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F-Center Production Efficiencies at Liquid-Helium Temperature*

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The efficiencies for *F*-center production (eV/*F* center) have been measured at liquid-helium temperature for KBr, KCl, LiF, and NaCl irradiated with 2.0-MeV electrons from a Van de Graaff generator and with x rays from a tungsten-target beryllium-window x-ray tube. Special dosimetric techniques were developed to measure the energy absorbed by the samples. The *F*-center production efficiencies for easily colored alkali halides are typically of the order of 5000 eV/*F* center for Van de Graaff irradiation, decrease to about 1800 eV/*F* center for 50-kV x-ray irradiation and then rise again to about 5000 eV/*F* center for 10-kV x-ray irradiation. NaCl follows the same general trend but is about six times as hard to color. Irradiations of KBr with x rays whose energies are just above or just below the *K* absorption edge of bromine indicate that the *K* edge does not play a dominant role in the coloration process. These results are discussed in relation to proposed mechanisms for the coloration process, and various quantitative and qualitative arguments are presented which indicate that inner shell ionization does not adequately account for either the magnitude of the observed vacancy production or the direction of its energy dependence. A correlation is made between the coloration efficiency and the ionization density along the tracks of the electrons generated by irradiation. It is concluded that mechanisms involving the single ionization of two adjacent halide ions are a more probable cause of the coloration than mechanisms involving either the single ionization of one halide ion or the multiple ionization of one halide ion. A calculation of the yield to be expected for this group of mechanisms is in reasonable agreement with experiment.

I. INTRODUCTION

An understanding of the formation of color centers in alkali halides by ionizing radiation involves two basic questions: First, what is the nature of the defect leading to a particular optical absorption band in an irradiated crystal; second, how is the energy of the absorbed ionizing radiation utilized in the production of a particular lattice defect? At room temperature one is faced with a rather complicated array of centers, many of which have not been correlated with a specific lattice defect. In addition, the coloration processes at room temperature are strongly structure sensitive, depending upon the presence of defects or impurities initially in the crystal prior to irradiation.[1,2] At temperatures near that of liquid helium the situation is considerably simplified. The nature of the dominant centers formed has been well established and the coloration has been demonstrated to be an intrinsic property of the perfect crystal lattice, showing none of the structure sensitivity present at room temperature.[3] Thus, at low temperature one can proceed more easily, perhaps, to a quantitative consideration of the mechanism of formation of the centers. That is, how is the energy which has been deposited in the crystal by ionizing radiation utilized in the formation of color centers?

The basic effect of ionizing radiation at low temperature appears to be the creation of an interstitial halogen atom leaving a vacancy in the lattice.[4,5] The *F* and *H* centers formed in this Frenkel-defect process are complimentary in that their recombination restores the perfect lattice. In addition, Klick and Patterson[6] have recently proposed that the alpha center,[7,8] the other prominent product of low-temperature irradiation, also arises from the same act of creation of Frenkel pairs in the pure lattice. The production of an interstitial halogen atom requires a transfer to the atom of both energy and momentum. In the case of low-energy x rays, which act through the photoelectrons they generate in the material, very little momentum is transferred directly to the halogen atoms, much less than would account for the experimentally measured defect production efficiencies. One must look, therefore, for a different, more indirect sort of displacement mechanism.

Several mechanisms of defect formation in alkali halides by ionizing radiation have been proposed by various authors.[1,5,9–14] In general, they involve the transfer of energy to the electronic system of the atom, and then its displacement to an interstitial position as a result of its altered electronic environment. These mechanisms may be divided into the following groups involving: (A) The *single ionization* of *one isolated halide ion*, or (B) the *multiple ionization* of *one isolated halide ion*, or (C) the *single ionization* of *two adjacent halide ions*.

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* A portion of this work was submitted to the faculty of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science (1962).

[1] F. Seitz, Rev. Mod. Phys. **23**, 328 (1951).

[2] H. W. Etzel and J. G. Allard, Phys. Rev. Letters **2**, 452 (1959).

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[4] W. Kanzig and T. O. Woodruff, Phys. Chem. Solids **9**, 70 (1958).

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[6] C. C. Klick and D. A. Patterson, Phys. Rev. **130**, 2169 (1963).

[7] H. Ruchardt, Phys. Rev. **103**, 873 (1956).

[8] H. Ruchardt, Z. Physik **140**, 547 (1955).

[9] D. E. McLennan, Can. J. Phys. **29**, 122 (1951).

[10] J. H. O. Varley, Nature **174**, 886 (1954); and J. Nucl. Energy **1**, 130 (1954).

[11] R. L. Platzman, in *Symposium on Radiobiology*, edited by J. J. Nickson (John Wiley & Sons, Inc., New York, 1952), Chap. 7.

[12] R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 1406 (1961).

[13] F. E. Williams, Phys. Rev. **126**, 70 (1962).

[14] F. Seitz, Phys. Rev. Letters **7**, 282 (1961).

An example of a mechanism in group A is that proposed by McLennan[9] in which the single ionization of a halide ion leads to a neutral atom which can then move off to an interstitial site under the temperature vibrations of the lattice. Presumably, at low temperature the movement of the neutral atom would be aided by the lattice agitation induced by the change in charge distribution. Alternatively, if the atom recaptures the electron before it diffuses away from its lattice site, the energy released by the recombination might induce the generation of vacancies by some exciton process.[14,15] A mechanism has also been proposed recently by Williams[13] in which momentum is acquired by a negative halogen molecule ion after the single ionization of a halide ion in the lattice. This momentum might then lead to separation of the molecule ion and the vacancy to produce Frenkel defects in the lattice.

Many workers have proposed mechanisms involving the multiple ionization of one isolated halide ion, i.e., mechanisms listed as group B. Varley[10,16] experimented with the fast electron irradiation of alkali halides and showed that a displacement collision model based on Rutherford scattering was insufficient to account for the coloration produced. He then proposed a mechanism in which a halide ion is multiply ionized in a single electron impact to form a *positive* ion. The strong repulsion caused by the six nearest-neighbor alkali ions then ejects the positive ion to an interstitial site. This leads to F and H centers which are separated from each other by several interatomic distances, a result consistent with paramagnetic resonance studies of these centers.[4] Various critiques of the Varley mechanism have been made by other workers.[17–19,12] A mechanism applicable to a variety of systems was suggested in 1950 by Platzman[11] who pointed out that disordering of a solid was possible even by low-energy electrons through the Auger effect. In this mechanism an inner-shell ionization is followed by an Auger cascade in which the atom is multiply ionized and a relatively large amount of energy is communicated to a small region of the solid. Frenkel-defect pairs could then be generated in this perturbed environment by some unspecified mechanism.[20] Models for color-center formation have been proposed by Klick,[5] by Howard *et al.*,[12] and by Williams[13] to avoid the objections to the Varley mechanism raised by Dexter.[19] Howard, Vosko, and Smoluchowski[12] have proposed a mechanism for KCl in which a positive chlorine ion, formed by multiple ionization, and a negative chlorine ion initially attract each other, and the two then interact through an exchange deexcitation interaction to form two neutral chlorine atoms. This transition produces about 3 eV of kinetic energy which might displace one of the chlorine atoms to an interstitial position if a series of focused collisions occurs.

Several mechanisms proposed recently[5,13] involve the single ionization of two adjacent halide ions, either directly by the ionizing radiation or indirectly from a doubly ionized halide ion capturing an electron from an adjacent halide ion. Thus these mechanisms can be classified in both groups B and C listed above. Klick[5] has suggested that the double ionization of a single halide ion or the single ionization of two adjacent halide ions leads to the formation of a small neutral halogen molecule which fits easily into one of the sites previously occupied by halide ion. The jump of a neighboring halide ion into one of the vacancies then might lead to a separated Frenkel-defect pair. Most recently, Williams[13] has suggested that the creation of two halogen atoms at adjacent halide ion sites, can lead to the formation of Frenkel pairs. In this model two negative halogen molecule ions are formed, each of which acquires momentum from interaction with the asymmetric crystalline field. "Billiard ball" collisions concurrent with tunneling of the positive hole then leads to separation of the halide vacancy and the molecule ion.

The experiment to be reported here was undertaken to try to determine which, if any, of the general classes of mechanisms listed previously was the most likely source of color-center formation in alkali halides at low temperature. The yield of these mechanisms would be expected to vary in different ways as the energy of the electrons generated in the material by irradiation was varied. Accordingly, comparisons of vacancy-production efficiencies were made for irradiations performed at liquid-helium temperature with high-energy electrons from a 2.0-MeV Van de Graaff and with low-energy x rays (hence, electrons) from a beryllium-window tungsten-target x-ray tube.

II. EXPERIMENTAL TECHNIQUES

A. Selection of Crystals

The following alkali halides were chosen as being particularly interesting to study: KBr, KCl, LiF, and NaCl. KBr was chosen as a typical alkali halide whose coloration properties have been studied by several workers.[21,3] In addition, the K-shell absorption edge in bromine is at an energy that permitted the use of the available x-ray tube to irradiate the crystal with x rays whose energies were all above or below the K edge. KCl

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[15] The generation of vacancies at low temperature by an exciton process would appear unlikely in view of the work of Inchauspe and Chiarotti (unpublished work) who found that no F or H centers were generated in KBr irradiated with uv light. Exciton-induced F-center growth at room temperature has been reported by J. H. Parker, Phys. Rev. **124**, 703 (1961) but not for the second stage of coloration that presumably is characterized by the formation of vacancies.

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[17] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1946), Vol. 2, p. 447.

