unknowns—the three components of resistivity. In principle, three such measurements were then sufficient; in practice, several more were made and a least-squares method used to actually compute the components.

APPENDIX II

The analysis of the data presents one peculiar difficulty. It will be noted that the contribution of a resistivity component to the actual resistance reading is weighted with a cosine dependence as well as a component of the lead separation. Since current is passed axially through the specimen, it is an unfortunate fact that $\cos(xz')$ is always much smaller than the other cosines. The x-direction is always close to the horizontal for a vertical current flow. To aggravate the matter, $\cos(xz')$ becomes smaller with slip. This has the effect of introducing a large amount of error in ρ_x.

To minimize this error, an attempt was made to choose crystals with orientations having as large a value of $\cos(xz')$ as possible, as well as representing crystals which remained well out of the double-slip region of the unit stereographic triangle. For this reason, $\cos(yz')\cong\cos(zz')\cong 0.7$. It is easy to see that the results listed in Table II for specimen 33, which represents an almost ideal orientation in these respects, are much more consistent than the others in its values of ρ_x; the results listed in Table III for specimen 32, which represents a poor orientation in these respects, are probably not reliable in values of ρ_x. The values of ρ_x must be regarded as the most poorly determined experimental quantity.

Another source of error is the deviation of the potential probes from the positions intended. To minimize this error, resistance measurements were made before extension and the positions corrected to agree with these measurements. In no case did the adjustment exceed the probe diameter. Following elongation, the calculated new positions of the leads were compared with those observed in a microscope. The agreement was better than 2%, which confirms the geometrical analysis used.

It is believed that a fair estimate of accuracy seems to be about 10% for strains less than 6% to 5% for larger strains. This is the case for ρ_y and ρ_z. In the case of ρ_x the corresponding errors were 50% and 20%.

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Structure Sensitivity of the X-Ray Coloration of NaCl Crystals*

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Room temperature measurements of the rate of coloring of NaCl crystals by x-rays at different depths below the irradiated surface and for different states of deformation and heat treatment are reported. From the results it is concluded that two mechanisms of coloring operate in these crystals. The first, or "rapid-type" coloring, approaches a saturation density of F-centers of the order of $10^{17}/\text{cm}^3$, and appears to result from the generation of color centers from vacancies already present in the unirradiated crystal. The second, or "slow-type" coloring, takes place at a constant rate until F-centers in excess of $10^{18}/\text{cm}^3$ are formed. This type of coloring, which is usually observed only near the irradiated surface, is due to the generation of F-centers at dislocations, and is responsible for the hardness and density changes produced by the x-rays. Rapid-type coloring is found to occur at essentially the same rate in deformed crystals and in carefully annealed crystals; recovery at low temperatures after deformation, however, decreases the colorability. These results indicate that the principal effects of deformation and heat treatment on colorability may be related to the state of dispersion of impurities.

I. INTRODUCTION

It is now well known that the principal center responsible for the coloration observed in alkali halide crystals after exposure to ionizing radiations (the F-center) consists of a negative ion vacancy which has trapped an electron. It is to be expected, then, that the rate at which F-centers form in a crystal subjected to irradiation (the "darkenability" or "colorability") will be a structure sensitive property. Seitz[1] has in fact suggested that since vacancies may be generated during plastic flow, the colorability of deformed crystals should be enhanced compared to that of annealed crystals. Another reason for anticipating increased colorability in deformed crystals is that F-centers can be generated at dislocations[2]; a deformed crystal should contain many more such sources for F-centers than a well-annealed crystal.

Experimental evidence pertaining to the effect of plastic deformation on darkenability is very inadequate. Much of the work in this field was carried out prior to 1930 by Smekal[3] and by Przibram.[4] In the case of rock salt irradiated with γ rays, Przibram found that a

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[1] F. Seitz, Phys. Rev. **80**, 239 (1950).

[2] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[3] A. Smekal, Z. Ver. deut. Ing. **72**, 667 (1928).

