Structure Sensitivity of *F*-Center Generation by X Rays at Low Temperatures*

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Recent internal friction and elastic modulus experiments suggest that *F* centers are formed at dislocations in the alkali halides during x irradiation even at liquid helium temperature, but that enhanced colorability is suppressed at low temperatures by the absence of diffusion of the generated centers. In the present experiments *F*-center growth curves were obtained for both as-received and plastically deformed (up to 15%) NaCl and KCl crystals at temperatures ranging from 10° to 325°K. From these data it is found that both the rate of capture of electrons by negative-ion vacancies and the final saturation concentration of *F* centers achieved are strongly temperature sensitive and that there exists an optimum temperature at which a given color center concentration is attained with a minimum amount of irradiation. The colorability of lightly deformed crystals is found to be enhanced only at temperatures where diffusion of *F* centers appears to be possible; otherwise a rapid saturation of the coloration is observed. However, the initial *F*-center growth rate in a heavily deformed crystal, relative to an undeformed one, becomes larger as the temperature is decreased, and can be interpreted in terms of the presence of a larger number of *F* centers formed near dislocations. With further x irradiation, this additional contribution saturates.

INTRODUCTION

OBSERVATIONS of the rate of formation of color centers in alkali halide crystals subjected to ionizing radiations have shown that vacancies are generated in these crystals even though the radiation is of insufficient energy to produce atomic defects directly.[1] Several indirect mechanism by which vacancies might be generated by x or γ irradiation have been proposed; these can be grouped into two classes, viz., those which occur in the bulk crystal and those which require the presence of dislocations. The possible importance of dislocations as a source of defects is suggested by the well-known phenomenon of dislocation climb through which large concentrations of vacancies can be formed by the motion of an edge dislocation line normal to its slip plane.

Although it was first thought that excess vacancies could be introduced into a crystal subjected to x irradiation by diffusion from external surfaces, experiments such as those of Duerig and Markham[2] showing that large concentration of *F* centers could be formed during irradiation at helium temperature demonstrated that the vacancies must be formed within the crystal. Seitz[3] proposed that the recombination of excitons in the vicinity of dislocations would release sufficient thermal energy to create vacancies by dislocation climb and to allow the vacancies so created to diffuse some 40 to 50 A away from their sources. From this model it would be expected that a crystal containing a large concentration of dislocations would color more rapidly under x irradiation than one containing fewer dislocations. Such an effect was first observed by Przibram[4] in 1927 and has been investigated more recently by Gordon and Nowick[5]

and Nowick.[6] These investigators concluded that there are two distinct mechanisms of *F*-center generation in operation during room temperature irradiation of NaCl (and, presumably the other alkali halides as well). The first, or "rapid-type" of coloring results from the formation of *F* centers from vacancies already present in the crystal. The second, or "slow-type" of coloring occurs at a constant rate and is due to the generation of new vacancies at dislocations. Nowick showed further that the slow-type coloration was greatly enhanced in a crystal in which the dislocation content had been increased by plastic deformation.

One potential difficulty with the dislocation mechanism discussed above was pointed out by Dexter[7]: If vacancies which become *F* centers are created at edge dislocations and remain within 50 A or so of their source, the *F* band due to these centers should be substantially broadened due to the elastic strain field which surrounds the dislocation. This broadening is not observed. Another difficulty arises in an experiment performed by Crawford and Young[8] who, using dislocation etching techniques, searched for direct evidence of dislocation climb during x irradiation of NaCl. Although it was expected that the effect would be observed easily, no evidence of climb was seen. This may, however, be because the ends of the dislocations intersecting the free surface were pinned by the first etch used.

In a recent paper, Mitchell, Wiegand, and Smoluchowski[9] propose an alternative mechanism for the generation of vacancies at dislocations which provides an explanation for their *F*-center growth curve data obtained on KCl. They propose the existence of two kinds of *F* centers (i.e., *F* centers in two distinct kinds of environments) in x-irradiated crystals. These ideas will be discussed later. It should be remembered that their data are mostly for much more prolonged irradiations

[1] H. W. Etzel, Phys. Rev. 100, 1643 (1955).
[2] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).
[3] F. Seitz, Phys. Rev. 89, 1299 (1953).
[4] K. Przibram, Z. Phys. 41, 833 (1927).
[5] R. B. Gordon and A. S. Nowick, Phys. Rev. 101, 977 (1956).

