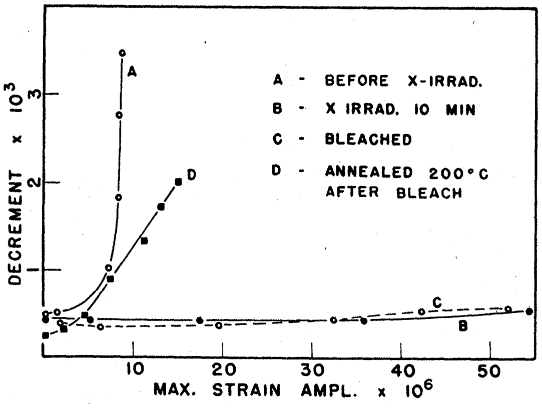

FIG. 5. Effects of x-irradiation at room temperature.

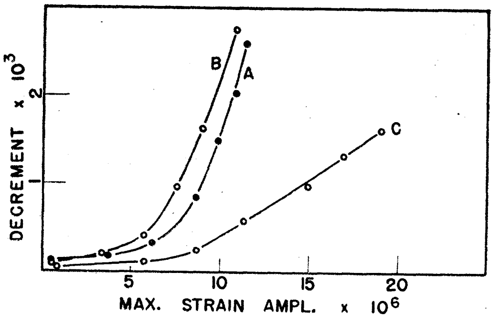

FIG. 6. Effects of x-irradiation at liquid nitrogen temperature. *A*—Before irradiation; *B*—cold irradiation, cold bleach; *C*—cold irradiation, room temperature bleach.

crystal is warmed to room temperature before bleaching, Δ is again markedly reduced.

The possibility that the reduction of Δ on x-irradiation is the result of some surface effect was investigated by etching off with water about 0.1 mm of the surface of a specimen after coloration and bleaching. The decrement remained extremely small, showing that the x-ray effect had taken place in bulk, or at least in appreciable depth. (Actually, the etching did result in a slight increase in Δ, but this occurred also in unirradiated specimens, as will be discussed below.)

Further details of the x-ray effect are shown in Fig. 7. It is particularly to be noted that after the extremely mild x-ray dosage of six minutes (per spot), the decrement of this specimen was nearly constant out to very large values of *U*, corresponding to stresses of about five times the static yield stress of annealed rock salt crystals.[7]

C. Effects of Mechanical Treatments

Application of static stress to the specimens was found always to increase their internal friction. The effects of the rather severe cold-working entailed in the grinding described above are illustrated in Fig. 8. Surface etching subsequent to the grinding was found also to produce an increase in Δ, showing that the plastic deformation on grinding is not confined to thin surface layers, but extends at least several tenths of a millimeter in depth. The amount of increase in Δ on etching was generally small compared to that on grinding.

As remarked above, even the mild handling of the specimen entailed in the cementing operation produced an appreciable increase in Δ. The amount of such increase, while extremely variable, was usually considerably less than that produced by grinding but appeared to be correlated with the initial magnitude of Δ; that is, the increase on handling was greater when Δ was initially large.

Finally, the vibrational stress applied in measurement also produced an increase in Δ, such that its value at a given driving voltage was increased after vibration under a higher voltage, as illustrated in Fig. 3.

D. Effects of Thermal Treatments

Heating a crystal to about 600°C and cooling it rapidly in air resulted always in high internal friction, in the neighborhood of the upper limit of the normal range. Furthermore, the Δ *vs* *U* curve was roughly the same for all specimens, regardless of the previous state; in other words, this high temperature treatment tends to obliterate all previous history.

Subsequent annealing for about 30 minutes at 200°C, with either slow (several hours) or rapid (few seconds) cooling, resulted in a considerable reduction in internal friction, particularly at high strain amplitudes, as shown in Fig. 9. Concurrently, there was an increase in the Young's modulus of about the same amount as occurs under coloration, *viz.*, about 0.1 percent.

Also shown in Fig. 9 and in more detail in Fig. 10 is the fact that considerable annealing takes place even at room temperature over a period of several days. Such annealing occurs after any increase in internal friction brought about by either cold-working or rapid cooling from high temperature. In numerous attempts to follow this annealing process over longer periods of time, the smooth decrease in internal friction was always interrupted, usually by small and variable increases probably resulting from accidental shock, but occasionally by a large increase and transition to the doubly valued type of Δ *vs* *U* curve. As remarked above, the reason for this behavior was not discovered.