[4] K. Przibram, Z. Physik **41**, 833 (1927); Wein. Ber. (IIa) **136** 43 (1927).

plastically deformed crystal colors more rapidly and reaches a deeper final color than an undeformed crystal. However, his observations were qualitative and complicated by the presence of various complex centers. Schröder[5] investigated the darkenability of deformed rock salt and, using ultraviolet light as his coloring radiation, observed enhancement of the darkenability of the deformed crystals. Unfortunately, Schröder's results may have been influenced by the large impurity content of his crystals (he reports that very pure rock salt cannot be colored by ultraviolet light). Although x-rays are widely used for the production of color centers in the alkali halides, there do not seem to be any quantitative experiments on the effect of deformation on x-ray colorability. It is the purpose of the present work (Sec. IV) to compare the colorability of deformed NaCl crystals with that of crystals which have received various heat treatments.

In attempting to study coloring rates during room temperature x-irradiation of NaCl crystals, it was found (in agreement with recent results obtained by Mador *et al.*[6]) that the growth of the F-band occurs in two distinct stages. First, there is an initial rapid growth which eventually tends to a saturation F-center density of about 10^{17} cm^{-3} throughout the whole crystal. Second, there is a continuing growth just below the irradiated surface which can lead to the formation of very high densities of F-centers. These results suggest the possibility that more than one coloring mechanism may be in operation during x-irradiation. Since thick crystals were to be used in investigating the effect of deformation on coloring, it seemed desirable first to extend the work of Mador *et al.* on the rate of growth of F-centers as a function of depth below the irradiated surface of the crystal. For this purpose thin crystal specimens were irradiated through rock salt filters of various thicknesses. These experiments are described in Sec. III.

II. EXPERIMENTAL

The optical measurements were made on NaCl crystals obtained from the Harshaw Chemical Company. The purity of such crystals has been reported.[7] The "thick" crystals used in the experiments on deformation and annealing were supplied already cleaved in the form of bars of square cross section 0.56 cm on an edge. The "thin" crystals were cleaved from larger blocks and ranged from 0.025 to 0.08 cm in the dimension parallel to the direction of the x-irradiation and the optical absorption measurement. The crystals were irradiated with x-rays obtained from a Machlett tube, having beryllium windows and a copper target, operated at 39 kv and 10 ma. All irradiations were at room temperature. The optical density at the maximum of the F-band was measured with a Bausch and Lomb "Spectronic 20" colorimeter-spectrophotometer. Optical density is reported as $\log_{10}(I_0/I)$, where I_0/I is the ratio of incident to transmitted intensity of F-light.

A crystal holder was constructed which made it possible to position the crystal reproducibly both in the spectrophotometer and in the x-ray beam. Precautions were taken to keep the crystals in darkness during the transfer from the x-ray unit to the spectrophotometer, to avoid optical bleaching. The procedure in determining curves of optical density *vs* x-ray dose was as follows. The crystal was irradiated for a given length of time, then removed from the x-ray unit and placed in the spectrophotometer, about two minutes elapsing between the termination of irradiation and the measurement of optical density. After another two-minute interval irradiation was continued. A small correction was made for the bleaching associated with each interruption and optical density measurement. It was found that, with this procedure, the same optical density *vs* dose curve was obtained for crystals in the same condition regardless of the number of optical measurements made during the course of the irradiation. The corrections involved do not shift any of the optical density curves shown in this paper by a significant amount.

All of the thin crystals were irradiated in the as-cleaved condition. Plastic deformation of the thick crystal bars was carried out by coating the ends with collodion and then compressing the bars lengthwise in a toolmaker's vise. The collodion coating prevents the ends of the bars from splitting during heavy deformation. All anneals were carried out in air; specimens were allowed to cool inside the furnace (at a rate such that the temperature dropped from 700°C to 400°C in one hour).

III. OPTICAL MEASUREMENTS ON THIN CRYSTALS

Comparison of F-band growth curves for crystals with and without NaCl filters is shown in Fig. 1, where the optical density is given as a function of irradiation time. The corresponding average density of F-centers, calculated by means of Smakula's equation[8] under the assumption of a uniform optical density throughout the thin plate specimens, is also shown. After the first 10 minutes of irradiation the increase in optical density for the crystal irradiated without a filter is linear with dose (Curve A) up to the practical upper limit of the spectrophotometer scale $[\log_{10}(I_0/I)\sim 0.7]$. Since the coloration near the irradiated surface is highly nonuniform in the absence of a filter, the actual density of color centers corresponding to a given optical density must be greater than the average density of centers obtained from Smakula's formula. Thus the density of F-centers formed near the surface after moderate irradiation is well above 10^{18} cm^{-3}.

