

work show damping loops more symmetrical with respect to a stress cycle than asymmetrical as demanded by the Granato-Lücke theory. The loops do exhibit some asymmetry at very low amplitudes, when the crystal has been well annealed, but this amplitude range is close to the limit of resolution of the present experimental method. Secondly, the stress dependence of the damping loops is not remarkably affected by rather large prestrains (about  $10^{-2}$ ), where the dislocations should be situated in a matrix of randomly distributed point defects, not pinned down with an excess solute concentration above the bulk concentration. It should be pointed out that the predicted stress dependence of the energy loss and decrement by both the Granato-Lücke theory and the one presented in the present paper are remarkably similar even though the dislocation models employed are quite different. This is a consequence of the fact that both theories assume the loss is proportional to the work done on the dislocation and distribution functions are employed to determine which network length breaks-away as a function of stress. Through our discussions with Prof. Lücke, it is understood that the Teutonico-Granato-Lücke theory, currently in press, may be more successful in explaining certain features of the present results than the Granato-Lücke theory.

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## Internal Friction of Additively Colored KCl Crystals

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The strain-amplitude dependence of internal friction at room temperature has been measured in both clear and additively colored KCl crystals. The additive coloring was made at several temperatures from 450°C to 600°C. The clear specimens which were subjected to the same heat-treatment as the one of the colored specimens, were prepared and the internal friction was measured in order to be compared with those of the colored specimens.

The concentration of the dominant pinning element,  $c$ , was estimated from the strain-amplitude dependent part of the Granato-Lücke's equation,  $\Delta_H$ , and also its concentration in bulk,  $c_0$ , was determined from the other independent measurements.

The binding energies of dominant pinning elements to dislocations were discussed from comparison of  $c$  with  $c_0$ , using the Cottrell's relation.

### 1. Introduction

When the coloration mechanism of alkali halide crystals is considered, measurements of their mechanical properties, especially of their internal friction, seem to be significant, because its experimental results suggest us the kind of pinning element to dislocations. This will be a fundamental step for considering the coloration mechanism.

Frankl<sup>1)</sup> has made an experiment on the

strain-amplitude dependence of the internal friction due to the theory proposed by Koehler<sup>2)</sup> (and developed by Granato and Lücke<sup>3)</sup> later) with X-rayed NaCl crystals at room temperature. He has found the fact that the strain amplitude dependence as well as the dynamic loss values of specimens were lost remarkably by X-ray coloration. In order to explain this results, he has shown the interpretation of dislocation pinning that cation vacancies will

be liberated from neutral vacancy pairs when F-centers are formed with photo-electrons and anion vacancies in neutral vacancy pairs and then they will migrate through the bulk crystal and will be captured by dislocations eventually. Seitz<sup>4)</sup> has suggested to this interpretation that vacancy clusters will pin down dislocations rather well reasonably than single vacancies. Recently, Bauer and Gordon<sup>5)</sup> has stated the significant conclusion that F-centers by X-ray coloration are formed in the vicinity of dislocations, comparing the effect of F-light bleaching on the ultrasonic attenuation at room temperature with those at low temperature. The situation of additive coloration is essentially different from that of X-ray coloration described above. Generally speaking, the process of additive coloration contains the specified heat treatment. It must be pointed out especially that specimens are subjected to a rapid quenching at the last stage of the heat treatment. Usually, the quenching gives rise to an increase of dislocation density<sup>6)</sup> and a hardening effect<sup>7)</sup> on alkali halide crystals. The quench-effect on the internal friction measurement of additively colored crystals, however, will be more complex since generated dislocations due to the quenching increase the dynamic losses and also the introduced F-centers and their coagulations lower those losses conversely. Therefore, it will be necessary to inspect the quench-effect carefully before estimating  $L_e$ , the average loop length between pinning elements, from the dislocation density and the additive quantity of alkali metal.

Very few papers for the mechanical properties of additively colored alkali halide have yet been published. Suzuki and Doyama<sup>8)</sup> have measured the hardness of additively colored KCl crystals and also have considered the coloration mechanism. They have stated that it is difficult to interpret the experimental results of dislocation pinning as the effect by the elastic interaction only between single F-centers and dislocations. They have also tried to consider the other interaction between dislocations and clouds of Debye-Hückel's type containing F-centers. In their experiment, however, they have not separated the above quench-effect so well in spite of their splendid consideration.

This paper will report on the strain amplitude

dependence of internal friction in clear and additively colored KCl crystals and also will discuss on the kinds of pinning element to dislocations corresponding to the variety of crystal situations.

