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PHOTOPLASTIC EFFECT IN PURE AND DOPED ALKALI HALIDES

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1. Introduction. — Dislocations in ionic crystals, particularly alkali halides, are electrically charged [1], [11]. Extensive measurements of that charge have been reported for pure as well as anion and cation doped crystals. This charge is supposed to influence a variety of mechanical, electrical, optical and diffusive properties of the crystals.

Recently, a detailed investigation of the photoplastic effect [12] in pure colored alkali halides has been performed in our laboratory and it is being reported elsewhere [13]. It has been shown that this effect can be basically understood in terms of the interaction between positively charged dislocations and electrons photoionized from F-centers. A number of properties of the effect, such as its dependence on light-wavelength, light intensity and strain rate can be semiquantitatively explained.

In this paper, the effect of impurity doping on the photoplastic effect is described. Hydrogen ions and a number of divalent cation impurities have been investigated. It is known that the magnitude of the electrical charge is strongly modified by doping and therefore drastic changes in the structure and properties of the effect are foreseen. In fact, the photoplastic behavior of doped crystals differs markedly from that observed for pure crystals. Its structure has revealed quite complex and the results reported here are not sufficient to provide a complete picture. It has clearly appeared that the ideas advanced to explain the effect in pure crystals are not adequate. However a qualitative scheme which rationalizes some of the data on doped crystals is tentatively proposed.

It is felt that the photoplastic effect constitutes an unique way to observe and measure the electrostatic interaction between dislocations and point defects in ionic crystals. Consequently it should provide an adequate test to current models dealing with such an interaction.

In a first part of this paper, the most significative features of the effect in pure crystals are briefly reported together with a short account of the model proposed. The emphasis is on the data which are relevant in connection with the work on doped crystals. This provides an adequate background for a comparative analysis of the data.

2. Experimental. — Nominally pure alkali halide crystals have been purchased from the Harshaw Chemical Co. Doped crystals have been supplied by Dr. F. Rosenberg of University of Utah. Pure samples were colored either additively, or by y-irradiation of by hydrogen doping followed by y-irradiation. Additive coloring was performed with the method advanced by Van Doorn. Hydrogen doping was achieved by additive coloring followed by treatment of the samples in high pressure (< 70 kg/cm²) hydrogen atmosphere at high temperatures (500-600 °C). Irradiations of pure or H⁺-doped crystals were carried out in a Co⁶⁰ swimming-pool type y-source. Cation doped samples were colored by X-ray irradiation at room temperature in a Siemens apparatus operating at 50 kV, 40 mA.

Colored samples 3 x 4 x 12 mm³ in size were then strained in compression in an Instron TT testing machine. At a certain point of the stress-strain curve they were subjected to light of a Xe-arc, Hg arc or tungsten filament (quartz-iodine) lamp either directly or through a Bausch-Lomb high intensity monochromator. In view of the small magnitude of the photoplastic effect, the most sensitive stress scale (0-1 kg) has been used combined with a displacement of the zero. Changes in load as small as 10 g can be detected.

For the low temperature work, a specially designed
cryostat was used. It has a set of aluminium-coated mirrors to drive the light into the sample compartment during straining. The experiments at 77 K were usually performed by immersing the samples into a liquid nitrogen bath inside a transparent cryostat. This system provided a higher illumination efficiency and consequently led to a larger size of the effect.

3. Photoplastic effect in pure crystals. — In nominally pure alkali halide crystals, which have been colored, a positive photoplastic effect is always observed as indicated in figure 1, for NaCl and KCl. It corresponds to room-temperature testing. When F-light is shone on the crystal a fast increase in flow stress is observed. Then a yield-point behavior appears leading to a region of steady flow. In some crystals, particularly at high illuminations intensities, an abrupt yield-drop is often found. On cutting the illumination, the flow stress essentially recovers the pre-illumination growth rate.

3.1 The effect is zero in the elastic region and increases strongly at the yield point. It remains practically constant for strain percentages in the range 2-8 %, except for NaCl where it increases monotonously with deformation. However the detailed shape of the dependence varies somewhat with the F-center concentration.

3.2 The effect is enhanced on lowering the strain rate or increasing the light intensity. A saturation value is obtained for high intensities.

3.3 The effect depends markedly on testing temperature. At all temperatures in the range 77-300 K the effect is positive.

3.4 The excitation spectrum of the effect closely follows the shape of the F-band at room as well as low temperatures, for lightly colored crystals. For heavily colored samples the excitation spectrum is broader and a marked dip appears at the F-band peak. This behavior is illustrated in figure 2, corresponding to KCl tested at room temperature. The shape of the spectrum for high colorations has been attributed to the non-uniform absorption of light in the sample. At the F-band peak most light is absorbed in a small fraction of the sample thickness.