In contrast, the F-center density of various crystals

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[5] J. Schröder, Z. Physik **76**, 608 (1932).

[6] Mador, Wallis, Williams, and Herman, Phys. Rev. **96**, 617 (1954).

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

[8] A. Smakula, Z. Physik **59**, 603 (1950). See also reference 2, footnote 1.

irradiated through NaCl filters approaches a saturation value of about 6×10^{16} cm^{-3} (as for example in Fig. 1, Curve *B*). For crystals irradiated through filters, the average *F*- center concentration calculated from Smakula's formula closely represents actual densities since coloration is very nearly uniform. Curve *C* in Fig. 1 shows that, within experimental error, a change of x-ray intensity without a change in filter thickness alters only the time scale of the coloring curve, not the saturation value. This implies that the number of *F*-centers formed depends to a first approximation only on x-ray dose and not on intensity. Similarly, measurements not presented in Fig. 1 show that curves for various filter thickness may be superimposed by a change of the time scale, with essentially the same saturation value attained in each case. It is especially worth noting that in Fig. 1 the intercept of the linear portion of Curve *A* is the same as the saturation value for Curves *B* and *C*.

The results reported show, in agreement with the earlier work of Mador *et al.*,[6] that *F*-center formation takes place in two stages. The first begins rapidly, then decreases in rate, eventually approaching a saturation density of about 10^{17} *F*-centers/cm^3. The second stage, which takes place detectably only near the surface where the radiant energy absorbtion is very high, eventually results in *F*-center densities well above 10^{18} cm^{-3}. With prolonged exposure, the region of intense coloration (where the number of *F*-centers $\gtrsim 10^{18}$ cm^{-3}) moves deeper into the crystal. The present work has shown that the second stage involves a linear increase in *F*-center density with time and that the contributions due to the two stages are additive.

IV. COLORATION OF DEFORMED AND ANNEALED CRYSTALS

Thick (0.56-cm) crystals are used for the plastic deformation experiments. Since a uniform distribution of color is not produced, the results of the optical measurements cannot be reported in terms of the density of color centers. Instead, only the observed optical density is reported.

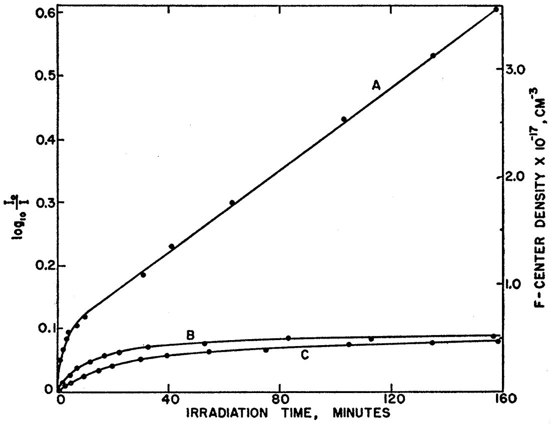

Fig. 1. Growth of the *F*-band as a function of irradiation time. Curve *A*: specimen 0.025 cm thick, no filter. Curve *B*: specimen 0.058 cm thick, NaCl filter 0.075 cm thick. Curve *C*: same as *B* but with incident x-ray intensity reduced by a factor of two. Optical densities for Curves *B* and *C* have been corrected to specimen thickness of 0.025 cm, to make results comparable with Curve *A*.

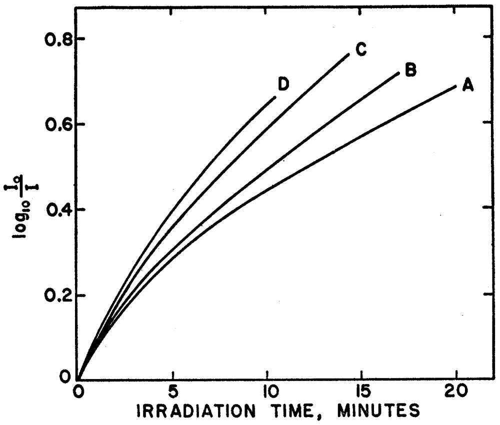

Fig. 2. Growth of the *F*-band in 0.56 cm thick NaCl crystals irradiated without a filter. Curve *A*: as-received crystal; Curve *B*: crystal deformed 3.9% in compression and allowed to recover five days at room temperature plus 1 hr at 100°C; Curve *C*: crystals deformed 3.9% and 8.1% in compression and measured 1 hr after deformation (data for both these crystals fell on the same curve); Curve *D*: as-received crystal, annealed at 700°C for 10 hr and furnace cooled.