## 2. Experimental Procedures

All specimens were arranged to  $1.0 \times 1.0 \times 10.0$  cm<sup>3</sup> in size by cleavage from ingots prepared by Kyropoulos method. After specimens were heated at various temperatures ranging from 450°C to 600°C during about 20 hours in potassium vapor, they were cooled to room temperature at the rate of about 10 degrees per minute. A rapid quenching could not be done since the possibility to generate cracks in specimens existed. Besides colored specimens clear one heat-treated in the same way had to be prepared for the comparison with colored ones.

For the measurement of internal friction, transverse vibration was adopted by means of electro-magnetic method. The vibration was originated with a RC oscillator and its frequency was in KC range. Two iron sheets,  $1.0 \times 1.0 \times 0.02$  cm<sup>3</sup> in dimension, stuck to the specimen, were used as a driving and a receiving element of the forced vibration. Specimens were suspended at two points with two fine tungsten wires and forced to vibrate electro-magnetically through a coil. A universal counter was used for the measurement of resonant frequencies and an optical microscope for the measurement of the strain amplitude directly.

## 3. Experimental Results

The dislocation density  $A$  of each specimen was measured by etching technique and shown as normalized in the following figures, assuming the linear relation to  $A_1$  according to Granato and Lücke's formula, as well as the applied frequency  $f$  was done. In the case of heat-treated and colored specimen,  $A$  was carefully inspected before and after the treatment.

Fig. 1 shows the strain amplitude dependence of logarithmic decrement in three clear "as cleaved" specimens each of which was taken from the upper, the middle and the lower part of the same ingot. The impurity concentration of each specimen is regarded to be different. That the point, where the curve

begins to rise, shifts to the larger amplitude side as the impurity concentration increases, may be explained to result from the decrease of  $L_c$  which is the mean loop length between pinning elements. On the other hand, the strain amplitude independent loss  $\Delta_I$  decreases clearly with the increase of the impurity concentration conversely.

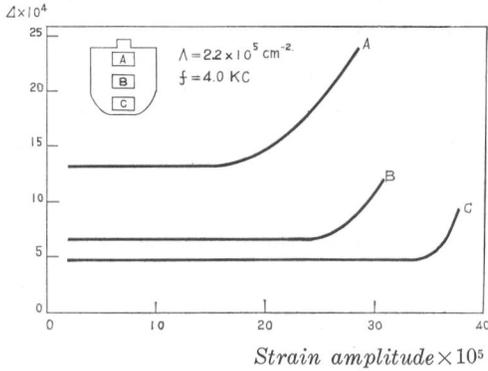


Fig. 1. Strain amplitude dependence of  $\Delta$  in three specimens cut from various locations of the same KCl ingot. [A: the upper part, B: the middle part, C: the lower part.]

Fig. 2 shows the strain amplitude dependence of  $\Delta$  in additively colored KCl specimens, compared with each original "as-cleaved" specimens. Curves  $A'$ ,  $B'$ ,  $C'$  and  $D'$  show the characteristics of  $A$ ,  $B$ ,  $C$  and  $D$  before coloration, respectively.

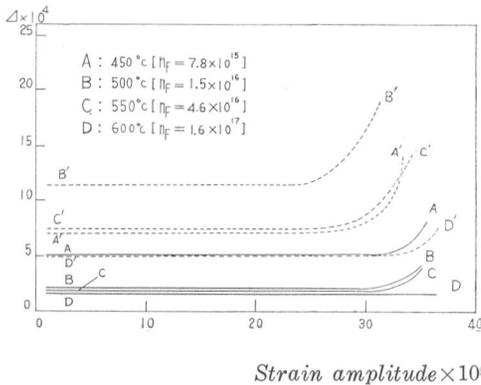


Fig. 2. Strain amplitude dependence of  $\Delta$  in additively colored KCl specimens, compared with each original as-cleaved specimens.

The internal friction of heat-treated clear specimens has been measured at the same time. Heat-treating processes for these specimens were just the same at that for additively colored specimens, because the comparison between the results of two kinds

was needed. Fig. 3 shows the strain amplitude dependence of  $\Delta$  in heat-treated clear KCl specimens, compared with each original as-cleaved specimens.