[6] A. S. Nowick, Phys. Rev. 111, 16 (1958).
[7] D. L. Dexter, Phys. Rev. 93, 985 (1954).
[8] J. H. Crawford and F. W. Young, Jr., J. Appl. Phys. 31, 1688 (1960).
[9] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. 121, 484 (1961).

than have been employed in most experiments in this field.

Rabin and Klick[10] have determined F-center growth curves at low temperatures for a number of the alkali halides and find that, in contrast to the results of room temperature experiments, the rate of formation of F centers with x irradiation at low temperature is not structure sensitive, i.e., crystals which show a marked difference in colorability at room temperature color at the same rate when irradiated at helium temperature. From this observation they conclude that the vacancies formed during low-temperature irradiation are created in the bulk, perfect crystal rather than at dislocations. The mechanism, given in detail by Klick[11] in a recent paper, is a modification of that first proposed by Varley[12] and involves the ejection of multiply ionized halogen atoms from their normal lattice sites by electrostatic forces. Experiments on H-center formation during low-temperature irradiation lend strong support to this mechanism. The mechanism apparently does not operate at room temperature.

The experimental evidence summarized above indicates that at room temperature a dislocation type of mechanism is the principal source of excess vacancies generated by ionizing radiation, while at helium temperature an interstitial type of mechanism such as that proposed by Rabin and Klick is the dominant source. This paper is concerned with the reasons for which the dislocation sources become inoperative at low temperature. To study this problem experimentally one needs a measuring technique which is sensitive to defect formation right at the dislocations as contrasted to the usual optical methods which measure an average of color center formation throughout the bulk of the crystal. The authors have recently shown that dislocation internal friction measurements provide such a technique,[13] the internal friction being used, in effect, as the detector in a spectrophotometer. The experiments are interpreted as follows: During low temperature x irradiation dislocation pinning points are created, each of which consists of a pair of dislocation jogs of opposite sign in close association with an F center located below the dislocation slip plane. Because the F center is in a region of dilation its absorption band is displaced towards the red by the dislocation strain field. Ionization of the F center by illumination with light of suitable wavelength results in the recombination of its vacancy with the dislocation jogs and, thus, in unpinning of the dislocation. Warmup allows the F center to diffuse away thereby creating a permanent pinning point (one which cannot be destroyed by optical bleaching). These internal friction experiments thus suggest that the energy

release at dislocations which results in vacancy formation is not sufficient in itself to allow the vacancies to diffuse away from their source and, therefore, that a dislocation can only be a source of vacancies in a coloring experiment if the temperature is sufficiently high to permit the thermally activated diffusion of F centers.

The experiments to be reported were undertaken in order to investigate the consequences of the above hypothesis on optical measurements of F-center formation during x irradiation. During the experiment some new observations on the temperature dependence of F-center formation from vacancies already present in the crystal were made and are also reported.

EXPERIMENTAL PROCEDURE

All optical measurements were performed with either NaCl or KCl single crystals purchased from the Harshaw Chemical Company. Large blocks of the crystals were deformed under water in a tool-maker's vise, permitting attainment of deformations ranging up to 15% in compression. Plates, approximately 1 mm thick, were cleaved from the deformed crystals and used for optical absorption measurements. The crystals were colored with 120-kv x rays from a tungsten anode and the F center concentrations were calculated by means of Smakula's formula.[14]

The optical measurements were made with a spectrophotometer especially constructed to accommodate the low-temperature cryostat which was the same as that used for the internal friction experiments of reference 13. It consisted of a Leiss single-prism monochromator, an incandescent light source, and an ultraviolet or infrared sensitive phototube used in conjunction with a Photovolt model 501-M photometer. A secondary optical path (through air) was used as the reference and eliminated the need to move the specimen for standardization of the photometer. Constant temperature baths used in the present experiments were: (1) liquid helium, (2) liquid nitrogen, (3) acetone and dry ice mixture, (4) ice and water mixture, and (5) room temperature water.