The curves in Fig. 2 show that the colorability is structure-sensitive to a certain extent. It was found that the curves of optical density *vs* irradiation time for various as-received crystals (i.e., crystals as received from Harshaw and subjected to no further cleaving) are almost identical. Crystals annealed by heating to 700°C for 10 hours followed by furnace cooling were observed to have a much greater colorability (Curve *D*). An as-received crystal after deformation in compression shows a colorability (Curve *C*) distinctly greater than that which it had prior to deformation but slightly less than that of an annealed crystal. (A 4% deformation is sufficient to activate a large density of slip planes in the crystal, as is revealed by the strong birefringence of the deformed crystals; the as-received and annealed crystals on the other hand are almost perfectly isotropic optically.)

The contribution to the over-all optical density made by the region of intense coloration near the surface should be negligible in the results of Fig. 2, due to the fact that thick crystals and short irradiation times are employed. However, it was decided to make certain of this point by irradiating the thick specimens through a 0.025-cm thick NaCl filter. The results of such experiments are shown in Fig. 3. (These data are not directly comparable to those in Fig. 2, since a slighlty different x-ray intensity was used.) The deformed crystal used in the measurements shown in Fig. 3 was one that had been first annealed at 700°C for 10 hours before deformation, in contrast to the case of Fig. 2 where an as-received crystal was deformed. In spite

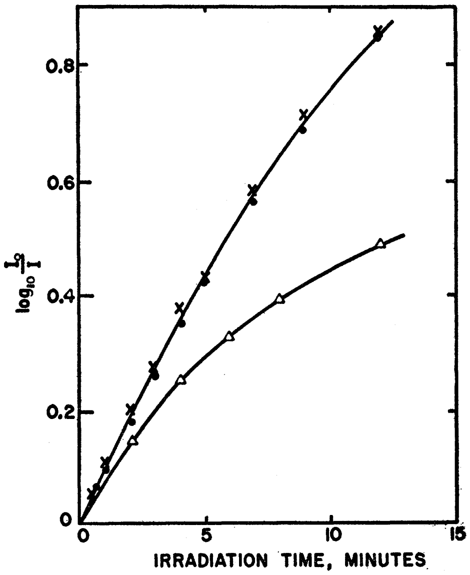

FIG. 3. Growth of the *F*-band in 0.56-cm thick NaCl crystals irradiated through a 0.025-cm thick NaCl filter. Triangles: as-received crystal; solid circles: annealed and furnace cooled; crosses: deformed 3.6% after annealing.

of these modifications, enhancement of the darkenability of the deformed and the annealed crystals with respect to as-received specimens is again observed in the data of Fig. 3. In both figures this enhancement is observed to increase with increasing irradiation time, i.e., the ratio of optical densities of various crystals is nearer to unity during the initial part of the irradiation curves than in the later part. This result implies that it is primarily the difference in saturation density rather than in initial coloring rate that determines the differences between curves. Unfortunately, the history of the as-received crystals is too uncertain to permit a direct interpretation of the differences between darkenability of such crystals, and those which are annealed or deformed. Comparison of Curves *B* and *C* of Fig. 2 shows, however, that a substantial decrease in colorability is produced by low temperature annealing after deformation.

The shape of the *F*-band in both the as-received and deformed crystals was examined in the region $3500 \leqq \lambda \leqq 6000\text{A}$ using thick crystals irradiated 15 minutes without a filter. While a possible slight broadening of the *F*-band was observed in the deformed crystal, no evidence of the presence of other bands was found in the wavelength region examined.

V. HARDNESS MEASUREMENTS

Marked increases in the hardness of rock salt have been observed by Li[9] and by Westervelt[10] after irradiation with x-rays. The optical measurements suggest that it is desirable to find how deeply below the irradiated surface these hardness increases occur. Hardness was measured using a Tukon hardness tester with a diamond pyramid indentor. Measurements of surface hardness showed an increase upon irradiation similar to the results of previous workers. It was also shown that the hardness increase is permanent at room temperature and is unaffected by bleaching; also, for a given irradiation the same increase was obtained for natural rock salt crystals (from the Stassfurt deposits) as for the Harshaw crystals.