3.5 The effect increases monotonously with F-center concentration. The theoretical model which has been proposed [13] to explain the photoplastic effect in pure crystals is schematically illustrated in figure 3. When F-light is shone on the crystal, electrons are photoionized from the F-centers and attracted to the charged dislocations (Fig. 3a). An electron cloud, determined by Boltzmann's law should then be formed around the dislocation core and be trapped at impurities or defects (Fig. 3b). Consequently the potential barrier generated by the electron cloud
opposes dislocation motion and induces hardening. This model accounts for a number of qualitative features of the effect and leads to the formula

$$\Delta \tau = \frac{C_1}{1 + C_2 v/I}$$

($$\Delta \tau$$ being the magnitude of the photoplastic effect, $$v$$ the average dislocation velocity and $$I$$ the light intensity) which provides a quantitative explanation for the role of strain rate and light intensity. $$C_1$$ and $$C_2$$ are constants.

It is worth mentioning that electric-field induced photo-ionization of electrons has to be invoked to account for the strong magnitude of the effect a 77 K for NaCl. This is not surprising if one considers the high electric fields to be expected in the neighbourhood of charged dislocation [14].

4. Photoplastic effect in doped crystals. — It is expected that impurity doping should introduce deep modifications in the structure and properties of the photoplastic effect. Both the plastic properties and color center behavior are altered by doping. In particular, anion as well as cation impurities change the magnitude (and even the sign) of the electrical charge on dislocations.

4.1 Photoplastic effect in crystals doped with U-centers. — The substitutional H\(^+\) ion, U-center, is electronically similar to the F-center and has, also, a well-defined absorption band in the UV region of the spectrum. The observation of the photoplastic effect in crystals doped with U-centers is of much interest since the results can be correlated with those observed for crystals with F-centers, and should help to confirm an adequate model.

For KCl, KBr and KI where the U-band peaks at 214, 228 and 270 mp respectively [15], a photoplastic effect, similar to that described for F-centers, has been observed at room temperature. A typical effect, as it appears for KCl, is depicted in figure 4a. In some cases a sudden decrease in flow-stress occurs on starting illumination, prior to the «normal» positive effect. For NaCl whose band falls far in the UV, the observation of the effect appears more difficult and has not been successful.

A detailed study of the characteristics of the effect has not been possible because of the low light intensity available in the U-band spectral region. However, in highly U-doped (4 x 10\(^{17}\) cm\(^{-3}\)) KBr, the spectral dependence has been obtained figure 4b. The effect is prominent in the U-band region although it presents some of the features found for heavily colored (F-centers) crystals. The marked decrease in the magnitude of the effect at the U-band peak has to be, again, related to the small penetration of the exciting light. Similar results have been obtained for KI.

It is worth mentioning that for nominally pure KI crystals, a very small photoplastic effect has been observed for light of wavelength close to the fundamental absorption edge [16]. It might be due to some impurities, especially OH\(^-\), which is known to be a common impurity in Harshaw crystals.

4.2 Photoplastic effect in cation doped crystals. — The investigation has been concentrated on divalent cation impurities. The following systems have been studied: NaCl: Zn\(^{2+}\) (5 x 10\(^{-3}\) mol), NaCl: Cd\(^{2+}\) (8 x 10\(^{-3}\) mol), NaCl: Ni\(^{2+}\) (5 x 10\(^{-4}\) and 2 x 10\(^{-3}\) mol) NaCl: Mn\(^{2+}\) (3 x 10\(^{-4}\) mol), KCl: Ba\(^{2+}\) (7 x 10\(^{-3}\) mol), KCl: Pb\(^{2+}\) (10\(^{-4}\) and 10\(^{-3}\) mol) and KCl: Sn\(^{4+}\) (10\(^{-3}\) mol).

At variance with the case of U-doped crystals the photoplastic effect is now markedly different from that appearing in pure crystals. Now, we will describe some features of the effect.
4.2.1 Structure of the effect. — Although marked differences are apparent among the various crystal systems, all impurities yield a photoplastic effect corresponding to one of the three typical patterns to be described next. In the first type, figure 5a, the flow stress experiences a fast decrease on illumination and then levels off to keep a small positive slope. On cutting the light off the stress rate is not appreciably modified. In the second type, figure 5b a mixed behavior is observed. Initially, there is a fast decrease in flow stress, as in the previous case, but afterwards the stress rate increases above the value corresponding to the «dark» curve. Finally, on cutting the light off, the flow stress decreases to reach the preillumination level as in the case of pure crystals. The third type is the standard positive effect, figure I, and is observed in some doped crystals at very low or rather high strain levels (see later). Exceptionally, a small positive effect has been always observed in NaCl : Mn⁺⁺. All these effects refer to room temperature testing. The illumination has been performed at the F-band peak.