RESULTS AND DISCUSSION

To observe through optical measurements effects due to the presence of dislocations, one would like to be able to make a comparison with the coloration of a dislocation free sample. Lacking such a sample, one must resort to comparison of F-center growth curves obtained for deformed and undeformed crystals; a 3% deformation is known to raise the dislocation density by a factor of about 100,[15] so a good indication of the effects due to the presence of dislocations can be achieved by using undeformed crystals for comparison. The first part of the present research is concerned with the temperature dependence of F-center formation in undeformed crystals.

[10] H. Radin and C. Klick, Phys. Rev. 117, 1005 (1960).

[11] C. Klick, Phys. Rev. 120, 760 (1960).

[12] J. H. O. Varley, Nature 174, 886 (1954); J. Nuclear Energy 1, 130 (1954).

[13] C. L. Bauer and R. B. Gordon, J. Appl. Phys. 33, 672 (1962).

[14] A. Smakula, Z. Physik 59, 603 (1930).

[15] C. L. Bauer, thesis, Yale University, 1959 (unpublished).

F-Center Generation in Undeformed Crystals

The concentration of F-centers in undeformed NaCl and KCl crystals was measured as a function of x-ray dose for irradiations at temperatures ranging from 78° to 325°K with results as shown in Figs. 1 and 2. Although it is known that the slopes of the F-center growth curves are quite different at 78° and 300°K,[10] the irradiations at intermediate temperatures produced larger F-center concentrations than had been expected. These large growth rates can be seen best in the curves for KCl shown in Fig. 2. The initial rate of the production of F centers is seen to increase with increasing temperature but saturation (with the possible exception of the 78°K curve) occurs at smaller concentrations. It is seen that there exists an optimum temperature at which a given concentration of F centers can be produced by a minimum amount of x irradiation. To investigate the rate of formation of F centers, $\dot{n}_F$, two processes must be considered, viz., the rate at which negative-ion vacancies are converted to F centers by x irradiation, k_C, and the rate at which F centers are destroyed (bleached) during x irradiation, k_B. Bleaching can occur in three distinct ways: by thermal or optical excitation and by direct recombination of trapped electrons with free holes. If n represents the concentration of available negative-ion vacancies, $\dot{n}_F$ can be expressed as

$$\dot{n}_F = k_C n - k_B n_F. \tag{1}$$

For moderate irradiations, the concentration of negative-ion vacancies may be expressed as

$$n = n_0 + k_v t - n_F, \tag{2}$$

if it is assumed that the concentration of vacancies, in addition to the initial negative-ion vacancy concentration n_0, increases linearly with x-irradiation time t. The proportionality factor k_v may also consist of two terms, one representing a bulk process, the other representing a process restricted to the region near dislocations. Combining Eqs. (1) and (2) and integrating yields

$$n_F = \left[\frac{k_C n_0}{(k_C + k_B)} - \frac{k_C k_v}{(k_C + k_B)^2} \right]$$
$$\times [1 - e^{-(k_C + k_B)t}] + \frac{k_C k_v t}{K_C + k_B}. \tag{3}$$

Hence n_F can be expressed as the sum of an exponential and a linear term. For long irradiation times Eq. (3) may not be valid because the original assumption that new vacancies are created at a constant rate [Eq. (2)] may not be valid when large concentrations of vacancies are located near the dislocations. However, good agreement can be obtained between theory and experiment if a proper choice of k_B, k_C, k_v, and n_0 is made.

From this simple analysis it is possible to make a number of observations pertaining to the dependence of F-center formation on temperature. If both k_B and
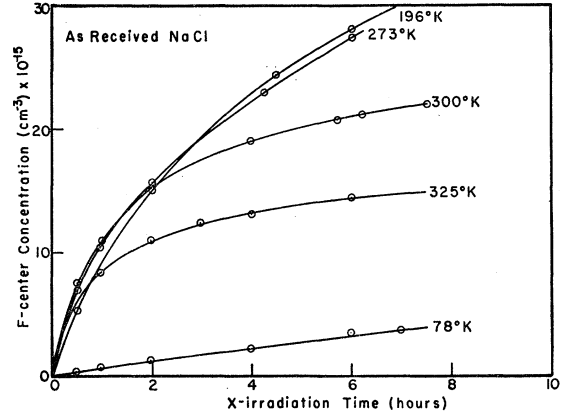