Measurements as a function of depth were made on a natural rock salt crystal 15 months after the specimen had been given an 8-hour irradiation, the crystal being cleaved through the darkened area so as to expose a face parallel to the direction of irradiation for measurements. The results (Fig. 4) show that the radiation induced hardness increase is largely confined to the surface layer about 0.02 cm thick, and that below 0.08 cm the hardness is indistinguishable from its value prior to irradiation. Thus the region of hardness change is essentially the same as the region of intense coloration. The results are in distinct contradiction to the impression of Pratt[11] that hardening occurs throughout the volume of the crystal.[12]

VI. DISCUSSION

The fact that *F*-band growth in the experiments on thin crystals could be described, in a purely formal way, as made up of two distinct stages suggests the possibility that there may be two mechanisms of coloring in these crystals. In order to give a more meaningful interpretation to the results, it will therefore be helpful to review briefly the accepted ideas about the mecha-

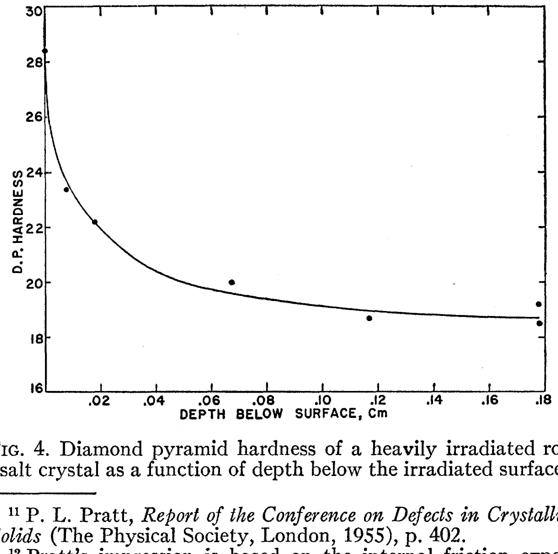

FIG. 4. Diamond pyramid hardness of a heavily irradiated rock salt crystal as a function of depth below the irradiated surface.

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[9] Y. Y. Li, Acta Metallurgica **1**, 455 (1953).

[10] D. R. Westervelt, Acta Metallurgica **1**, 755 (1953).

[11] P. L. Pratt, *Report of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 402.

[12] Pratt's impression is based on the internal friction experiments of Frankl, where the decrease in damping due to irradiation was shown to occur throughout the volume of the entire crystal. This latter effect, which has been verified and extended by the present authors (work to be published) is apparently of different origin than the increase in hardness.

nism of formation of F-centers. It has been widely suggested that the vacancies required for the formation of color centers are generated at dislocations during x-irradiation. Experimental evidence which supports this mechanism is as follows.

(1) F-center concentrations of the order of 10^{18} to 10^{19} cm^{-3} can be attained by x-irradiation whereas comparison of the mass density of a crystal as measured hydrostatically with that calculated from x-ray data shows[13] that the concentration of vacancies present in an annealed crystal probably does not exceed about 10^{17} cm^{-3}, counting both free vacanies and those associated in clusters.

(2) It has been shown by Smekal[14] and by Etzel[15] that x-irradiation enhances the darkenability of a crystal in ultraviolet light. Since ultraviolet light is presumably not energetic enough to generate vacancies, it is concluded that the x-rays must be able to do so.

(3) X-irradiation decreases the density[16] and increases the length of NaCl crystals.[17]

The experimental results just quoted were apparently obtained on crystals irradiated under conditions where the major effects might be attributed entirely to the intense coloration near the surface of incidence of the x-rays. Thus, there is no question that the formation of a region of intense coloration near the surface must involve the generation of new vacancies. Furthermore, the fact that coloration can take place readily at temperatures too low for vacancy diffusion over appreciable distances implies that the sources of these new vacancies must be dislocations rather than external surfaces. The principal question of mechanism then concerns the earlier stage of coloring which results in a saturation density of the order of 10^{17} F-centers/cm^3. It is desirable to determine whether this stage is also primarily due to the generation of new vacancies in the crystal, or whether it results from the utilization of vacancies or small vacancy clusters already present in the crystal prior to irradiation.