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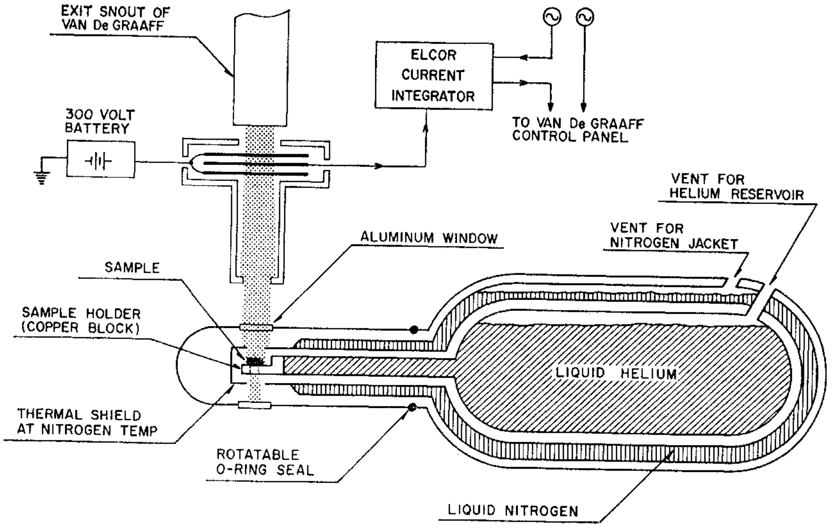

FIG. 1. Schematic of the helium Dewar used for the 2.0-MeV electron irradiations. The ionization chamber directly under the Van de Graaff exit snout was used to automatically terminate the irradiation after a preset dose was delivered to the sample.

and LiF were chosen because they have attracted considerable theoretical attention.[12,19,20] NaCl was chosen as one of the typically "hard-to-color" alkali halides observed by Rabin and Klick.[3]

Single crystals obtained from the Harshaw Chemical Company were cleaved along their principal planes with a razor blade. All the specimens of a particular alkali halide were cleaved from the same large source crystal to ensure uniform composition of the samples. Rabin and Klick have shown that the coloration efficiency at helium temperature is relatively insensitive to impurity content, but the above procedure was adopted as a precautionary measure. The crystals were cleaved into pieces approximately 8 mm square and of various uniform thicknesses. A list of the crystal thicknesses for the x ray and Van de Graaff irradiations is given in Table I. Two criteria were used in selecting the thickness for a particular alkali halide exposed to a particular irradiation energy. First, the crystal had to be thick enough to permit accurate measurement of the energy absorption with the available dosimetry systems. Second, the crystal had to be of a thickness that would provide a narrow well-defined energy spectrum of absorbed x rays or electrons. This would sharpen any possible energy dependence of the coloration process and facilitate any theoretical calculations that might be made. The requirement for a narrow absorbed-energy spectrum usually required that the crystals absorb as small a fraction of the incident radiation as possible. Thus, the requirements for the dosimetry systems and for narrow spectral distributions were directly opposed, and in practice some compromise was made between them.

TABLE I. Summary of crystal thicknesses, in inches.

Material	2.0-MeV electrons	50-kV x rays, 1-mm Al	50-kV x rays, unfiltered	15-kV x rays	10-kV x rays
KBr	0.015	0.010	0.008	0.010	0.009
KCl	0.021	0.009	0.008	···	0.022
LiF	0.027	0.046	0.035 0.350	···	0.075
NaCl	···	···	0.071	···	0.025

B. Irradiation Techniques

1. X-Ray Irradiations

The stainless-steel Dewar used for the x-ray irradiations was similar to the ones used by previous workers.[3] Optical measurements were made during periodic interruptions of the x-ray exposures at the same temperature as the irradiation temperature. The Dewar was moved to a Cary model 14MR recording spectrophotometer (Applied Physics Corporation) for these measurements. A germanium resistance thermometer indicated that the sample holder was at about 5.1°K. X-ray irradiations were performed with a Machlett OEG 60 tungsten-target, beryllium-window x-ray tube energized by a three-phase full-wave rectified power supply with about 5% ripple. This essentially constant potential power supply facilitated calculation of the spectral distribution of emitted x rays. The x-ray tube and power supply were inherently stable so that no special stabilization circuits were required to ensure reproducible (±1%) x-ray doses to the samples.

2. Van de Graaff Irradiations

The Naval Research Laboratory 2.0-MeV Van de Graaff generator provided an intense electron beam directed vertically downward. The stainless-steel Dewar described above could not be used with this machine since it was designed for operation in a vertical position during irradiation and subsequent measurements in the spectrophotometer. A glass Dewar designed for operation in a horizontal position under the Van de Graaff and in a vertical position in the spectrophotometer was available, however, and was used for the high-energy electron irradiations. The arrangement of this Dewar under the Van de Graaff is shown schematically in Fig. 1. The beam intensity available from the Van de Graaff was far greater than that available from the x-ray tube. It was considered desirable to adjust the beam current of the Van de Graaff so that the rate of energy deposition in the sample was the same as for the x-ray runs. Any gross differences in sample heating could be eliminated by this technique. Difficulty was encountered in delivering determinate doses to the sample on successive runs at these low-beam currents because of fluctuations in the machine output. The transmission monitor chamber shown in Fig. 1 was designed to monitor this rather erratic output during irradiations. The electron beam from the accelerator passed through the monitor chamber's three 0.0005-in.-thick aluminum electrodes and then through a 0.005-in.-thick aluminum window in the Dewar. The output of the chamber was fed to a current integrator (Elcor Corporation), which indicated the instantaneous current as well as the total charge accumulated during an exposure. The integrator was connected so that it automatically cut off the Van de Graaff when a certain preset charge was reached. The reproducibility of successive doses delivered to the sample with this system was better than 0.1%.

C. Measurement of Energy Absorption

1. *X-Ray Irradiations*

The measurement of the energy absorbed by an alkali halide crystal exposed to a plane parallel x-ray beam falls naturally into two separate operations: First, a measurement of the beam intensity (eV/cm^2-sec) incident upon the sample is made; second, the fraction of this incident intensity that is absorbed by the sample is determined. These two measurements may be done with completely different techniques if desired. The intensity of an x-ray beam at some point of interest may be measured by the *total* absorption of the x rays arriving there, using as the absorber some material which changes in a measurable way as a known function of the energy absorbed per unit area. Examples of standard well-understood dosimeters are the calorimeter, in which the absorbed radiation causes a rise in temperature of the absorber, and the Fricke ferrous sulfate solution dosimeter in which the absorbed radiation causes a change in the chemical composition of a solution. These dosimetric systems are difficult to use, however, in the sample holder geometry of the Dewars used in this experiment. One can avoid this difficulty by using a different dosimetric system, such as the radiation-induced darkening of glass, which is more adaptable to the Dewar geometry. This sort of dosimeter need not be absolute in itself since it can be calibrated against one of the previously mentioned standard dosimeters, i.e., the Fricke dosimeter in this experiment. In addition it should be pointed out that there is no convenient way to use a dosimeter directly to measure the energy absorbed by the crystal during an irradiation at liquid-helium temperature. The conditions of the irradiation can be re-established at a later time, however, when the Dewar and sample are at room temperature. The dosimetry can then be performed under more tractable conditions.

Rabin and Klick[3] and Ritz and Cheek[22] have used glass-block dosimeters to measure the intensity of low-energy x-ray beams and to determine the fraction of the incident intensity absorbed by thin alkali halide crystals. These blocks ($1\times1\times0.3$ cm thick) are made of a silver-activated metaphosphate glass developed by Schulman *et al.*[23] Irradiation with ionizing radiation induces an optical absorption band which encroaches upon the visible part of the normally transparent spectrum. This absorption causes the block to turn brown. The change in coloration when the x-ray beam is totally absorbed in the block can then be used as a measure of the intensity of the incident radiation.

One must know the relationship between the radiation-induced coloration of the blocks and the energy absorbed by the blocks. This was done in the present experiment by calibrating the blocks against the Fricke ferrous sulfate solution dosimeter.[24] The x-ray beam was collimated by a diaphragm of known cross-sectional area and totally absorbed in oxygenated ferrous sulfate solution. The radiation oxidized the ferrous sulfate and the resulting ferric ion concentration was determined by measurements on the solution at 304 mμ in the thermostatted cell of a Beckman model DU spectrophotometer. A knowledge of the "G value" (the number of ferric ions formed per 100 eV absorbed by the solution) then permitted a computation of the energy absorbed by the solution.[24] The placement of a glass block in the plane of the diaphragm under identical x-ray exposure conditions and a measurement of its radiation-induced change in optical density yielded a quantitative relation between the coloration of the block and the beam intensity derived from the ferrous sulfate measurements. The blocks were calibrated in this fashion for each of the different x-ray conditions used in the experiment, i.e., 10-, 15-, and 50-kV exciting potentials with inherent filtration (1.5-mm beryllium) and 50 kV with an added 1 mm of aluminum filtration.[25]

The intensity impinging upon a sample in the Dewar was determined by replacing the crystal with a glass-block dosimeter. The fraction of this incident intensity absorbed by an alkali halide crystal was then measured

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[22] V. H. Ritz and C. H. Cheek (to be published).

[23] J. H. Schulman, C. C. Klick, and H. Rabin, Nucleonics **13**, 33 (1955).

[24] Natl. Bur. Std. (U. S.) Handbook 78 (1961).

[25] This calibration indicated that Rabin and Klick (Ref. 3) underestimated the energy absorbed by the alkali halides used in their experiment by approximately 70% as a result of the assumption that the energy required to produce a given level of coloration in the blocks was the same for both Co^{60} γ rays and low-energy x rays (see Ref. 22).