![Graph](image)

**Fig. 5.** Typical photoplastic effects in cation-doped alkali halides. Pure negative effect a) and mixed-type effect b).

The difference between the structure of the effect in pure and doped crystals is also readily apparent if the experiments are performed in the plastic relaxation after keeping the strain constant, figure 6. Effects depicted in figure 5 have some peculiar properties which are essentially different from those observed in pure crystals. If, after completing an illumination period, a new illumination is started, the new photoplastic effect depends very markedly on the strain elapsed between the successive illuminations, figure 7. In fact, if that strain is ≥ 0.2 %, there is not second effect if the first one was pure negative (Fig. 7a). If the first effect was of a mixed type, the second one is «standard» positive (Fig. 7b). It is to be stressed that the parameter is the strain and not the time elapsed between the illuminations. This behavior is at variance with that found in pure crystals where the effect is clearly repetitive (Fig. 7c).

4.2.2 Influence of concentration and thermal treatments. — The effect of impurity concentration has been investigated in two systems, KCl : Pb²⁺ (concentrations : 10⁻⁴ and 10⁻³ mol) and NaCl : Ni⁺⁺ (concentrations : 5 × 10⁻⁴ and 2 × 10⁻³ mol). In both cases the effects are small and clear systematic differences have not been detected, for equal dose irradiations.

On the other hand quenching is known to alter considerably the state of aggregation of the impurity. The influence of a quenching treatment has been studied in several systems. Crystals were kept at 400 °C for one hour and then rapidly cooled on a metal plate. After this treatment they were X-irradiated and tested at room temperature. Significant results have been obtained for NaCl : Mn⁺⁺, NaCl :
PHOTOPLASTIC EFFECT IN PURE AND DOPED ALKALI HALIDES

ON OFF

ON OFF

1-

\[ KC_1 + Ba^{++} \]
quenched

\[ KC_1 \]
untreated

INCREMENTAL STRAIN, %

FIG. 7. — Repetitivity of the effect in doped and pure crystals. Shortly after the completion of an illumination period a very small photoplastic effect is observed in quenched KCl : Ba++ a). If the effect was of a mixed type a small positive effect is observed on reillumination b). Positive effect in pure crystals is clearly repetitive.

Erratum: The values of the three abscissas must be read 1.2.3... instead of 1 2 3...

Zn++ and KCl : Ba+++. In these cases the negative effect is clearly enhanced by the treatment and in the case of NaCl : Mn++ where the effect is positive in untreated samples, becomes negative in the treated ones. The greater changes are observed in KCl : Ba++ where the effect increases almost one order of magnitude. The effect keeps its magnitude after about one week in the dark.

4.2.3 Dependence on strain level. — As a general rule the size of the negative photoplastic effect increases with strain at low strains, then levels off and finally decreases and changes to a mixed type for higher strains. In some systems the effect becomes positive as in pure crystals. In figure 8 data for NaCl : Ni++, NaCl : Zn++ and KCl : Sn++ are given. In KCl : Ba++, which has been quenched prior to irradiation, the effect is essentially constant in a wide strain range. This allows for studying the dependence of the effect on some variables (strain-rate, light-intensity and wavelength) on the same sample.

4.2.4 Dependence on F-center concentration. — The magnitude of the effect increases with irradiation dose or F-center concentration. Data for a reasonable range of concentrations have been obtained for NaCl : Zn++, figure 9. Each point corresponds to an average of two or three experiments on different samples. The dispersion of the data with regard to that average is as high as ~ 50 %.

4.2.5 Dependence on light intensity. — The dependence on light intensity is similar to that for pure crystals. The range 1-50 × 10^4 phot/cm².s has been obtained by using neutral screen-type optical filters on the higher intensity light beam. On increasing intensity the magnitude of the negative effect grows but a tendency to saturation is observed. Significant data have been obtained for quenched KCl : Ba++ and are displayed in figure 10.
4.2.6 Dependence on strain rate. — The general trend of this dependence is again, similar to that found in pure crystals, figure 11. The data correspond to quenched KCl: Ba^++. The effect is greatly enhanced for low strain rates. Monochromatic light corresponding to the F-band peak has been used to excite the effect.

4.2.7 Dependence on light wavelength. — Figure 12 shows the data obtained for quenched KCl: Ba^++. The effect is prominent at the F-band region, although the photoplastic excitation spectrum appears broader and a small valley is observed just at the F-band peak. This behavior has to be compared to that found in pure crystals (Fig. 2) and should be, again, attributed to non-uniform absorption of the light throughout the sample thickness. One should take into account that F-center concentration is ~10^{17} cm^{-2} for this experiment.

It is, then, clear that for doped as well as pure alkali halides, F-band excitation is primarily responsible for the photoplastic effect.