After x-irradiation, when the internal friction is already very low, the room temperature annealing effect does not appear. Furthermore, in this case, the

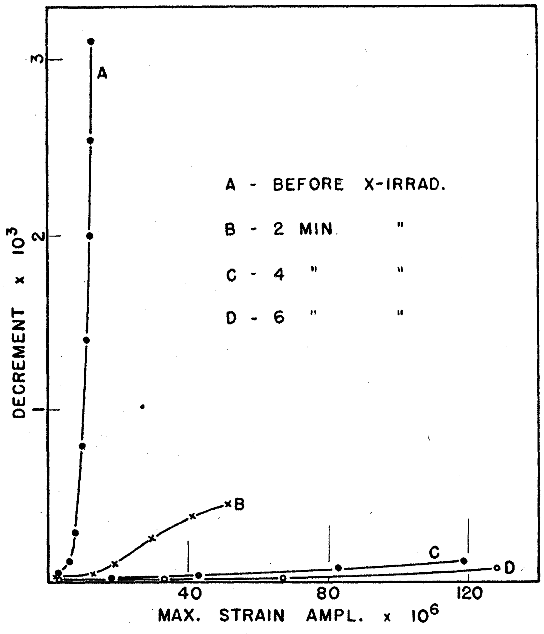

FIG. 7. Showing the rate of reduction of Δ by x-irradiation at room temperature. (This specimen had previously been heated to 600°C and cooled in a few seconds.)

200-degree anneal increases the decrement, though never to the magnitude it had had before the x-irradiation (see Fig. 5).

IV. DISCUSSION

A. The Dislocation Model

The normal internal friction (Fig. 1) and the change in the Young's modulus (Fig. 2) found for rock salt are similar to the corresponding properties of metallic crystals,[1–3] which suggests that the mechanism of damping is essentially the same in the two types of solids. We adopt here the currently accepted viewpoint that this mechanism consists of the oscillatory motion of dislocations.

The model, then, is a crystal containing some number of dislocation lines, as well as numbers of various "point" imperfections such as foreign ions and lattice vacancies. These point imperfections may interact with the dislocations, in the manner described by Cottrell,[13] to form "pinning points" at which the dislocation line is immobilized under moderate stresses, but from which it may be "broken away" under sufficiently high stress. Then, as shown by Koehler,[3] the major contribution to the damping is given by the longer segments of dislocation lines lying between the more widely spaced pinning points.

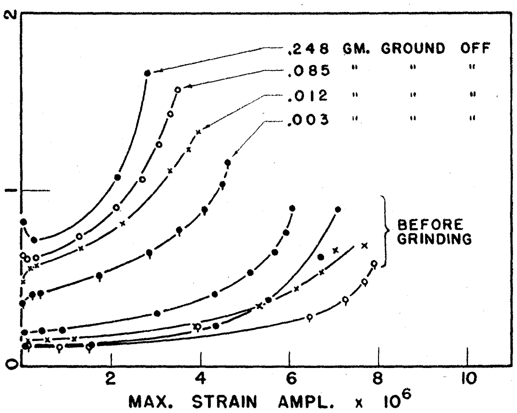

FIG. 8. Increase in Δ resulting from dry grinding on abrasive paper. The "before grinding" curves were obtained after many days of room temperature annealing.

In the following it will be shown that this model is adequate to account, at least qualitatively, for most of the observed phenomena. It should, however, be pointed out that other mechanisms, namely the relaxation of various thermodynamic potential differences, are also operative but give only linear damping and are therefore not important here.

B. The Abnormal Amplitude Dependences

The large increase in damping which leads to the doubly valued dependence of Δ on U (Fig. 3) can be accounted for by assuming the sudden breakage of large numbers of pinning points. Now, Koehler[3] has pointed out that a shear stress causes the exertion of stronger forces on widely spaced than on closely spaced pinning points. Hence, the initial breaking of only relatively few points under the increased stress may, for a suitable configuration of pinning points, give rise to an avalanche of unpinning, leading to the greatly increased decrement.

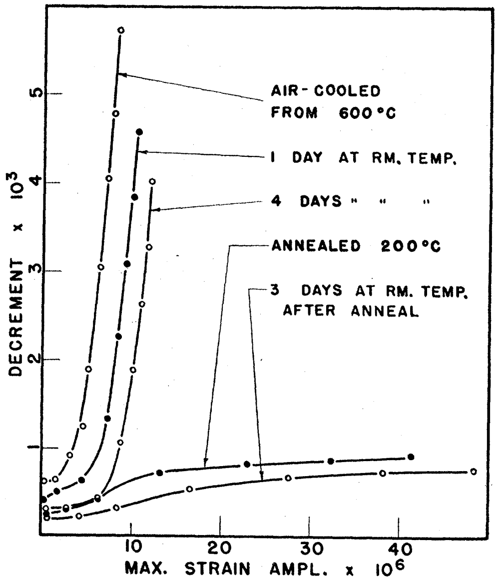

FIG. 9. Effects of thermal treatments. (Curves are labeled in chronological order.)