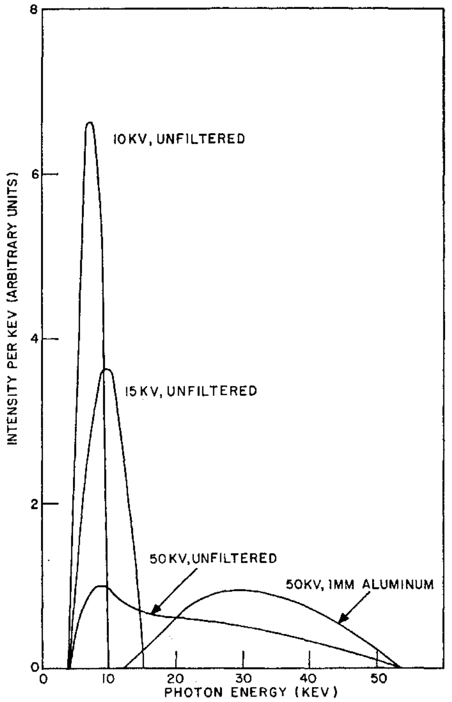

FIG. 2. Spectra of the beryllium-window x-ray tube for various exciting potentials and filtrations. The spectra have been normalized so that the areas under each curve are equal.

by irradiating another block with the sample interposed between the block and x-ray tube target. The difference in the reading of these two blocks yielded the fraction of the incident intensity absorbed by the crystal.[3]

An alternate method of measuring the fraction of the incident intensity absorbed by the sample is to calculate it from theory. This method has the advantage of also yielding the spectral distribution of the x-ray energy absorbed by the crystal, information which is necessary for a comparison of the experimental results with theory.[20] This calculation requires a knowledge of the spectral distribution of the x rays incident upon the sample and of the thickness and energy-transfer coefficients of the sample.[26]

X-ray emission spectra under 50-kV excitation have been measured by Ehrlich[27] for a tungsten-target beryllium-window tube similar to the Machlett OEG-60. Her paper also presents a method of calculating the emission spectra by theoretical means. One uses the spectrum generated by the thin-target theory of Sommerfeld and corrects it for electron backscattering from the target, and for self-absorption of the bremsstrahlung in the target. The methods of Ehrlich were applied here to generate x-ray tube emission spectra for exciting potentials of 10 and 15 kV. The spectra are shown in Fig. 2. The 50-kV spectrum filtered with 1 mm of aluminum was derived from Ehrlich's experimentally measured 50-kV unfiltered spectrum by straightforward application of the exponential absorption law. The comparatively narrow distributions of the 10- and 15-kV x rays are the result of the strong absorption by the beryllium window which cuts out almost all photons with energies of less than 5 kV. Both the experimental and calculated spectra are approximations to the actual physical situation since some fine structure (i.e., the *L* absorption and emission lines of the tungsten target) was not resolved by the scintillation spectrometer[28] or included in the calculation presented here (e.g., the *L* emission line). This approximation was felt to be adequate in view of the uncertainties in the *F*-center production mechanism calculations to be considered here.

The spectral distributions of the x-ray energy *absorbed* by the KBr crystals of Table I, when exposed to the incident spectra of Fig. 2, are shown in Fig. 3. Note that in one of the irradiations (50 kV, 1 mm aluminum) all of the x-ray energy is in the spectral-energy region above the *K* edge of bromine, and for another (10 kV, unfiltered) all of the energy is concentrated between the *K* and *L* edges. In Fig. 4 distributions are shown for the x rays absorbed in LiF. An additional very thick crystal of LiF was used in the 50-kV unfiltered x-ray efficiency runs. The spectral distribution for this crystal (10 times as thick as the other one exposed at this energy) is shown as the dashed curve

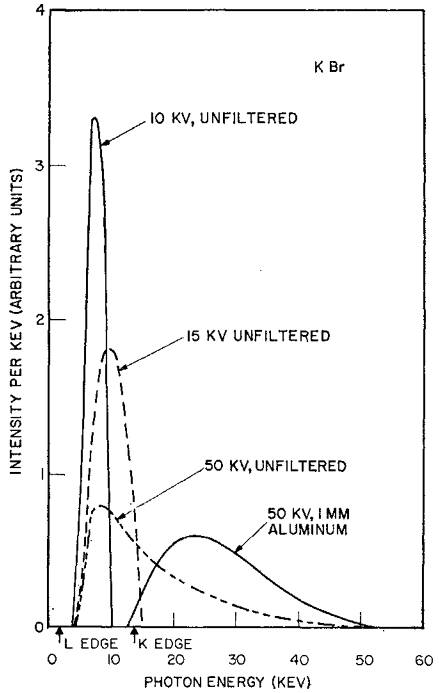

FIG. 3. Spectra of the x rays absorbed by the KBr crystals used in the experiment. The areas have been normalized as in Fig. 2. The *K* and *L* absorption edges of bromine are indicated by arrows on the abscissa.

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[26] R. T. Berger, Radiation Res. **15**, 1 (1961).

[27] M. Ehrlich, J. Res. Natl. Bur. Std. **54**, 107 (1955).

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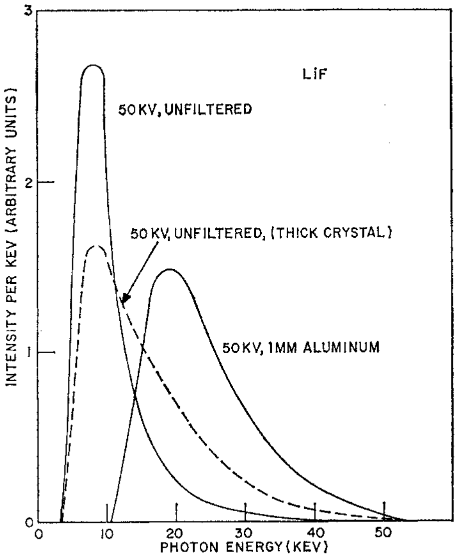

FIG. 4. Spectra of the x rays absorbed by LiF crystals used in the experiment. The spectra have been normalized as in Fig. 2.

in Fig. 4. These spectra illustrate that a significant change of the spectral distribution in the crystal can be caused by a variation of the crystal thickness as well as by varying the energy of the incident x-ray beam. The thicknesses of the alkali halides used for the 10- and 15-kV x-ray irradiations were chosen so as to totally absorb the beam. The spectral distributions of x rays absorbed by the crystals for these radiation qualities are therefore the same as the distributions shown in Fig. 2 for the incident x rays.

The uncertainties in the absolute calibration of the glass-block dosimeters involved the following: area of the defining diaphragm and timing error, 0.5%; "*G* value" for the ferrous sulfate solution dosimeter in this x-ray energy range, 3%; ferrous sulfate concentration determination, 0.5%; optical density measurements on the blocks, 0.5%. Combining these as random errors one obtains 1.1% as the probable error in the calibration of the blocks. For cases in which the crystals absorbed the entire x-ray beam, an additional uncertainty of 0.5% was involved in the intensity determination in the Dewar. Crystals which absorbed a fraction of the beam (10–80%) involved an additional dosimeter reading which introduced 2–5% uncertainty. Thus the probable error in the energy absorption measurements was less than 6%.

The fraction of the intensity absorbed by crystals as calculated from the x-ray spectra was generally within about 15% of that measured by the blocks. This agreement is more of a reflection on the adequacy of the x-ray spectra than on the accuracy of the glass-block dosimeters. The dosimeters were used as the basis for the vacancy-production efficiencies presented in this paper. The reasonable agreement of the results derived from calculations involving the x-ray spectral distributions and those obtained by the glass-block dosimeters indicates that the spectral distributions of Figs. 2–4 are not grossly in error.

2. *Van de Graaff Irradiations*

The dosimetric techniques used to determine the amount of energy absorbed (eV/cm^2) by the alkali halides exposed to 2.0-MeV electrons were similar to those used for the x-ray irradiations. The measurements again required a knowledge of two things: the intensity of the electron beam incident on the sample, and the fraction of this intensity that was absorbed by the sample.

The intensity incident upon the sample was measured with the glass-block dosimeters[22] by re-establishing the conditions of the irradiation at room temperature after the sample irradiation was completed. The glass block was placed in the sample position of the Dewar shown in Fig. 1. The blocks were calibrated against a Faraday cup to determine the relationship between their coloration and the absorbed energy. The electron beam was passed through a defining diaphragm into a Faraday cup. The current from the cup was measured by means of vibrating-reed electrometer employed in a Townsend null circuit. The voltage produced on an accurately calibrated ($\pm 0.1\%$) polystyrene dielectric capacitor was balanced by a calibrated potentiometer ($\pm 0.1\%$). This measurement determined the electron flux (electrons/cm^2-sec) at the plane of the diaphragm. The voltage on the Van de Graaff (and hence the electron energy) was known to about $\pm 1\%$ by calibration with the Be(γ,n) reaction. Thus the beam intensity could be determined in eV/cm^2-sec at the plane of the diaphragm. Placement of a glass-block dosimeter in the plane of the diaphragm then served to calibrate its response. A correction ($\approx 5\%$) was made for the energy carried off from the block by backscattered electrons and bremsstrahlung.[29,30]

A cross check on the absolute accuracy of the calibration of the blocks for 2.0-MeV electron irradiations was made by irradiating blocks in a Co^{60} gamma-ray source. The spectrum of electrons generated in the blocks by Co^{60} gamma rays is similar to that produced by 2-MeV electrons, so that the coloration efficiency of the blocks should be the same for these two irradiations. A source at the Naval Research Laboratory has been calibrated with a graphite ionization chamber and the Fricke dosimeter to an absolute accuracy of 1%.[31] The energy absorbed by blocks placed in this gamma-ray field was calculated by the methods described in N.B.S. Handbook 78.[24] A correction of 4% was applied to the blocks for the additional energy deposited in them by low-energy scattered gamma rays present in the source.[31]

In summary, the Van de Graaff calibration of the

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[29] R. H. Schuler, in *Proceedings of the Second Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), Vol. 21.