FIG. 1. Dependence of the F-center growth rate on temperature for NaCl.

k_C are temperature dependent, Eq. (3) can give a qualitative explanation of the behavior of the experimental observations. At high temperatures, both k_B and k_C are large and hence the initial growth rate is large, although the final saturation concentration of F centers is relatively small. As the temperature decreases both k_B and k_C decrease, which causes the initial growth rate to decrease but the final saturation concentration to increase. Furthermore, from Eq. (1), the initial slope should be equal to

$$(dn_F/dt)_{t=0} = k_C n_0. \tag{4}$$

For the temperature range bounded by 78°K and room temperature, $(dn_F/dt)_{t=0}$ for both KCl and NaCl was found to obey an Arrhenius equation. That is, k_C, which is a measure of the probability that a vacancy can trap an electron, decreases exponentially with decreasing temperature. Hesketh[16] also made observations of the initial F-center growth rate in x-irradiated NaCl crystals and had found that the rate can be represented by
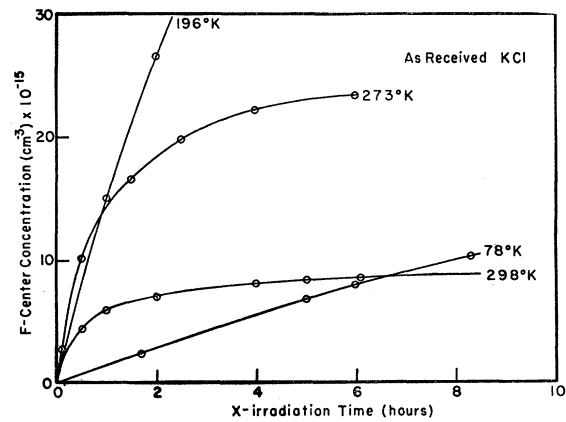
$$(dn_F/dt)_{t=0} = \dot{e}Ce^{-E/kt}, \tag{5}$$

FIG. 2. Dependence of the F-center growth rate on temperature for KCl.

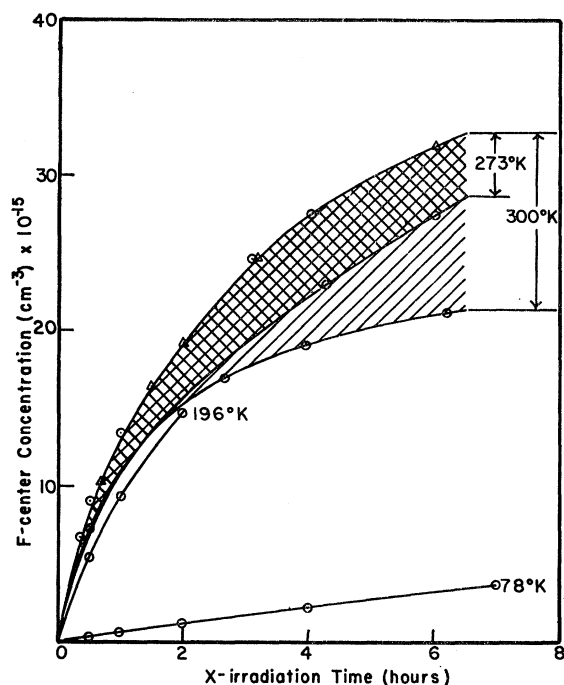16 R. V. Hesketh, Phil. Mag. 4, 114 (1959).

FIG. 3. Deformation contribution at various temperatures to the total F-center concentration (shaded areas) in NaCl crystals deformed 2.86% in compression. At 196°K and 78°K deformed and undeformed crystals color at the same rate.

at temperatures ranging from 78°K to room temperature. Here $\dot{e}$ is the rate of liberation of electrons, C is a constant of the order of unity, and E is an activation energy with a value of about 0.05 ev. However, data taken at liquid helium temperature show that Eq. (5) does not hold when the temperature approaches absolute zero.