It is known that at least under some conditions vacancies already present prior to irradiation control the colorability of crystals. A striking example is the effect of prior proton irradiation in enhancing considerably the x-ray coloration produced deep inside a crystal.[18] This result is readily explained in terms of the creation of vacancies in large numbers by the proton irradiation. Another illustration is in the effect of impurities in enhancing the colorability of alkali halide crystals. (Divalent and multivalent impurities are especially effective by virtue of the fact that they must be accompanied by vacancies in order to maintain charge neutrality of the ionic crystal.) These effects are reviewed and interpreted by Schulman.[19] In view of these impurity effects, we must assume either that impurities also play a significant role in the coloring of the present (Harshaw) crystals or else that the impurity content is too low to be important in these crystals. Schulman argues in favor of the former view, since he finds by extrapolation of data on the effect of divalent impurities on colorability that observed colorabilities of "pure" crystals can be accounted for by impurity contents of the order of 10 parts per million. Such contamination is well within the impurity content of normally available "pure" alkali halide crystals, as is shown by recent analyses.[7]

The alternative view is to deny the existence of vacancies in quantities of the order of 10^{17} cm^{-3} in "pure" crystals prior to irradiation, and to claim that even the early stage of coloring is due primarily to the generation of vacancies from dislocations. It might then be anticipated that this coloring is directly dependent on the dislocation density in the crystal. This prediction is clearly in contradiction to the results of Figs. 2 and 3 (since the deformed crystals may be expected to have at least 100 times the dislocation density of the annealed crystals). To explain the lack of dependence of colorability on dislocation density would then require the assumption that, although vacancies are generated at dislocations, recombination of electrons and holes also occurs at dislocations. Thus the two effects may possibly cancel each other, leaving a net colorability independent of dislocation density. With such an assumption, however, it then becomes difficult to explain why the colorability should show any structure sensitivity at all, e.g., the decrease in colorability after low temperature annealing (Fig. 2).

As a result of these considerations, it seems most reasonable to recognize a difference in mechanism between the two stages of coloring. The early stage will be referred to as the "rapid-type" coloring, since it takes place readily even deep inside a thick crystal. The second stage, which is responsible for the region of intense coloration near the surface, will be called the "slow-type" coloring. Thus, we have concluded that while slow-type coloring is due to generation of vacancies at dislocations, rapid-type coloring is most reasonably attributed to vacancies and/or vacancy clusters present in the crystal prior to irradiation. In the Harshaw crystals used in the present experiments and in those of Mador *et al.*, the density of these vacancies must then be of the order of 10^{17} cm^{-3}.

The saturation density of color centers for rapid-type coloring (in the present case 6×10^{16} cm^{-3}) should not be regarded as precisely the number of vacancies in the crystal prior to irradiation. The work of Harten[20]

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

[14] See K. Przibram, *Verfärbung und Lumineszenz* (Springer-Verlag, Vienna, 1953).

[15] H. W. Etzel, Phys. Rev. **98**, 1531A (1955).

[16] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949); Primak, Delbecq, and Yuster, Phys. Rev. **98**, 1708 (1955).

[17] K. Sakaguchi and T. Suita, Tech. Repts. Osaka Univ. **2**, 177 (1952).

[18] W. Leivo and R. Smoluchowski, Phys. Rev. **93**, 1415 (1954).

[19] J. H. Schulman, J. Phys. Chem. **57**, 749 (1953).

[20] H. V. Harten, Z. Physik **126**, 619 (1949).

demonstrates that the saturation density increases with decreasing temperature. This result is best explained by recognizing that x-rays produce bleaching as well as coloration and that these two effects, which are balanced at saturation, may vary with temperature in different ways. In these experiments, Harten used filtered radiation (wave lengths in the range 0.2 to 1.0 A) and relatively short exposure times. Thus, in terms of the present concepts, he was dealing with the rapid-type coloring only. Harten did report, however, that concentrations of F-centers in excess of 10^{18} cm^{-3} were obtainable after extremely long irradiations. This result supports the contention that slow-type coloring involves a relatively low quantum efficiency. Thus, it can be obtained detectably only after relatively long exposures to x-radiation of low absorption coefficient, or after short exposures to soft x-rays, as in the layer of intense coloration obtained near the surface of a crystal exposed to unfiltered radiation.