[30] K. A. Wright and J. G. Trump, J. Appl. Phys. **33**, 687 (1962).

[31] V. H. Ritz and F. H. Attix, Radiation Res. **16**, 401 (1962).

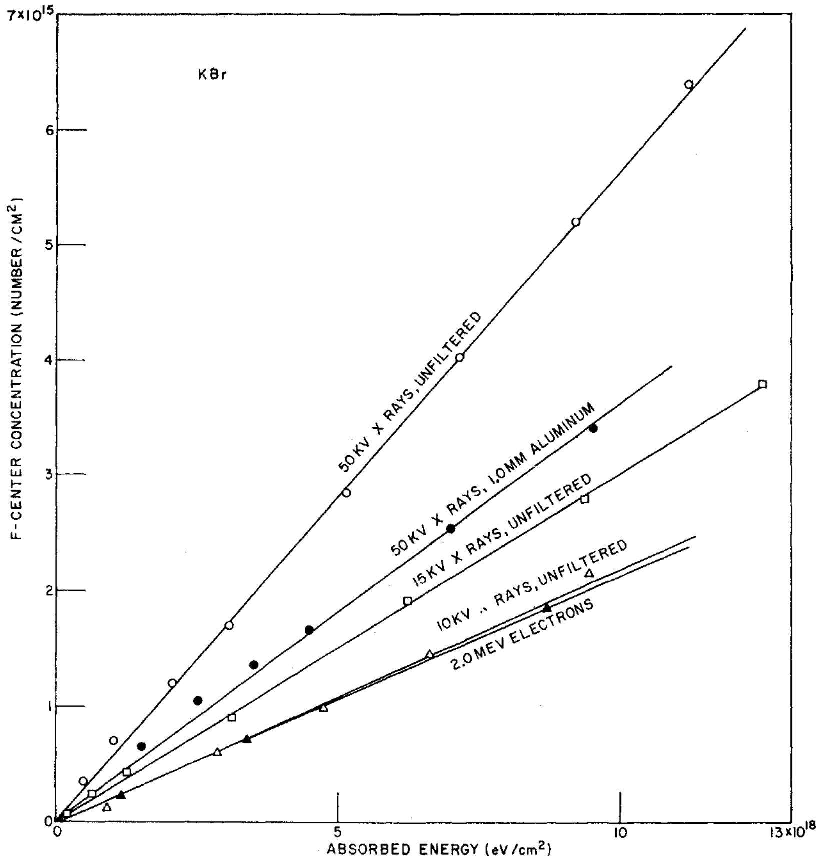

Fig. 5. Growth of the *F* band in KBr as a function of absorbed energy for various radiations.

blocks involved the energy of the incident electrons, the proper operation of the Faraday cup to measure the incident flux, and the corrections for backscatter. The Co^{60} calibration of the blocks involved the source calibration in roentgens per unit time and the use of appropriate conversion factors and corrections to determine the energy absorption in the blocks. The Van de Graaff and Co^{60} gamma-ray calibrations of the blocks agreed to within 4%, indicating that the calibration procedures were valid and accurate.

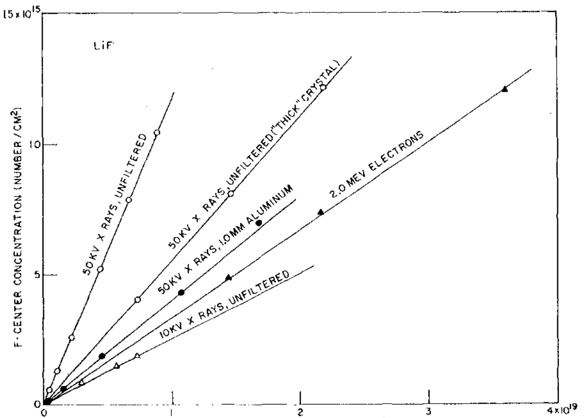

Fig. 6. Growth of the *F* band in LiF as a function of absorbed energy for various radiations.

The fraction of the incident radiation that was absorbed by the alkali halide crystals was measured by the same glass-block dosimeter substitution method that was used for the x-ray irradiations, i.e., blocks were exposed with and without an interposed sample. The backscatter corrections were applied to these measurements to compensate for the different backscatter characteristics of the alkali halides and the dosimeters.

An alternate method of determining the energy absorbed by the samples is to measure the incident electron beam intensity (eV/cm²-sec) and then to make use of a "depth-dose" curve to determine the fraction P of the incident intensity that is absorbed by the sample. The depth-dose curves can be expressed for low-atomic-number materials[32] in terms of a generalized sample thickness:

$$R=\frac{\rho L N_A}{E}\sum_i f_i\left(\frac{Z}{A}\right), \tag{1}$$

where ρ is the density (g/cm³), L the thickness (cm), N_A the Avagodro's number, E the initial electron energy (MeV), f_i the fraction by weight of each element, Z the

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[32] C. H. Cheek and V. Linnenbom, N.R.L. Report 5448, 1960 (unpublished).

atomic number, and A the atomic weight. The above treatment must be modified for high-atomic-number materials in which an appreciably greater amount of electron scattering takes place in the material. This increases the path of the electrons in the sample and results in a larger absorption of the incident-electron energy than would be expected from Eq. (1) and the depth-dose curves. A correction for this increased path length due to scattering can be made[33] using the theory of Yang.[34] The value of R calculated from Eq. (1) is multiplied by the Yang correction to give a corrected value of R. A revised value for P is then obtained from the depth-dose curves of P versus R.

The depth-dose curves are expressible in terms of dP/dR versus R as well as P versus R. This suggests that one could measure dP/dR experimentally with a dosimeter at $R=0$ (i.e., on the surface where the electron beam enters the sample) and at some other value of R (i.e., on the surface where the electron beam exits from the sample). The ratio of the exit dose to the entrance dose may then be used to determine an experimentally derived value of R from the dP/dR curve. It is interesting to note that this value of R requires no Yang correction since the dosimeter measurement includes any effects caused by increased electron scattering in high atomic number materials. This value of R can then be used to find P from the P versus R curve. A suitable dosimeter for this sort of measurement should be very thin and of low atomic number to avoid perturbation of the electron flux. Polyethylene terephthalate film (Dupont Mylar) in 0.00025-in.-thick sheets has these properties and has been used to measure absorbed dose in the range of dose encountered in this experiment.[35] Mylar films were placed on top and bottom of the crystal and irradiated with the electron beam to determine dP/dR and, hence, P as described above.

Three different techniques for measuring the fraction of the incident intensity that was absorbed by the crystals have been described. They are: (1) the substitution method using glass-block dosimeters, (2) a theoretical calculation involving depth-dose curves and the Yang correction, and (3) a measurement of the entrance and exit doses at the surfaces of the crystal with the Mylar-film dosimeter and subsequent use of the depth-dose curves. A comparison of these three methods was made for the irradiation of a 0.015-in.-thick KBr crystal with 2.0-MeV electrons. The fraction of the incident intensity absorbed by this crystal was found to be 0.186, 0.166, and 0.210 for methods (1), (2), and (3), respectively. The agreement between these different methods indicates that the fraction of the incident intensity absorbed by the crystal was known to about 10%. It was felt that the glass-block dosimetry was the most accurate of the three methods, and it was used for the vacancy-production efficiencies reported in this paper.

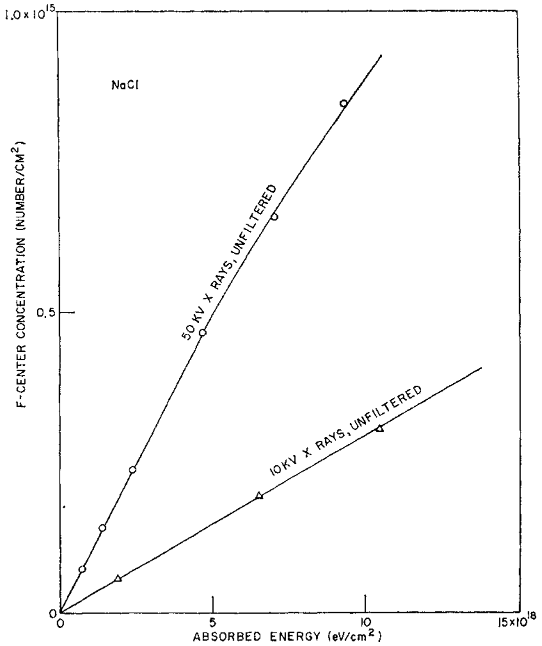

FIG. 7. Growth of the F band in NaCl as a function of absorbed energy for various radiations.

The crystal thicknesses for the Van de Graaff irradiations were chosen so that approximately 20% of the incident intensity was absorbed by the crystals. This produced an electron flux in the samples that was orders of magnitude higher in energy than that of the x-ray irradiations. On the basis of a continuous slowing-down model of electron-energy loss one would estimate that the electrons in the crystal had energies between 1.6 and 2.0 MeV. However, some fast "knock-on" electrons of low energy are undoubtedly produced. The fraction of the total energy absorbed that is carried by these lower

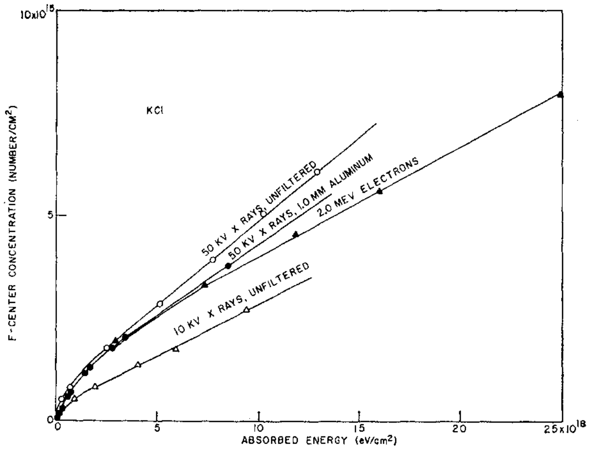

FIG. 8. Growth of the F band in KCl as a function of absorbed energy for various radiations.