In any event, it has been shown that a qualitative description of the rate of growth of F centers as a function of temperature, which agrees with experimental results, can be obtained by assuming that only a single type of F center exists. A large concentration of F centers can be obtained in a moderate time interval by x irradiating at a temperature somewhere between 78° and 298°K. It is this temperature region which produces the optimum balance between growth rate and bleaching rate. This phenomenon could not have been detected simply by examining the F-center growth curves at 78° and 300°K (for example, see Fig. 2).

F-Center Generation in Deformed Crystals

The dislocation internal friction experiments mentioned in the introduction suggest that F centers are formed at dislocations during x irradiation even at liquid helium temperature, but that enhanced colorability is suppressed at low temperatures because the F centers are unable to diffuse into the bulk of the crystal. Once the behavior of the undeformed crystals is known at various temperatures, the enhanced colora-

bility produced by deformation can be obtained by repeating the growth curve experiments, this time using crystals cleaved from a deformed block of NaCl.

The rate of coloration during x irradiation at low temperatures was found to be identical for both lightly deformed and undeformed crystals but a large additional increase of the F-center concentration was observed in the deformed crystals as the irradiation temperature approached room temperature. This observation shows conclusively that the enhanced colorability of the deformed crystals does not arise from excess vacancies generated during the deformation process. Figure 3 shows the F-center growth curves for both deformed and undeformed NaCl crystals at various temperatures. The shaded areas represent the dislocation contribution to the F-center concentration.

An increase in the dislocation density due to deformation should only affect k_v as it has been shown that n_0 remains unchanged during deformation. Hence, the additional colorability of the deformed crystals must be due to that part of Eq. (3) which contains k_v. At high temperatures the dislocation contribution to the F-center concentration should be approximately linear (as $k_B + k_C$ is large), while at low temperatures the exponential term will be affected by the presence of dislocations and a deviation from linearity would be
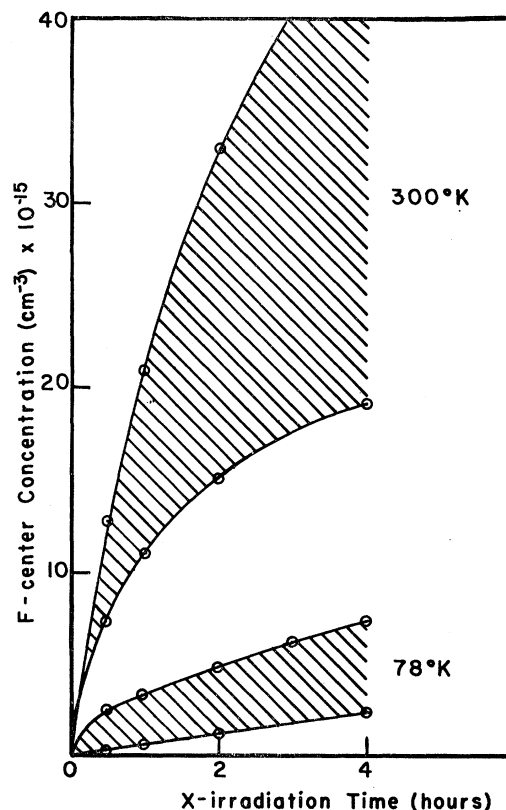

FIG. 4. Deformation contribution to the total F-center concentration (shaded areas) in NaCl crystals deformed 14% in compression.

expected. By taking the difference between the curves, for a given temperature, from Fig. 3 it can be seen that the dislocation contribution does start out linearly. The fact that the high temperature (300°K) of Fig. 3 gives the most prolonged linear relationship can be taken as qualitative evidence that a linear F-center growth should predominate after the exponential term has saturated. The present data do not extend to long enough time to successfully test this prediction.

Figure 3 clearly shows that the dislocation-enhanced coloration only becomes appreciable at temperatures where dislocation pinning by x irradiation becomes irreversible.[17] It is apparent that dislocations do play an active role in the production of F centers in NaCl at room temperature. At lower temperatures, either dislocations no longer act as potential sources of vacancies or diffusion confines the migration of these vacancies to the immediate vicinity of the dislocations, the latter possibility being indicated by the dislocation damping experiments. To distinguish between these possibilities by optical measurements, the percentage of the volume of the crystals near dislocations would have to be enlarged in order to magnify the effects so that they can be observed directly. The simplest way this can be accomplished is to substantially increase the dislocation density, Λ.