4.2.8 Dependence on testing temperature. — There are preliminary data [17] indicating that dislocations might change their sign to positive when plastic straining is performed at low temperature (liquid nitrogen or better liquid helium temperature). This behavior suggests that the structure and magnitude of the photoplastic effect might change at low temperatures. The role of testing temperature was investigated by making experiments at liquid nitrogen temperature on KCl: Ba^++ and NaCl: Zn^++, both quenched and untreated. Samples were X-irradiated for 30 min and illumination was performed at the F-band peak corresponding to 77 K. Main results are the following: 

i) In quenched KCl: Ba^++, the effect is positive at 77 K for very low strain levels. On increasing the strain the effect becomes negative but much smaller (~1/5) than at room temperature. In untreated samples, the effect is always zero or small positive.

ii) In NaCl: Zn^++, quenched as well as untreated, the effect is always positive at 77 K.

It can, then, be concluded that testing temperature has a marked influence on the sign and magnitude of the photoplastic effect. It becomes less negative or even positive on going down to liquid nitrogen temperature.
5. Discussion of the effect on doped crystals. — In principle, the data on the photoplastic effect in U-doped crystals seem to confirm the model proposed for pure crystals. The effect is related to excitation of the U-centers. Although U-band absorption does not lead to photoconductivity, except at its high energy tail, one can invoke field-induced ionization of the excited U-center as for the low temperature effect in pure crystals. However, it is not completely clear why dislocations should be positively charged in this case. One has to conclude that U-band illumination or the combined effect of a dislocation moving near an excited U-center ejects the hydrogen ion and leaves an empty vacancy swept along with the dislocation.

On the other hand, the model proposed for the photoplastic effect in pure crystals does not appear suitable for divalent cation doped crystals. In fact, this type of doping increases the negative charge of the dislocations prior to irradiation. It might be, then, reasonably expected that irradiation cannot reverse the sign of the charge to positive. In that case electrons liberated by the light are pushed away from the dislocations core. A cloud of positive charge formed by the empty vacancies will be produced around the dislocations. The scheme discussed in section 3, would again predict an increase in flow stress due to the electric field opposed by the positive vacancy cloud. This is at variance with experiment.

Let us think of the negatively charged dislocation as dragging an excess of $\text{Cl}^-$ ions at the core, figure 13.

![Fig. 13. — Schematic illustration of the processes occurring during F-light illumination of a divalent cation doped crystal. The excess of $\text{Cl}^-$ ions on the dislocation line recombine with the empty anion vacancies generated by the light and electrical charge is neutralized.](image)

It appears quite reasonable that these ions might easily recombine with empty anion vacancies and regenerate the perfect crystal. This would provide a simple mechanism to remove the negative charge of the dislocations. In fact this is the mechanism invoked to account for the reversal of sign in colored samples. The role of illumination in the photoplastic effect, should be to increase the concentration of empty vacancies and therefore enhance their rate of capture by the moving dislocations.

The removal of the dislocation charge should be responsible for the decrease in flow-stress. Once the dislocation is uncharged, no further change in flow stress is expected on cutting the light off. This is in agreement with the pure negative effect shown in figure 5a. Furthermore, if a new illumination is started no effect will be observed unless enough straining in the dark has taken place as to recharge again the dislocation line figure 7a.

If the illumination is proceeded enough time, the above mechanism can reverse the sign of the charge to positive and then the model proposed for pure crystals should be operative. Hardening sets in and cutting the light leads to a decrease in flow stress. This is the type of effect depicted in figure 7b.

The evolution in the magnitude of the effect with strain, and particularly the change in sign for high strains is not readily understood. It is probably related to changes in dislocation charge during straining.

The role of quenching treatments is, in principle, consistent with the scheme proposed. The dissolution of impurity aggregates carried by the treatment should favor the negative charging of the dislocations. In fact, Turner and Whitworth [18] have detected (in NaCl : Mn$^{++}$) a large increase in negative charge after quenching, which is qualitatively in agreement with our findings. The change in the sign of the photoplastic effect at low temperatures appears, to be consistent with the change in the sign of the dislocation charge when the straining is performed at low temperature [17].

Finally, the data on the influence of light-intensity and strain rate can be qualitatively understood in terms of our scheme. Higher light intensity implies a higher concentration of empty anion vacancies and consequently a higher positive charge to be acquired by the dislocation. Furthermore, it is reasonable that the processes for removal or loss of charge be more operative on increasing dislocation charge and it leads to a saturation of the effect. On the other hand, lower strain-rates, i.e. lower dislocation velocities, imply a higher dislocation charge after the dynamical equilibrium between the rates of capture and loss of charge have been established.

Although, a mathematical model for this scheme can be developed, more detailed data on the properties of the effect are needed before the model can be successfully tested.

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