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[33] W. D. Compton and G. W. Arnold, J. Appl. Phys. **31**, 621 (1960).

[34] C. N. Yang, Phys. Rev. **84**, 599 (1951).

[35] V. H. Ritz, Radiation Res. **15**, 460 (1961).

energy electrons could not be determined easily since the Spencer-Fano theory of electron-energy dissipation has not been evaluated for this particular sample geometry.[36] The tabulations of McGinnies[37] are available, however, for the case of a uniformly distributed electron source in an infinite medium. More secondary electrons would be produced in that geometry than in the present experiment, so that an upper limit on the number of secondary electrons can be determined. Data from the work of Compton and Arnold[33] derived from the tabulations of McGinnies indicate that no more than 5% of the secondary electrons will have energies below 100 keV.

III. EXPERIMENTAL RESULTS

A. Growth of the *F* Band

The growth of the *F* band in KBr, NaCl, LiF, and KCl as a function of absorbed energy for various ionizing radiations is presented in Figs. 5–8. The x-ray irradiated crystals were colored nonuniformly because of their large x-ray absorption coefficients and the nonmonochromatic nature of the incident x rays. This made it difficult to determine *F*-center concentrations in units of *F* centers per cm^3. It was found to be more convenient to express the concentration in units of *F* centers per cm^2. This was done by recasting the Lorentzian form of Smakula's equation[38] as follows:

$$Nt=2.97\times10^{17}[nDW_{1/2}/(n^2+2)^2f], \tag{2}$$

where Nt is the *F*-center concentration (*F* centers/cm^2), D the optical density at absorption peak, f the oscillator strength, n the refractive index, and $W_{1/2}$ the half-width (eV). The oscillator strength was assumed to be 0.8 for all the alkali halides, and the other quantities on the right-hand side of Eq. (2) were either measured or taken from the literature. The *F*-center concentrations (*F* centers/cm^2) obtained from Eq. (2) are plotted in Figs. 5–8 as a function of the absorbed energy (eV/cm^2) as measured by the various dosimetric techniques. The *F*-center production efficiencies (eV/*F* center) are equal to the reciprocals of the slopes of these curves.

Inspection of the growth curves for KBr in Fig. 5 reveals that, while the *F*-center production efficiency is strongly influenced by the type of incident radiation, the curve shape is the same, i.e., linear, for all types of incident radiation. The growth curves of LiF and NaCl in Figs. 6 and 7 exhibit the same behavior. Thus for these materials the slope and, hence, the *F*-center production efficiency are a constant for any particular type of radiation.

The growth curves for KCl in Fig. 8, however, are markedly nonlinear at the outset but then achieve a constant slope as the irradiations progress. One possible explanation might be that there is an initial high concentration of negative ion vacancies in the crystal which could produce *F* centers by simply trapping an electron.[8] This requires much less energy than the actual displacement of a halide ion from its lattice site and could serve as a "cheap" source of *F* centers. If this supposition were correct one might expect a delay in the onset of *H*-band growth in the early stages of coloration. Unfortunately the *H* band is much smaller than the *F* band, and, consequently, could not be measured accurately in the region of 1×10^{15} *F* centers/cm^2, where the *F* band is growing nonlinearly. The *F*- to *H*-band ratio was measured and found to be constant in the linear portion of the growth curve. Another possible explanation of the initial nonlinearity could be that varying amounts of the absorbed energy go into the production of other vacancies, i.e., alpha centers, as the irradiation progresses. This possibility is consistent with the idea recently put forth by Klick and Patterson[6] that *F* and alpha centers have a common origin in a Frenkel-defect vacancy creation event. Experiments in this laboratory[39] have indicated that the *F*- to alpha-band ratio is constant in KCl for *F*-center concentrations up to at least 2×10^{16} *F* centers/cm^2. This was as far as measurements were carried on the vacuum uv spectrophotometer. It would appear that the relative proportions of *F* and alpha centers are constant so that the enhanced *F*-center production observed early in the growth curve cannot be accounted for by a decrease in the number of alpha centers produced.

The possibility that the initial nonlinearity of the KCl growth curves was due to some impurity was investigated briefly. Cape[40] has reported photochemical *F*-band formation in KCl under uv irradiation in crystals with high OH concentrations. Since KCl luminesces under x-ray irradiation, the possibility existed that the initial nonlinearity of *F*-band growth observed here was due to some photochemical process. A KCl crystal whose OH content was 0.04 of that of the Harshaw crystals used previously was x rayed and found to have a growth curve identical to that of the Harshaw crystal. This result would seem to eliminate OH as a factor in the nonlinearity.

The following treatment of the growth curves of Fig. 8 indicates that something present in the bulk of the crystal may be involved, however. The linear portions of the growth curves were extrapolated to intersect the ordinate. The *F*-center concentrations (*F* centers/cm^2) obtained at these intersections increase in proportion to the volume of the crystal that is actually colored by the radiations; i.e., if the growth curves were plotted in terms of *F* centers/cm^3 they would all extrapolate to approximately the same point on the ordinate. The Van de Graaff data yielded a vacancy concentration (*F* plus alpha centers) of 1.7×10^{-6} in units of the mole fraction of vacancies to the total number of chlorine ions. This concentration is comparable to the bromine concentra-

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[36] L. V. Spencer and U. Fano, Phys. Rev. **93**, 1172 (1954).

[37] R. T. McGinnies, Natl. Bur. Std. (U. S.) Circular 597 (1959).

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

[39] V. H. Ritz and D. A. Patterson (unpublished work).

[40] J. A. Cape, Phys. Rev. **122**, 18 (1961).

tion ($\approx 7\times10^{-5}$) found as an impurity in KCl by Kobayashi and Tomiki,[41] but it is difficult to say whether or not the bromine would enhance the *F*- and alpha-center production.[42] The initial-vacancy concentration ($\approx 10^{17}$ vacancies/cm^3) would appear to be larger than the isolated negative ion vacancy concentrations ($\approx 10^{16}$/cm^3) found in other alkali halides.[43] In the absence of experimental evidence one cannot correlate the initial nonlinearity directly with either the bromine concentration or the number of negative ion vacancies present in the crystal.

In lieu of an extensive investigation of the initial coloration rate this paper will assume that the linear portions of the KCl growth curves are probably more characteristic of the actual generation of halide ion vacancies in the lattice. Thus the *F*-center production efficiencies for KCl were derived from the linear portions of the growth curves of Fig. 8.

B. Summary of Efficiency Measurements and General Observations

The *F*-center production efficiencies derived from the slopes of the growth curves of Figs. 5–8 are listed in Table II. These efficiencies were obtained by dividing the *F*-center concentration by the energy absorbed by the crystal and thus are indicative of the *F-center* production efficiency rather than the *vacancy*-production efficiency, i.e., *F* centers plus alpha centers.[44] The results listed in Table II are also presented pictorially in Fig. 9, where the *F*-center production efficiencies are arranged in order of the ionizing ability or "quality" of the radiation. The spacings along the abscissa are roughly proportional to the stopping power (energy lost per unit path length) of the electron flux that is generated in the sample by the incident 2.0-MeV electrons or low-energy x rays. It must be emphasized, however, that Fig. 9 is really just a convenient presentation of the data of Table II. For example, all of the alkali halides irradiated with 50-kV x rays filtered with 1 mm of aluminum have been grouped together at the same point along the abscissa. Actually the electron fluxes in these crystals are quite different because (1) the spectrum of absorbed x rays is slightly different for each of them, and (2) the spectrum of fast photoelectrons will be different for each one due to the varying positions of the x-ray absorption edges.

TABLE II. Summary of *F*-center-production efficiencies, eV/*F* center.

Material	2.0-MeV electrons	50-kV x rays, 1-mm Al	50-kV x rays, unfiltered	15-kV x rays	10-kV x rays
KBr	4700	2740	1700	3300	4600
KCl	3750	2900	2400	...	4000
LiF	3000	2500	850 1800	...	3800
NaCl	...	...	10 100	...	34 000

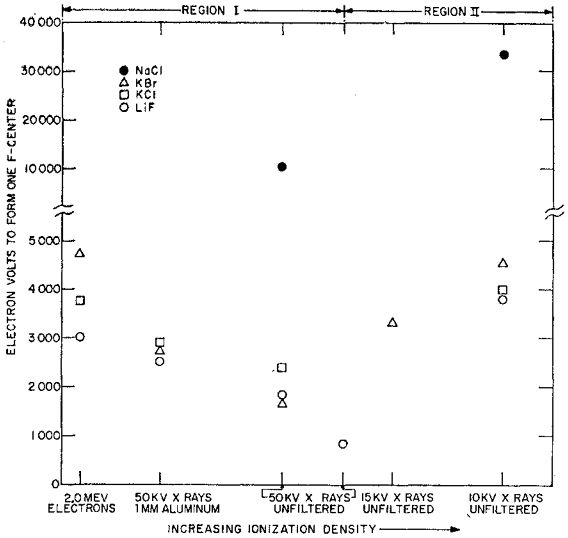

FIG. 9. Summary of the *F*-center production efficiencies of Figs. 5–8. The results have been arranged in order of the ionization density along the paths of the electrons generated in the crystals by the irradiations.