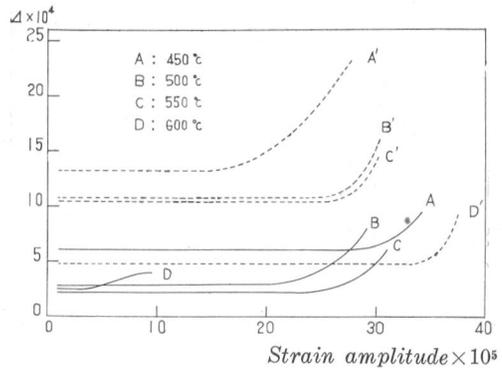


Fig. 3. Strain amplitude dependence of  $\Delta$  in heat-treated clear KCl specimens, compared with each original as-cleaved specimens.

The curves,  $A'$ ,  $B'$ ,  $C'$  and  $D'$ , show the characteristics of  $A$ ,  $B$ ,  $C$  and  $D$  before heat-treatment, respectively.

For comparison of the colored specimen characteristics with the clear specimen characteristics, Fig. 4 was presented, which is quite the same as Fig. 2 and Fig. 3. The curves,  $A$ ,  $B$ ,  $C$  and  $D$ , show the characteristics of colored specimens and the curves,  $A'$ ,  $B'$ ,  $C'$  and  $D'$ , show the corresponding characteristics of clear specimens.

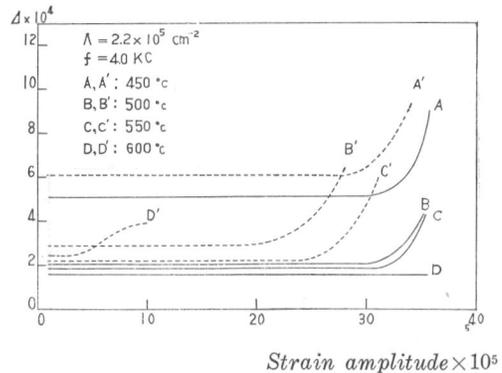


Fig. 4. Strain amplitude dependence of  $\Delta$  in additively colored KCl specimens, compared with heat-treated clear specimens.

Fig. 5 shows a typical spectral distribution of the optical absorption in colored specimens. From this curve, the concentration of F-center,  $n_F$ , was determined, using Smakula's formula<sup>9)</sup>.

Fig 6 shows the ionic conductivity curves of the as-cleaved specimens in Fig. 1. The

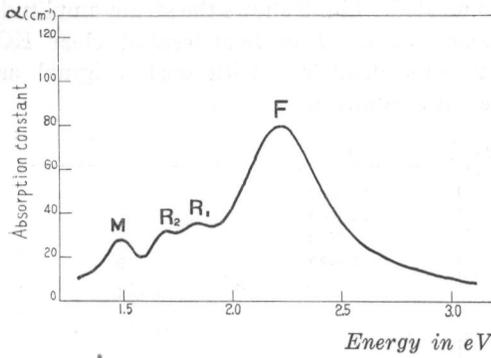


Fig. 5. A typical spectral distribution of the optical absorption.

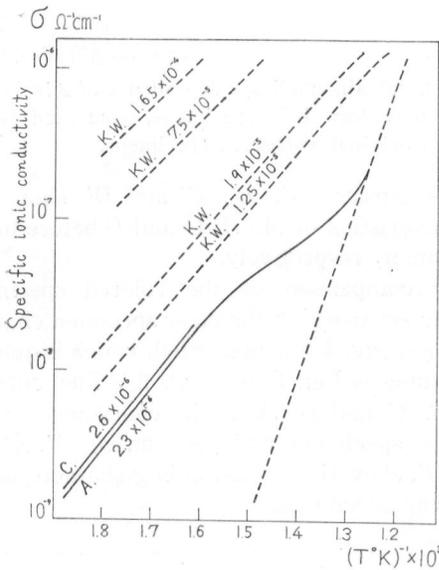


Fig. 6. Ionic conductivity of the as-cleaved specimens in Fig. 1.

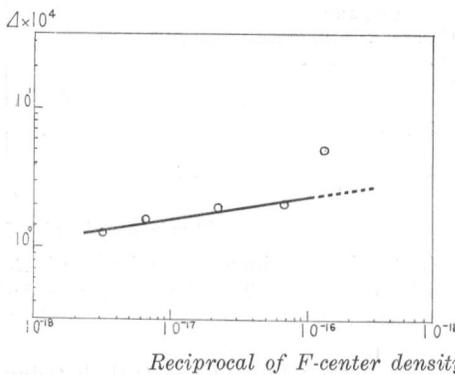


Fig. 7. Relation between  $\Delta_1$  and  $n_F^{-1}$  in additively colored KCl crystals.