It is possible to make a rough calculation of the percentage of the total volume of a crystal that is within a given radius, r, of a dislocation. If V_T is the total volume of the crystal and $V(r)$ is the volume located within a distance r of a dislocation, then

$$100V(r)/V_T = 100\pi r^2 \Lambda, \qquad (6)$$

provided that $V(r) \ll V_T$. If $r = 50$ A, the volume near a dislocation in an undeformed crystal will be about 0.000 01% of V_T. Even for a 3% deformation the value will only be about 0.001%. Only when Λ approaches
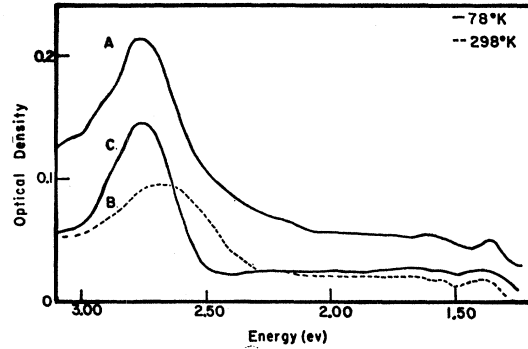
FIG. 6. Shape of the absorption spectrum of a 15% deformed NaCl crystal after (A) x-irradiation at 78°K, (B) warmup to room temperature, (C) recooling to 78°K.

10^{10} cm^{-2} will the volume near a dislocation begin to become detectable.

An attempt was made to obtain deformed crystals which might have dislocation densities large enough to show a contribution to F-center production even at low temperatures. Two crystals were cleaved from a block of NaCl which had been compressed 14% under water. One crystal was x irradiated at 300°K and the other at 78°K. The F-center growth curves for these two crystals compared to curves for two undeformed samples are shown in Fig. 4. Although the growth rates are larger for the 300°K curves, the relative dislocation contribution is less, at least in the early stages. In other words, the heavily deformed crystals become more structure sensitive at low temperatures. This is in contrast to the observations reported by Rabin and Klick[10] who found that the coloration of NaCl crystals became less structure sensitive as the temperature of irradiation was lowered.

To ascertain whether the effect of large deformation can influence the rate of F-center generation at still lower temperatures, an NaCl crystal, deformed 15% in compression, was x irradiated at 10°K and its F-center growth rate compared with the two 78°K curves of Fig. 4. The results are shown in Fig. 5. It is apparent that the enhanced colorability is still present even for irradiation at 10°K. In fact, it seems that the enhancement is about equal to that observed at 78°K.[18]

There are two possible explanations for the structure sensitivity of the low-temperature coloration of the heavily deformed crystals. The formation of F centers at dislocations may be contributing to the optically observed coloring or the very heavy deformation may have generated a large vacancy concentration which is thereby increasing the amount of rapid-type coloration. Evidence has not been obtained in the present experiments to distinguish positively between these two possibilities. The following observations on the shape of the F band support the first hypothesis: The x irradiation of heavily deformed crystals at low temperature causes some broadening of the F band as shown in Fig. 6.
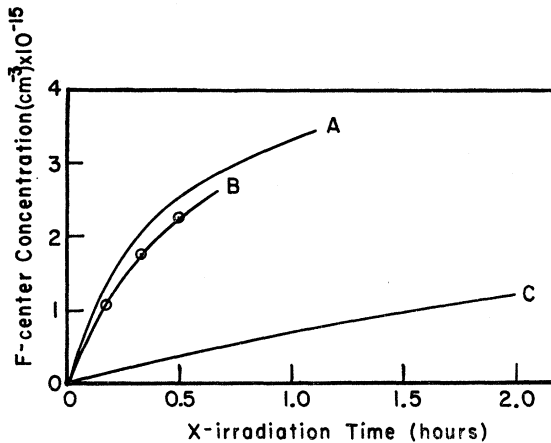

FIG. 5. F-center growth rate in: (A) NaCl specimen deformed 14% and x-irradiated at 78°K, (B) NaCl crystal deformed 15% and x-irradiated at 10°K, (C) an undeformed NaCl crystal x-irradiated at 78°K.