There are two rather striking features about the *F*-center production efficiencies presented in Fig. 9. First, the energy required to produce an *F* center is strongly dependent upon the sort of radiation used to color the crystal. Second, all of the alkali halides used in the experiment exhibit the same variation in coloration efficiency with the ionizing ability or "quality" of the radiation. They are fairly difficult to color with 2.0-MeV electrons, become easier to color at moderate x-ray energies, and then rapidly become difficult to color again at low x-ray energies.

It is interesting to note that NaCl follows the same general trend as KBr, KCl, and LiF but is much harder to color at all energies. This behavior is consistent with the results of Rabin and Klick[3] who found that NaCl was more difficult to color than the previously mentioned alkali halides. They have correlated the *F*-center production efficiency with the space available in the crystal lattice for the accommodation of an interstitial atom and have found that NaCl might, indeed, be expected to be more difficult to color. This correlation did not include *all* the vacancies produced but it is unlikely that the ratio of *F* to alpha centers differs enough among the alkali halides to invalidate their conclusion.

The fact that the *F*-center production efficiency depends upon the "quality" of the radiation to which the crystal has been exposed indicates that the crystal might filter the x-ray beam enough to modify its colorability. Two LiF crystals were exposed to 50-kV un-

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[41] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **15**, 1982 (1960).

[42] H. Bauser and F. Luty, Phys. Stat. Solidi **1**, 608 (1961).

[43] H. Rabin, Phys. Rev. **116**, 1381 (1959).

[44] The vacancy-production efficiency, as distinguished from the *F*-center-production efficiency, is discussed later in this paper.

filtered x rays to test this hypothesis. As noted in Table I, one of these crystals was ten times as thick as the other. The spectral distribution of absorbed x-ray energy in these crystals was presented in Fig. 4. Reference to Table II and Fig. 9 indicates that there is quite a significant change in the ease of coloration as the thickness of the crystal is varied. This sort of effect may account for the apparently anomalous behavior of LiF coloration reported by Rabin and Klick[3] who found that it did not fall on their curve correlating *F*-center production efficiency with interstitial space available in the lattice. All of their alkali halide samples were cleaved to the same thickness so that LiF, with its much lower atomic number, may have been irradiated with a significantly different x-ray and photoelectron flux.

The dependence of the coloration efficiency upon the intensity of the radiation field (eV/cm^2-sec) was checked for KBr and KCl with 10- and 50-kV unfiltered x rays.[45] The intensity was reduced to about a fifth of the intensity used in the irradiations shown in Figs. 5 and 8 by reducing the emission current of the x-ray tube. The *F*-center-production efficiencies were found to be within a few percent of those obtained at the higher dose rates. Thus, the *F*-center efficiency at helium temperature depends upon the type or "quality" of the radiation, but not upon the intensity of the radiation.

IV. DISCUSSION

A. Introduction

Only a few of the papers on vacancy-production mechanisms cited in the introduction have calculated the yield to be expected as the energy of the electrons generated in the sample by irradiation is varied. In particular, the papers of Varley,[10,16] of Howard *et al.*,[12] and of Durup and Platzman[20] have concerned themselves with this problem. When low-energy x rays impinge upon a sample they interact predominantly by the photoelectric process. This gives rise to a flux of fast secondary electrons which dissipate their energy in a very large number of inelastic collisions, losing of the order of 10 eV per collision. Thus, most of the ionization is produced by the secondary electrons, rather than by the initial photoelectric interaction of the x rays in the sample. To make a quantitative comparison of the results of this experiment with the various proposed mechanisms one must know the spectral distribution of the electrons generated in an irradiated sample. One can utilize available information on the nature of the electron "degradation" spectrum generated in a material when initially monoenergetic electrons slow down and degrade in energy. These electrons lose energy both by a continuous slowing-down process[46] and by the production of energetic "knock-on" electrons which enrich the low-energy portion of the electron spectrum. The general formulation of the degradation spectrum problem is due to Spencer and Fano,[36] and extensive tabulations have been made by McGinnies.[37] The LiF irradiations of the present experiment were chosen for such a calculation because the starting photoelectron spectrum is simpler in this material as a result of the positions of the x-ray absorption edges. The photoelectron spectra derived from Figs. 2 and 4 were degraded with the aid of the tabulations of McGinnies,[37] and the results are presented in Fig. 10. This represents a snapshot picture, in effect, of the electron spectrum seen at a point in the crystal at any time. One sees that although the incident x-ray spectrum may be rather narrowly defined, the degraded electron spectrum extends to much lower energies. These spectra are used in conjunction with the results of Fig. 9 in the discussion which follows. For convenience, the data of Fig. 9 are divided into two regions: region I consisting of the fairly energetic irradiations to the left of the 50-kV, unfiltered x-ray points and region II consisting of the low-energy irradiations to the right of the 50-kV, unfiltered points.

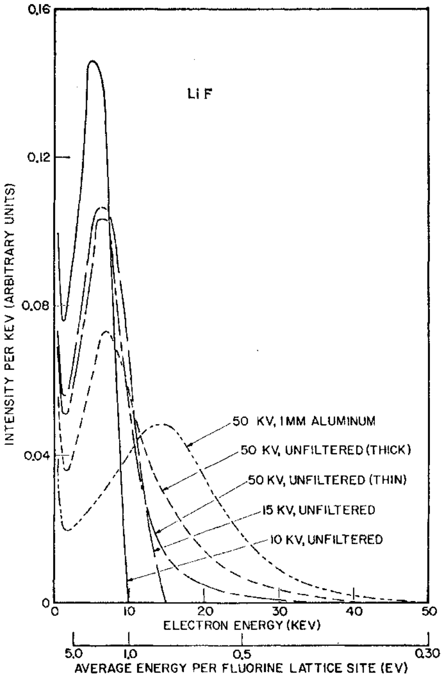

FIG. 10. Electron-degradation spectra generated in LiF by various x-ray irradiations. The lower scale gives the amount of energy that is dropped, on the average, at a fluorine lattice site traversed by an electron of a particular energy.

B. Mechanisms of Group B: The Multiple Ionization of One Isolated Halide Ion

Varley[10] originally estimated the efficiency of vacancy production from the fact that about 10% of the ionizations produced in rare gases by electron bombardment

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[45] The glass Van de Graaff Dewar failed before the intensity dependence of coloration could be checked.

[46] H. A. Bethe and J. Ashkin, in *Experimental Nuclear Physics*, edited by E. Segré (John Wiley & Sons, Inc., New York, 1953), Vol. 1, Part II.

were double ionizations. In a later paper[16] he considers the displacement process in more detail. Concerning himself with *direct* multiple ionizations occurring in one event (i.e., no Auger cascades are invoked), he first estimates the degree of multiple ionization needed to eject a halide ion to an interstitial position. Then, using estimates of the probability for multiple ionization for different halides which were interpolated from the rare gas data of Massey and Burhop,[47] the most efficient values of vacancy-production efficiency were obtained for LiF (750 eV/vacancy), KCl (760 eV/vacancy), KBr (900 eV/vacancy), and NaCl (600 eV/vacancy) for the case in which the halide ion must be doubly ionized to effect displacement. These values are in rough agreement with the results of Rabin and Klick[3] for *F*-center production efficiencies if *F* centers are the only vacancies formed. The inclusion of alpha centers[6,8,42] would indicate vacancy-production efficiencies of about 200–400 eV/vacancy. These values are slightly lower than Varley's results which, however, may be more efficient if multiple ionizations resulting from Auger cascades are included.[48] In relation to the present experiment, however, it is more important to consider the energy dependence predicted for this mechanism. In Varley's calculation the cross sections for various degrees of direct multiple ionization in a single event are independent of the incident-electron energy for energies above the ionization energies of the various shells. This schematization is consistent with the work of Stanton and Monohan[48,49] who found that the cross section for the formation of He^{2+} by electron impact relative to that of He^+ was constant for energies above 1.4 keV. Thus, some energy dependence of the vacancy production might be expected but only at very low energies where the energy drops below the threshold for ionization, and one might expect a diminution in yield. Reference to Fig. 9 indicates, however, that the coloration efficiency is strongly energy dependent in region I where an energy-independent response is predicted. In addition the electron-degradation spectra of Fig. 10 imply that the decreased yield observed experimentally in region II would appear to occur at much higher electron energies than would be expected from this model. Thus the direct multiple ionization of single halide ions does not seem to account for the experimentally observed energy dependence of *F*-center formation.

Howard, Vosko, and Smoluchowski[12] have estimated the efficiencies for inner-shell single ionization in KCl. Presumably these ionizations would be followed by Auger cascades which initiate vacancy production. In their model the efficiencies are energy-independent for the *L* and *M* shells and equal to 600 and 65 eV/ionization, respectively. The *K*-shell efficiency is energy dependent and equal to 24 000 eV/ionization at 20 keV and 60 000 eV/ionization at 2.0 MeV. The results reported in the present paper, in conjunction with the measurements of Klick and Patterson[6] on the *F* and alpha bands, indicate that only about 400 eV are required to generate a vacancy in KCl. This suggests that the *L* or *M* shells must be involved because of their high efficiency for defect formation. The energy independence of the yield predicted by Howard *et al.*[12] for these shells does not appear to be compatible with the results of Fig. 9.