$\text{Ca}^{++}$  impurity concentration, which is shown by spectroscopic analysis to be predominant in the present case, was determined by the

calibration to the curves of Kelting and Witt's ionic conductivity<sup>10</sup>.

Fig. 7 shows the experimental relation between  $\Delta_1$  and  $n_F^{-1}$ , the reciprocal of F-center density, in additively colored specimens. Four points for the colored specimens at various coloring temperatures above 500°C are on a straight line, but the one point for the specimen colored at 450°C is far apart from the line. This line is described as

$$\Delta_1 \propto (n_F)^{-1/6}.$$

Actually speaking, the reason why the points for higher coloring temperatures above 500°C are situated on a straight line has not been understood yet, but it seems to be significant that the point for the coloration at 450°C is far apart from this line. It will be discussed later.

#### 4. Discussions

According to the formulation of internal friction by Granato and Lücke<sup>3</sup>, the logarithmic decrement  $\Delta$  is divided into two terms in the KC range, that is, a  $\Delta_I$  term independent of the strain amplitude, and a  $\Delta_H$  term dependent on the strain amplitude. Since  $\Delta_H$  is considered quantitatively to be more reliable than  $\Delta_I$ , the present study has been done by mainly analyzing  $\Delta_H$ . At first, from the slope of the experimental curve,  $\log(\epsilon \cdot \Delta_H)$  versus  $1/\epsilon$ ,  $K\eta c$  has been obtained, where  $\epsilon$  means the strain amplitude,  $K$  the Cottrell's force factor,  $\eta$  the misfit of the pinning element and  $c$  the concentration of the pinning elements in the neighbourhood of dislocations. If there is some information about  $K$  and  $\eta$ ,  $c$  can be estimated.

According to Cottrell's theory<sup>11</sup>, there is the famous relation of elastic interaction between  $c$  and  $c_0$ , that is

$$c = c_0 \exp [E/kT],$$

where  $c_0$  is the concentration of the pinning elements in the bulk at equilibrium. In this study,  $c_0 [c]$  for clear crystals has been estimated by means of ionic conductivity measurements, using the results of Lidiard's calculation<sup>12</sup> on the concentration changes of divalent impurity ions associated with positive ion vacancies. Then,  $c_0 [F]$  for additively colored crystals has been estimated directly by means of measurements of the optical absorption. As far as clear KCl crystals are concerned, the

defects in question are separated  $\text{Ca}^{++}$  ions and positive ion vacancies, and  $\text{Ca}^{++}$  ions associated with positive ion vacancies, that is, "complexes", because  $\text{Ca}^{++}$  are clearly predominant among the many types of impurity ions, according to spectroscopic analysis. On the other hand, in the case of additively colored crystals, the defects in question are negative ion vacancies, F-centers and other more complex centers, besides the three kinds of defect mentioned above.

The concentration  $p$  of complexes can be discussed according to the results of Lidiard's calculation. Since the  $\text{Ca}^{++}$  concentration of the present specimens was of the order of  $10^{-6}$  mol,  $T(p=1/2)$ , the temperature when  $p$  reaches  $1/2$ , can be estimated as follows,

$$T(p=1/2) = (0.07 \sim 0.08) \frac{e^2}{\epsilon r_0 k}$$

Here,  $\epsilon$  denotes the static dielectric constant,  $r_0$  the minimum distance between positive ion sites,  $k$  Boltzmann's constant, and  $e$  the static electric charge. Since  $T(p=1/2) = 350^\circ \sim 400^\circ\text{C}$  in this case,  $\text{Ca}^{++}$ 's are considered to be almost completely associated with positive ion vacancies at room temperature. The specimens in Fig. 1 were nearly in thermal equilibrium at room temperature, so that the predominant pinning elements at room temperature are probably complexes. It is very difficult, however, to estimate the binding energy of a complex to a dislocation, because there is no information about  $K$  and  $\eta$  of the complexes.

Heat-treated clear specimens in Fig. 2 are considered to preserve at the measuring temperature the imperfection concentrations nearly characteristic of the annealing temperatures, namely,  $450^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $550^\circ\text{C}$  and  $600^\circ\text{C}$ . Meanwhile, since  $p$ , the concentration of complexes, decreases rapidly as the temperature rises, dissociated  $\text{Ca}^{++}$  ions and positive ion vacancies become predominant at temperatures above about  $450^\circ\text{C}$ . On the contrary,  $p$  becomes a negligible quantity. Since the concentration of  $\text{Ca}^{++}$  is the same as the concentration of positive ion vacancies in this temperature range, the one which has a larger binding energy to dislocations should constitute the pinning element. Fortunately, the total concentration of  $\text{Ca}^{++}$  has been estimated through the ionic conductivity measurements. By using the appropriate corrections for this concentration from Lidiard's calculation,  $c_0/c]$