The fact that the points for decreasing driving voltage nearly duplicate those for increasing voltage shows that the time for repinning of dislocations is short compared to the few seconds required for a measurement. In this connection, it is essential to recognize that the points of the Δ *vs* U curves cannot be traversed truly in sequence. Rather, by virtue of the modulus shift described above, each change of driving voltage throws the system off resonance by an amount sufficient to reduce the amplitude of vibration

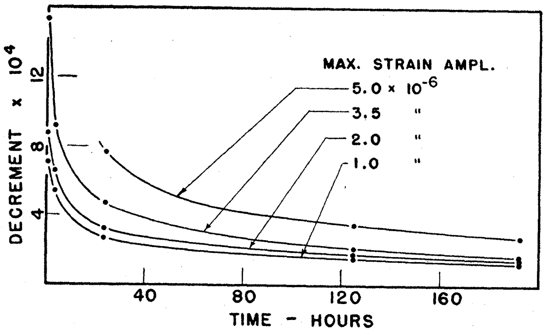

FIG. 10. Example of room temperature annealing following grinding of the specimen.

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[13] A. H. Cottrell, *Bristol Conference on the Strength of Solids* (Physical Society, London, 1948), p. 30.

to a small fraction of its resonant value. The measurement is completed by tuning the driving signal to the new resonance and simultaneously balancing the bridge, these operations requiring several seconds to perform. Presumably the repinning of dislocations takes place during these intervals. While the method of measurement does not permit the determination of the path along which the system approaches the steady-state resonant vibration, this path must, for points on the upper branch of the curve, necessarily go through strain amplitudes at least as large as that at which the reversal occurs.

On the other hand, the fact that the high decrement persists at the reduced amplitude shows that repinning does not take place during the resonant vibration. We therefore postulate that when the dislocation moves at high velocity through the pinning point, repinning cannot occur; but when the dislocation is nearly stationary at the pinning point, repinning takes place very rapidly.

The phenomenon of doubly valued amplitude dependence, while not previously observed, is nevertheless, closely related to two well-known phenomena, the only essential difference being in the time scale. In the first instance, the cataclysmic breaking of pinning points occurs also in the yield-point phenomenon in static loading of metals, but the repinning time is much longer since the dislocations are permanently removed from their initial positions and the recovery process can occur only by diffusion of the pinning imperfections over appreciable distances. In the second instance, it has been observed that the decrement of some metallic crystals increases with time under vibration at a constant strain amplitude. Therefore, if the vibration were carried out under constant driving voltage, it would be found that the decrement would increase and the amplitude decrease with time. And, by waiting sufficiently long, it would be possible to obtain an amplitude smaller than that previously observed under a lower driving voltage. The present case differs only in that the required time is unobservably short under the experimental method employed.

The discontinuous amplitude dependence (Fig. 4) again suggests a cooperative breaking of pinning points. In this case, however, it is not clear why the breaking does not proceed further under the higher driving voltages.

C. The X-Irradiation Effects

In reference 12, a mechanism was proposed to account for the observed effects of coloration and bleaching (Figs. 5 and 6). Briefly, this consists of the liberation of cation vacancies from their association in pairs with anion vacancies by the trapping of electrons in the latter to form the *F* centers, and the diffusion of the liberated cation vacancies to dislocations, where they act as pinning points. This mechanism accounts not only for the reduction of internal friction on x-irradiation, but also for its independence of subsequent bleaching, and, especially, for the absence of the effect on low temperature coloration and bleaching, when the liberated vacancies cannot undergo the required diffusion.

Furthermore, this mechanism is plausible in the light of present knowledge of the properties of lattice vacancies in ionic crystals. Firstly, the work of Tubandt[14] has shown that, except at extremely high temperatures, the mobility of the cations is some 10^4 times that of the anions. Etzel and Maurer[15] have determined the activation energy for cation migration to be 0.85 ev, from which the jump rate of the cation vacancies may be estimated[16] as about one $\sec^{-1}$ at room temperature. Thus, it is not unreasonable to suppose that in an interval of a few minutes the cation vacancies may, in the presence of a stress field, migrate several hundred ion spacings, while the anion vacancies are essentially immobile. Secondly, Reitz and Gammel[17] have calculated the binding energy of a cation-anion vacancy pair to be 0.89 ev, which suggests that the existing vacancies will, at room temperature, be largely associated into pairs (or perhaps larger clusters). The binding energy of an *F* center, on the other hand, should be roughly comparable to the optical excitation energy, i.e., of the order of 2 ev, so that it is likely that an electron can, indeed, displace a cation vacancy from a vacancy pair.