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[17] As reported in reference 13, this is approximately 250°K.

[18] Curves A and C are the same curves shown in Fig. 4 for 78°K.

This would be expected if, because of suppressed diffusion, it were difficult for the F centers to escape from the strain fields of dislocations at which they were formed. If this hypothesis is correct, warmup to room temperature after irradiation should cause the F band to return to its normal width. As shown in Fig. 6, the F band does appear to narrow during a room-temperature anneal in a manner compatible with the above discussion. It is possible, however, that subsidiary absorption bands, which lie beneath the F band, contribute to the broadening and anneal at room temperature. It was also observed that a section of the same heavily deformed crystal, when x irradiated at room temperature, shows no excess F-band broadening.

CONCLUSION

The optical absorption experiments performed at various temperatures agree with the prediction of the dislocation pinning model, developed from internal friction experiments, that edge dislocations always act as sites for vacancy formation during x irradiation. When the temperature is below that needed for diffusion of F centers, and the dislocation density is of the magnitude ordinarily present in rock salt, the dislocations are unable to enhance the optically observed F-center growth rate. The transition temperature between the passive and active role of dislocations in the generation of color centers falls at about $250°K$ for NaCl.

In general, the present experiments indicate that bulk

F centers are formed at all temperatures either from vacancies already present or by a mechanism such as that proposed by Rabin and Klick. All aspects of the Rabin and Klick interstitial mechanism, which is the only effective source of additional vacancies at low temperatures, are compatible with the ideas presented here. However, as the temperature is increased the interstitial mechanism either stops or becomes relatively ineffective and the dislocation mechanism becomes active. The present experiments also emphasize a well-known but often overlooked fact: When F centers are located in the strain field produced by imperfections (mainly edge dislocations), they no longer retain the characteristic properties of F centers, i.e., their characteristic absorption band is displaced.

Mitchell, Wiegand, and Smoluchowski[9] have concluded from their analysis of the growth rate of F centers in crystals deformed up to 3% that the initial, deformation sensitive portion of the F-center growth curves is due to an additional concentration of vacancies created during the deformation process. If this were the correct description, it would be expected that the deformation contribution would be observed at all temperatures of irradiation. The present optical absorption measurements do not substantiate this type of behavior. A strong temperature dependence of the deformation contribution to F-center concentration is observed as shown in Fig. 3. This strongly suggests that the excess vacancies are formed during the irradiation.

Interaction of Antiferromagnetic Spin Waves with a Bloch Wall*

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The interaction of an antiferromagnetic spin wave with a 180° Bloch wall is studied from the theoretical point of view. Our formulation includes the anisotropy and exchange energies of the crystal together with the characteristics of the wall such as its stiffness and viscosity. The anisotropy is assumed to be of a general orthorhombic form. We show that there exists a bound wall excitation branch as well as a free spin-wave excitation branch, and we derive a restrictive set of relationships between the excitations on two different sublattices. Further, we show that there exist special values of the energy for which the spin waves are degenerate and the restrictions no longer apply. Finally, we determine the change of phase of the spin waves on passing through the Bloch wall as a function of the wavelength, demonstrate that the phase change decreases as the wavelength increases, and compare our results with those of the analogous ferromagnetic case.

I. INTRODUCTION

THE existence of antiferromagnetic domains has been experimentally demonstrated both by neutron and optical studies.[1] These domains usually arise from ordinary crystal imperfections such as dislocations,

grain boundaries, and crystallographic twins (see Fig. 1). Within these domains, it is possible to excite antiferromagnetic spin waves. It is the purpose of this paper to determine the effect of the domain wall on the transmission of antiferromagnetic spin waves from one domain to another. The analogous ferromagnetic case has been considered by Boutron[2] and by Winter.[3]

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[1] W. Roth, J. Appl. Phys. **31**, 2000 (1960).
[2] F. Boutron, Compt. rend. **252**, 3955 (1961).
[3] J. M. Winter, Phys. Rev. **124**, 452 (1961).