TABLE III. Vacancy production by 1.0-MeV electrons.[a]

Element	Shell	eV/vacancy
F	K	14 000
	L_{I}	300
Cl	K	260 000
	L_{I}	12 000
	L_{II}, L_{III}	2500
	M_{I}	500

[a] J. Durup and R. L. Platzman, Discussions Faraday Soc. 31, 156 (1961).

The most complete and elegant treatment of inner-shell ionization yields produced in alkali halides by ionizing radiation is that of Durup and Platzman.[20] They consider alkali halides irradiated with monoenergetic electrons whose initial energies range from 0.6 keV to 4.0 MeV. The treatment of Durup and Platzman is superior to those cited previously in that they utilize available information on the electron-degradation spectrum[37] and make extensive calculations of the cross sections for inner-shell ionization. Their results provide the yield (number of inner-shell ionizations per 100 eV absorbed) for each of the shells as a function of incident monoenergetic electron energy. The removal of an electron from the *K*, *L*, or *M* shells of a low-atomic-number material presumably leads to an Auger event and multiple ionization. Estimates of the vacancy-production efficiency can be derived from these yields if every inner-shell ionization is assumed to lead to vacancy creation through some, as yet, unspecified mechanism. The efficiencies for individual shells in F and Cl irradiated with electrons of initial energy T_0 equal to 1.0 MeV are given in Table III. One notes that the yield increases roughly by an order of magnitude for each shell as one progresses to the outer shells. This is a general consequence of the fact that, according to Bohr-Bethe theory, the probability that a particular bound electron will be ionized by an interaction with a fast electron traversing the material is roughly proportional to the reciprocal of its binding energy. Table IV lists some of the values of the *K*-shell efficiencies for chlorine and fluorine for different monoenergetic incident electrons. The energy required to form a vacancy increases rather slowly with decreasing electron energy and then rises rapidly near the *K* edge as more of the

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[47] H. S. W. Massey and E. H. S Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, Oxford, 1952).

[48] Varley points out that the empirical measurements of multiple ionization in gases[47] may include some Auger events if they are performed with electrons whose energies are higher than the threshold for such events.

[49] H. E. Stanton and J. E. Monahan, Phys. Rev. **119**, 711 (1960).

TABLE IV. Vacancy production by K-shell ionization.[a]

Initial electron energy	eV/vacancy Chlorine	Fluorine
1.00 MeV	260 000	14 000
0.41	300 000	15 500
0.10	350 000	16 800
0.016	630 000	21 000
0.006	1 600 000	26 000
0.0025	...	43 000
0.0012	...	140 000

[a] J. Durup and R. L. Platzman, Discussions Faraday Soc. 31, 156 (1961).

available energy of the degradation spectrum slips below the K edge. The energy dependence for the L and M shells was not calculated by Durup and Platzman, but it would be expected to be less energy-dependent than the K shell, with the rapid decrease in yield occurring at lower energies near the appropriate edges. A comparison of the estimates of Durup and Platzman in Table III with the data of Fig. 9 indicates that K-shell ionization cannot account for the observed F-center production rates which are 5 to 60 times larger than the prediction. If one includes the alpha centers in the experimental vacancy-production efficiencies[6] for KCl, then one must go to the outermost shells to achieve agreement with experiment. The ratio of F to alpha centers in LiF is unknown, so that the vacancy-production efficiency in this material is rather speculative. However, the F-center production efficiency alone would seem to eliminate the K shell as the source of vacancy production. In KBr the vacancy-production yields would be presumably lower than those for KCl, so that the observed vacancy-production rates again would seem to exclude inner-shell ionization. Thus one can say that the experimental data presented in Fig. 9 argue strongly against inner-shell ionization as the dominant factor in the coloration process.

The calculation of Durup and Platzman[20] predicts a constantly *decreasing yield* for vacancy production as the incident electron energy is reduced. The data in region I of Fig. 9 indicates, however, that the yield actually *increases* as the initial electron energy goes from 2 MeV to a few kilovolts. This response also argues against the importance of K-shell ionization. The predicted response for the outer shells is rather energy-independent, so that even the outer shells, which are in fair agreement with the observed vacancy-production efficiencies, cannot account for the direction of the observed energy dependence in region I. The energy required to produce an F center does increase in region II of Fig. 9 as the electron flux in the samples decreases in energy. However, this rise would appear to occur at much higher energies than were predicted by Durup and Platzman, especially if outer-shell ionization is involved. In LiF, in particular, where the K and L edges are at 0.6 and 0.04 keV, respectively, the change in the amount of energy in the vicinity of the edges as the x-ray energy is varied would appear to be relatively small. The fact that the coloration process may be very efficient if all the vacancies are counted suggests that the decrease in yield observed at low energies is attributable to an effect involving something other than the absorption edges. Similar conclusions can be reached for KCl where K-shell ionization fails to account for the high vacancy-production rates and L- or M-shell ionization must be invoked to achieve agreement with experiment.

The energy dependence of the vacancy yield for KBr was not calculated by Durup and Platzman, but there does not appear to be any reason why arguments similar to those discussed above for KCl and LiF should not be applicable to this material. The magnitude of the vacancy-production efficiency indicates that inner-shell ionizations are not dominant, and a parallel trend of efficiency with electron energy would be expected.

If the process of low-temperature coloration begins with an inner-shell ionization, one might look for some change in the x-ray coloration efficiency near the various absorption edges in alkali halides. Sharama and Smoluchowski[50] have reported preliminary results of such an investigation at the K edge of chlorine in KCl. They have performed irradiations at liquid-nitrogen temperature using both "white" x rays generated at exciting potentials above and below the K edge and, more recently, monochromatic x rays from a bent crystal monochromator. An apparent increase in colorability has been reported for irradiations above the K edge, but no absolute F-center production efficiencies have been reported as yet. A similar experiment was done here at helium temperature for KBr at the K edge in bromine (13.5 keV). As indicated by Fig. 3, the x-ray spectral energy was supplied to the crystal above the K edge by the 50-kV, 1-mm aluminum filtration irradiation, and between the K and L edges by the 10-kV, unfiltered irradiation. Reference to Fig. 9 reveals that it is indeed easier to color KBr when it is irradiated with x rays above the K edge; a result consistent with the findings of Sharama and Smoluchowski for KCl. However, one should note that the other alkali halides of Fig. 9 also exhibit the same variation in coloration efficiency with x-ray energy. The K edges of these other crystals all lie below 3 keV. The x-ray emission spectra of Fig. 2 indicate that all of the irradiations for materials other than KBr were done with x rays whose energies were well above the K edge in these materials. The result, then, is the KBr follows the general trends of the other alkali halides even though it is the only one irradiated below its K edge. This would indicate that the K absorption edge in bromine does not play a dominant role in the coloration of KBr. This would also be inferred, of course, from a comparison of the yields calculated by Durup and Platzman for other alkali halides with the experimental vacancy-production efficiencies.

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[50] J. Sharma and R. Smoluchowski, Bull. Am. Phys. Soc. 7, 178 (1962); 8, 251 (1963).

It should also be noted that if Auger effects are important the behavior of KCl and KBr might be different in view of the different probabilities for *K*-shell Auger events.[26] The apparent increase in colorability of KCl above the *K* edge in chlorine has been cited by Sharma *et al.*[50] as evidence for the importance of multiple ionization resulting from the Auger effect. It should be borne in mind, however, that a change in colorability as the edge is crossed is a *necessary* but not a *sufficient* condition for the dominance of the Auger effect. The flux of photoelectrons in the material also changes as the edge is crossed and hence the probability for the single ionization of two adjacent halide ions which could lead to vacancies through the mechanisms listed previously in group C.

C. Mechanisms of Group C: The Single Ionization of Two Adjacent Halide Ions

The energy required to produce a vacancy by mechanisms involving the single ionization of two adjacent halide ions was not calculated in the references cited in the introduction.[5,13] This sort of mechanism is rather appealing in view of the efficiency results in region I of Fig. 9. All of the alkali halides exhibit an increased ease of coloration as one passes from the 2.0-MeV electron irradiation data to that of the 50-kV x-ray irradiations. The stopping power of the electrons comprising the electron flux in the crystals increases markedly in this interval. This change in stopping power increases the probability that two adjacent halide ions will be ionized. If mechanisms involving the simultaneous ionization of two adjacent halide ions are dominant, one should observe a decrease in the energy required to produce an *F* center as the ionization density along the paths of the electrons increases. This is indeed the behavior observed in region I of Fig. 9.

In region II all of the alkali halides become more difficult to color as lower energy x rays are used. One can postulate that at these low energies the ionization density along the electron tracks is so high that some of the energy that went into *F*-center formation at higher energies is now wasted. Figure 10 indicates that a significant portion of the electron spectrum lies in a region in which the ionization density along the track is quite high. The possibility that vacancies are annealed out by the high ionization density of the same electron track that created them suggests itself, although the quantitative calculation of such self-annealing would seem to be rather difficult. Another possible explanation for the decreased yield of vacancy production at low energies might be that more energy proportionately is going into excitation than into ionization. It would appear, however, from calculations of the energy required to produce an ion pair in gases[51] that a decreased yield would be expected only for electron energies below a kilovolt. The spectra of Fig. 10, in conjunction with the calculations of Howard-Flanders,[52] indicate that too little energy is concentrated in that spectral region to account for the change in yields. In addition, a rough calculation of the vacancy annealing to be expected as vacancies are annealed by fast photoelectrons other than those which created them can be made along the lines suggested by Compton and Arnold.[33] In this calculation the fast photoelectrons generated by irradiation are assumed to expend their energy by random walking in a spherical volume; all the vacancies present in this volume are annealed out in the process. The most pronounced effect would be expected in KBr where the large absorption coefficient for low-energy x rays results in the greatest surface coloration. For the 10-keV x-ray irradiations one finds that 5-keV electrons interacting at every lattice site will random walk so as to affect about 5% of the lattice sites. This effect would be an order of magnitude smaller for LiF because of its smaller x-ray absorption coefficient. Thus, some other process would appear to be responsible for the observed variation in colorability at low energies.