It must be supposed that a cation vacancy is less strongly bound to a dislocation than to an anion vacancy, since otherwise the stable configuration would be that giving the extremely low internal friction. This supposition is further borne out by the fact (Fig. 5, curve D) that the vacancies are evaporated from the dislocations at only slightly elevated temperature.

Pinning of dislocations by vacancies may also occur in metals, as has been suggested by Seitz.[18] However, the situation in ionic crystals differs in one essential respect, owing to the fact that the Burgers vector must be twice the interionic distance, since otherwise the motion of the dislocation in the slip plane could not leave behind a perfect lattice. In metals, on the other hand, the fundamental slip vector may be a single interionic distance. In view of this difference, the interaction of edge dislocations with vacancies in the two types of crystals may be compared as follows: In metals (a) condensation of a single vacancy in the edge of a straight portion of the dislocation will leave the cross-section configuration unchanged, but merely moved to the adjacent slip plane; the resulting jog in the disloca-

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[14] C. Tubandt, *Handbuch der Experimental Physik* (J. Springer, Berlin, 1932), Vol. 12, Part 1.

[15] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[16] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[17] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

[18] F. Seitz, Advances in Physics (Supplement to Phil. Mag.) **1**, 43 (1952), see p. 73 ff.

tion line may act as a pinning point; (b) condensation of vacancies will actually occur most probably at preexisting jogs; this will merely move the jog one step along the dislocation line, leaving the same configuration, with no increase in pinning; (c) condensation of a complete row of vacancies will merely move the entire dislocation to the adjacent slip plane. In ionic crystals, on the other hand, (a) condensation of a single vacancy in the dislocation edge will result in an essential change in the cross-sectional configuration; (b) condensation of a single vacancy at a jog will also result in an essentially different configuration of the dislocation, with one additional pinning point; (c) condensation of a complete row of single vacancies will leave the dislocation completely pinned. This does not imply that such complete pinning is energetically possible; however, the results shown in Fig. 7 suggest that the pinning vacancies are, indeed, very closely spaced.

Finally, it may be remarked that pinning by cation vacancies provides a likely mechanism for the strong hardening effects of divalent substitutional impurity cations and of F centers in ionic crystals.

D. The Mechanical Effects

The increased internal friction observed after application of stress means, on the assumed model, that the number of long unpinned dislocation segments has been increased. This could come about either through multiplication of dislocations or through breaking of pinning points. The fact that appreciable increase in Δ occurs even under static stress far below that required to produce observable plastic deformation suggests that the latter mechanism predominates. Then, the observed correlation of the amount of increase in Δ with its initial magnitude is in general agreement with Koehler's aforementioned prediction of easier breakability of the more widely spaced pinning points. Finally, the increase in Δ on etching may be interpreted as the effect of plastic deformation under the unbalanced internal stresses.

E. The Thermal Effects

At the high temperature of 600°C, it is likely that the vacancies and impurity ions will be largely evaporated from the dislocations, so that the rapid cooling from this temperature will result in a large number of long unpinned dislocation segments, giving the observed high internal friction. The fact that the Δ *vs* U curves following such treatment are roughly independent of previous history suggests that the total length of dislocation line, pinned and unpinned, is essentially unchanged by the various other treatments.

At room temperature, on the other hand, the only imperfection which can give strong pinning and which also has appreciable mobility is the cation vacancy. (Theoretical calculations by Dienes[19] indicate that vacancy pairs also have appreciable mobility; however, as indicated above, these cannot give such pronounced pinning.) Thus, the room temperature annealing is probably also the result of diffusion of cation vacancies to the dislocations, the slow rate of this effect as compared to the x-irradiation effect being a statistical result of a smaller vacancy concentration.

The results of annealing at intermediate temperature (200°C) require the assumption that another type of pinning imperfection, presumably foreign ions, is also operative. Then the decrease in Δ when such annealing is carried out following the high temperature treatment and essential completion of the room temperature anneal (Fig. 9) is the result of the increased mobility of these ions. On the other hand, when the 200-degree anneal is carried out after x-irradiation, the impurity pinning process is overbalanced by the evaporation of vacancies, leading to the observed partial increase in Δ, as shown in Fig. 5.

V. ACKNOWLEDGMENT

The writer wishes to express his appreciation for the advice and encouragement of Professor Thomas A. Read, under whose guidance this investigation was conducted.

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[19] G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).