in Cottrell's equation has been determined. Supposing  $K$  of  $\text{Ca}^{++}$  ion is equal to  $1/50 \sim 1/2$  and  $\eta$  is  $20 \sim 30\%$  in clear KCl crystals, the binding energy is obtained as  $E = 0.7 \sim 0.9$  eV at  $450^\circ\text{C}$ . On the other hand, if the misfit  $\eta$  of a positive ion vacancy in KCl crystals is assumed to be equal to about  $0.5 \sim 1.5\%$ <sup>4)</sup>, its binding energy is obtained as  $E = 0.9 \sim 1.1$  eV at  $450^\circ\text{C}$ . Therefore, it is for heat-treated clear KCl crystals that the positive ion vacancies must predominantly pin dislocations.

As for additively colored specimens, it is clear from the measurement of optical absorption that F-center exist in much larger concentration than the other centers. The main problem is to compare the number of F-centers with the number of positive or negative ion vacancies and also to compare the binding energies with one another. In the specimen colored at  $450^\circ\text{C}$  the density of F-centers  $n_F$  is estimated as  $7 \times 10^{15}$ , which is far smaller than the total  $\text{Ca}^{++}$  density, that is,  $2.3 \times 10^{16}$ , so that the number of positive ion vacancies is much more predominant than the number of F-centers. Therefore, if the binding energy of both kinds are considered to be of almost the same order, the main pinning elements must be positive ion vacancies. In fact, as shown in Fig. 7, only the point for the specimen colored at  $450^\circ\text{C}$  is situated at some distance from the curve

$$A_I \propto (n_F)^{-1/6},$$

contrary to the results that points for all the other specimens are on this curve. The specimens colored at the temperatures above  $450^\circ\text{C}$  have densities of F-centers, corresponding to each coloring temperature, which are almost the same order or larger than the total  $\text{Ca}^{++}$  density. Therefore, it may be concluded naturally that the pinning elements in the specimen colored at  $450^\circ\text{C}$  must be positive ion vacancies and the pinning elements in the specimen colored at above  $450^\circ\text{C}$  must be F-centers. This results coincides partly with that of hardness measurements by Suzuki and Doyama<sup>9)</sup>. Referring to the misfit of F-centers in NaCl calculated by Gourary and Adrian<sup>10)</sup>, the misfit  $\eta$  has been assumed to be  $0.5 \sim 5.0\%$  and  $K$  to be  $1/50 \sim 1/2$ . Thus, the binding energy of the F-center is obtained in this way as  $E = 0.7 \sim 1.0$  eV. This value is almost the same as that of positive or negative ion vacancies. However, all the calculated values

of F-center concentration in the neighbourhood of dislocations are larger than the order of  $10^{-1}$ . This suggests that F-centers in the neighbourhood of dislocations are likely to coagulate.

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### DISCUSSION

**Lücke, K.:** You explained how to obtain the loop length from the measurements of  $\Delta_H$ . My question is how large are these loop length, in particular, how does the length change with temperature and what is the interaction energy resulting from the Cottrell's formula.

**Sakamoto, M.:** Assuming  $K \simeq 1/50 \sim 1/2$  and  $\eta \simeq 30\%$  for clear crystals at  $450^\circ\text{C}$ , and  $600^\circ\text{C}$ , the loop lengths  $L_e$  of pinning elements are calculated as  $2.7 \times 10^{-7}$  cm and  $5.2 \times 10^{-8}$  cm, respectively, and the interaction energy resulting from the Cottrell's formula

$$\ln \frac{c_1}{c_2} = \frac{E}{k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

is obtained as 1.0 eV, which is not consistent with the value  $0.7 \sim 0.9$  eV calculated from using  $c_0$  in the paper. Assuming  $K$  is the same and  $\eta \simeq 1.5\%$  for clear crystals at both temperatures,  $L_e$ 's are calculated as  $1.4 \times 10^{-8}$  cm and  $2.6 \times 10^{-7}$  cm, respectively, which seem to be partly unreasonable. Qualitatively speaking, however, it seems to keep still reasonability, because the interaction energy resulting from the above formula is also obtained as 1.0 eV, which seems to be almost consistent with the value calculated from using  $c_0$  in the paper. That is the reason why the main pinning element for clear crystals at above  $450^\circ\text{C}$  may be considered as positive ion vacancy.