A measure of the relative efficiency of the rapid-type and slow-type coloring may be obtained from the ratio of initial to final slopes of any F-band growth curve, provided that the relative effectiveness of the different x-ray wave lengths in producing color centers is the same for both mechanisms (see the Appendix). Actually curves obtained without a filter (e.g., Curve A, Fig. 1) show so large a curvature near the origin that a determination of the initial slope is difficult. On the other hand, for irradiation through a filter, the final slope is so small that it cannot be determined with precision. Thus it is possible to give only a lower limit to the ratio of coloring efficiencies. Examination of the various coloring curves, such as those of Fig. 1, shows that the ratio of initial to final slope is at least 100. It is therefore concluded that if the assumption discussed in the Appendix is valid, the energy to form an F-center in rapid-type coloring is initially of the order of 10^{-2} or less of that for the slow-type. In terms of the suggested mechanisms of the two types of coloring, this result is in accord with Seitz' prediction[1] that the solvent action of excitons and/or electrons and holes produced by irradiation on "incipient vacancies" at dislocations should be much weaker than the action on vacancies in small clusters.

The conclusion that rapid-type coloration depends on vacancies and vacancy clusters present in the unirradiated crystal should lead one to expect that this type of coloring is structure sensitive. An extreme example of this structure sensitivity was already mentioned earlier in this discussion, i.e., the effect of proton irradiation in greatly enhancing the x-ray colorability deep inside the crystal. Less striking effects are obtained through heat treatments. For example, it is well known[14,21,22] that quenched crystals color more rapidly than slowly cooled crystals. Another effect of heat treatment is demonstrated in the present experiments, which show that annealing increases the colorability of an as-received crystal.[23] This result seems similar to the observation, reported in the early literature,[14] that natural or solution grown crystals show a low rate of coloring (compared to melt grown crystals) but that the colorability may be increased by annealing. Finally, it is widely reported[14] that cold working increases the colorability. In the present experiments, this was only true for the as received crystals; the colorability of an annealed crystal was almost unchanged after deformation.

The differences in colorability between crystals treated in different ways may be explained in terms of the excess vacancies produced by the particular treatments. For example, this explanation certainly fits the experiments on proton irradiated crystals. One might explain in the same way effects of heat treatment and of cold-working. The effect of quenching in enhancing colorability may be attributed to the quenching in of vacancies which were in equilibrium at high temperatures. Presumably, then, even the rather slow rate of cooling of the annealed crystals in the present experiments is not sufficient to permit complete removal of the vacancies present in equilibrium at the annealing temperature. Rather, it may be supposed that these vacancies are either unable to coalesce, or else that they aggregate at most into small clusters which are capable of being redissolved upon x-irradiation. It has been proposed[1] that cold working generates an excess of vacancies or vacancy clusters and that this phenomenon accounts for the enhancement of colorability in deformed crystals. In these terms, the agreement between the colorability of annealed and of cold-worked crystals in the present experiments may be somewhat coincidental. Furthermore, it is somewhat difficult to explain the close agreement between the rates of coloring of crystals deformed 4 percent and those deformed 8 percent (Curve C, Fig. 2).

An alternative explanation for the effects of heat treatment and deformation may be given in terms of the concept that colorability is controlled primarily by vacancies which are in equilibrium with divalent (and multivalent) impurities dissolved in the crystal. Since such impurities generally have very low solubilities, it is reasonable to suppose that the principal effects of heat treatment and deformation on colorability are to produce changes in the degree of dispersion of such impurities. The vacancy concentration is then only indirectly controlled by the given treatment. A concept of this sort was first suggested by Smakula[8] and more recently considered by Schulman.[19] In terms of this concept, heat treatment gets impurities into solution, but even upon relatively slow cooling there is insufficient

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[21] R. Smoluchowski, *Report of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 252.

[22] F. A. Cunnell and E. E. Schneider (private communication).

[23] Harshaw crystals are grown from the melt in large sizes. Presumably, the original rate of cooling of the crystals is much slower than the rate of cooling after annealing in the present experiments.

time for complete precipitation. The work of Matthai[24] supports this contention by showing the presence of ultramicroscopic colloidal particles after anneals below 400°C which may be dissolved by heat treatments at high temperatures. It may be supposed that cold working disperses impurities, but only if they are not already in solution (i.e., if colorability is not already high as a result of heat treatment), while recovery after deformation would permit precipitation of impurities near dislocations, thus decreasing the colorability (as observed in Curve *B* of Fig. 2). In these terms it would appear that the various observations reported in the literature on the enhancement of colorability upon deformation may have involved no more than such impurity effects.[25] Clearly, experiments on extremely high purity crystals are needed to make possible a more certain separation of effects due to impurities from those due to vacancy clusters. In the absence of such information, however, it is worth noting that further support for the importance of impurities may be obtained from studies of ionic conductivity. It is well known that ionic conductivity of alkali halides at temperatures well below the melting point is controlled principally by the concentration of multivalent impurities.[2] It has been observed[26,27] that annealing generally increases the ionic conductivity in the same way as it enhances the colorability. This fact seems to suggest that the dissolution of impurities at high temperatures and their failure to precipitate out during cooling at normal rates is responsible for the effect of annealing on both properties. The alternative interpretation, that the enhancement of colorability by annealing may be due to the formation of small vacancy clusters, would not be suitable to explain the enhancement of the ionic conductivity; probably only single vacancies have both the net charge and the mobility required to produce ionic conductivity.

The structure sensitivity of the slow-type coloring should be of an entirely different character, showing a rapid increase with increasing dislocation density.[28] Furthermore, the generation of 10^{18} vacancies/cm^3 at edge dislocations should have the effect of raising the extra half-plane of a dislocation about 1000 atom distances (taking a dislocation density of 10^8/cm^2). This implies a drastic change in the dislocation structure and is in accord with the observed result that the hardness change takes place only in the region of slow-type coloring. The severity of the damage produced by slow-type coloring is also indicated by the formation of more complex color centers. For example, it has been observed[6] that the *M*-band appears to a much higher density, relative to the *F*-center concentration, in the region of intense coloration near the surface. Also, the present authors have observed that the change to a blue color ("Blauumschlag"[14]) which occurs upon optical and thermal bleaching of *F*-centers, takes place only in the region of slow-type coloration This effect must be associated with the coagulation of simple centers to form more complex centers (e.g., *R*-centers). In general, then, it may be concluded that the generation of vacancies from dislocations, involved in the slow-type coloration, produces severe damage to the crystal structure.

VII. CONCLUSIONS

The enhancement of the colorability of deformed crystals over that of annealed crystals, predicted on the basis of the generation of vacancies by dislocations during plastic flow,[1] is not observed. It appears that the sensitivity of coloring rates to particular treatments, as observed in the present experiments and widely reported in the early literature, may be related to the state of aggregation of impurities in the crystals, rather than to structural imperfections alone. If this interpretation is correct, ideally pure crystals should show only slow-type coloring.

APPENDIX

It is assumed that in each element of volume of the irradiated crystal the rate of formation of *F*-centers is proportional to the rate at which radiant energy is absorbed. Suppose that $\mu(\lambda)$ is the absorption coefficient for x-rays of wavelength λ, $I_\lambda d\lambda$ the x-ray intensity in wavelength range $d\lambda$, and $K'(\lambda)$ and $K''(\lambda)$ are measures of the coloring efficiencies for rapid-type and slow-type coloring, respectively, for radiation of wavelength λ. If $\dot{n}_F'$ and $\dot{n}_F''$ are the over-all rates of formation of *F*-centers in rapid-type and slow-type coloring, respectively, then

$$\dot{n}_F' = \int_x \int_\lambda K'(\lambda) I_\lambda \mu(\lambda) d\lambda dx,$$

$$\dot{n}_F'' = \int_x \int_\lambda K''(\lambda) I_\lambda \mu(\lambda) d\lambda dx.$$

If $K'(\lambda)/K''(\lambda)$ is a constant independent of λ, then

$$\dot{n}_F'/\dot{n}_F'' = K'/K'',$$

i.e., the ratio of coloring rates for the two mechanisms equals the ratio of coloring efficiencies.

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[24] R. Matthai, Z. Physik **68**, 85 (1931).

[25] On the other hand, some of these observations may have involved primarily slow-type coloring.

[26] F. Quittner and A. Smekal, Z. physik. Chem. **B3**, 162 (1929); F. Quittner, Z. Physik **68**, 796 (1931).

[27] G. A. Russell and R. Maurer (private communication).

[28] Recent experiments by one of the authors (A. S. N., to be published) confirm this prediction.