The vacancy-production efficiency for mechanisms of group C can be calculated along the lines of the following rather crude and highly stylized model. Suppose that the single ionization of any two adjacent halide ions leads to a vacancy through the mechanisms of group C. However, if any of the nearest-neighbor halide ions surrounding the pair is ionized, vacancies are not produced because of some unspecified annealing process. Thus, only isolated pairs are counted as producing vacancies in this schematization. The object of the calculations to be performed in this section and in the Appendix is to estimate the number of isolated pairs generated along the paths of electrons of a particular energy as they traverse the lattice. This requires a knowledge of two things: (1) the probability p for the production of any ionization along the electron track and (2) the fraction of these ionizations that produce isolated pairs of ions. This information, combined with the degradation spectra of Fig. 10 and an assumption as to the energy required to ionize a halide ion, permits an estimation of the yields (vacancies/eV) to be expected for the various irradiations used in this experiment. In the model adopted here the yield will be calculated for two cases: (1) a one-dimensional line of halide ions and (2) a three-dimensional array of halide ions arranged in a cubic lattice. If p is the probability for any random ionization and b is the band gap (eV), then the yield (vacancies/eV) as calculated in the Appendix on a random statistical basis is given by $n_1=p(1-p)^2/4b$ for the one-dimensional case and $n_3=6p(1-p)^{18}/4b$ for the three-dimensional case. Both of these yields are based on either lines or arrays of ions which are infinite in

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[51] R. L. Platzman, Intern. J. Appl. Radiation Isotopes **10**, 116 (1961).

[52] P. Howard-Flanders, in *Advances in Biological and Medical Physics*, edited by H. Curtis, L. Gray, and B. Thorell (Academic Press Inc., New York, 1958).

extent.[53] The behavior of these yields as p increases indicates that the yields for both cases increase, reach a peak, and, then, decline as pairs that are not isolated are discounted. The initial yield for the three-dimensional case is higher and the peak is reached at lower p than for the one-dimensional case simply because more nearest neighbors are available around a pair in three dimensions.

TABLE V. Vacancy-production efficiencies for mechanisms involving the single ionization of two adjacent halide ions, as calculated from Eqs. (3) and (4) for LiF.

Radiation	Calculated (eV/vacancy) n_1	n_3	Experiment[a]
2-MeV electrons	9200	1680	3000
2-MeV electrons (deg.)	6900	1300	
50-kV x rays, 1 mm Al	870	410	2500
50-kV x rays (thick)	660	425	1800
50-kV x rays (thin)	565	445	850
15-kV x rays	540	450	···
10-kV x rays	465	510	3800

[a] F centers only.

The selection of an appropriate value of p presents some difficulties since the probability of ionization along the individual electron tracks is desired rather than the average probability for the whole bulk of the crystal. This approach seems justified in view of the intensity independence of coloration which indicates that intersecting tracks are not an important factor. In addition, the vacancy-generation mechanisms of group C require neither intersecting tracks nor interactions between distant points in the crystal. The probability for an ionization is much higher along the electron tracks, of course, than in the whole bulk of the crystal. For example, an electron with a few kilovolts energy has such a large stopping power that it will interact at almost every lattice site it traverses. Thus the probability for the occurrence of an ionization along the track is practically unity, even though the average probability for the entire crystal is many orders of magnitude smaller. The problem, then, is to estimate the probability for any ionization p in the vicinity of the electron track. As a first approximation the energy dissipation may be considered as continuous along the tracks. A more detailed description would consider a series of discrete excitations and ionizations occurring in the vicinity of the tracks. A complete description of the situation at this level would require a knowledge of the nature and spatial distribution of the separate events.[54] Some information as to the detailed physical situation can be adduced from cloud chamber observations of electron tracks in gases, but details as to the portion of a solid that is sampled by a degrading electron are more obscure.[55] The probability p can be calculated in a straightforward manner for the idealized one-dimensional case with the result derived in the Appendix. The estimation of p for the three-dimensional case leads to some conceptual difficulties since the yield function n_3 applies to an infinite lattice rather than to a limited region surrounding a tortuous electron track. The procedure to be followed here is to assume that, for an electron of a given energy, p is the same for the three-dimensional case as for the one-dimensional case calculated in the Appendix. The two cases presented here may be viewed as complimentary estimates of the coloration efficiency. The probability for any ionization, p, along the electron track as calculated for the one-dimensional case using the Bethe-Bloch stopping power is fairly straightforward. However, the one-dimensional yield function n_1 underestimates the efficiency since the electrons actually sample a three-dimensional lattice in which more nearest neighbors are available than in one dimension. On the other hand, the three-dimensional yield function n_3 approximates the physical situation more closely, but the use of the p derived for the one-dimensional case overestimates the probability for any ionization. Thus the best calculation probably lies somewhere between these two estimates, depending upon the number of lattice sites sampled as the electrons degrade in energy and travel in more tortuous and condensed paths.

The combination of the one-dimensional probability function, p, with the one- and three-dimensional yield functions derived in the Appendix produces the following results for electrons with an energy E:

$$n_1=\frac{S(E)\rho d}{8b^2}\left(1-\frac{S(E)\rho d}{2b}\right)^2, \tag{3}$$

$$n_3=\frac{3S(E)\rho d}{4b^2}\left(1-\frac{S(E)\rho d}{2b}\right)^{18}, \tag{4}$$

where $S(E)$ is the electron stopping power for halide ion interaction (eV-cm^2/g), ρ the density (g/cm^3), d the halide ion spacing (cm), b the band gap (eV). These expressions were evaluated for LiF by integrating over the electron-degradation spectra of Fig. 10. Electron stopping powers were interpolated from the tabulations of Nelms[56] for energies down to 10 keV and scaled from proton stopping powers for energies below 10 keV.[57] No corrections were applied for inner-shell binding.[58] The energy carried by the Auger electrons was included in the calculation but, in the absence of detailed knowledge of the Auger cascades, their energy spectrum was

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[53] H. Rosenstock, J. Soc. Ind. Appl. Math. **9**, 169 (1961); and (private discussion).

[54] J. W. Boag, Radiation Res. **1**, 323 (1954).

[55] A comprehensive discussion of "track effects" in radiation physics and chemistry is given by R. L. Platzman, in *Radiation Biology and Medicine*, edited by W. D. Claus (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), Chap. 1.

[56] A. T. Nelms, Suppl. Natl. Bur. Std. (U. S.) Circular 577 (1958).

[57] M. Rich and R. Madey, U. S. Atomic Energy Commission Rept. UCRL-2301, 1954 (unpublished).

[58] Natl. Bur. Std. (U. S.) Handbook 79 (1961).

assumed to be the same as the degraded photoelectron spectrum. The halide ion spacing was assumed to be 2.8 Å. The results are given in Table V, under the assumption that 20 eV (twice the band gap[59]) are required to ionize a fluorine ion although less energy may actually be required.[60] The two entries for 2.0-MeV electrons refer to monochromatic electrons and to the degraded spectrum which occurs when the incident electrons are totally absorbed in the sample. Experimentally, the situation was somewhere between these two cases since about 20% of the incident-electron energy was absorbed. The *F*-center-production efficiencies measured in this experiment are also listed in Table V. It should be borne in mind that an additional, indeterminate, number of vacancies in the form of alpha centers are probably also present in LiF.

Fairly good agreement is obtained between the calculations and experimental results listed in Table V. The three-dimensional calculated yields are in better quantitative agreement with experiment for the Van de Graaff irradiation than the one-dimensional yields, but both calculations exhibit the proper trend with radiation quality in passing from the Van de Graaff to the x-ray irradiations. At x-ray energies both calculations are more efficient than experiment, so that additional energy is available to account for other vacancies. The predicted variation of efficiency with radiation quality is greater than experiment in region I and much less than experiment in region II. This would seem to indicate that some loss mechanism other than the one adopted in this simple model is operative. The annealing of vacancies along the electron tracks at the time of their creation would appear to be a possible explanation for the experimental decrease in yield at high ionization densities. As mentioned above, the yield function n_3 reaches a peak at lower p than n_1. This is evident in Table V where the peak efficiency for n_3 is reached between the Van de Graaff and x-ray irradiations, while the efficiencies calculated from n_1 are still rising even at the lowest x-ray energies.

The vacancy-production efficiencies expected for KBr and KCl on the basis of the model described here were not calculated because of the complications added by the x-ray absorption edges. In general, the variation in colorability of different alkali halides would not be expected to be too large, since the variables in Eq. (3) and (4) do not vary too much from one alkali halide to another.[61] The variation of coloration efficiency with electron energy would also be expected to be about the same for all the alkali halides, since the ratio of electron stopping powers (and, hence, ionization density along the track) at any two electron energies is approximately independent of the atomic number of the absorber[56] for electrons with energies above the threshold of the inner shells. Evaluation of Eq. (3) for LiF, KCl, and KBr traversed by 2.0-MeV monoenergetic electrons which do not degrade in energy yields vacancy-production efficiencies of 9300, 10 000, and 4500 eV/vacancy, respectively. For 10-keV electrons the efficiencies are 910, 990, and 580 eV/vacancy, respectively. A similar calculation using the model of Eq. (4) yields efficiencies of 1650, 1800, and 850 eV/vacancy for LiF, KCl, and KBr traversed by 2.0-MeV electrons. At 10 keV the predicted efficiencies are 330, 300, and 270 eV/vacancy for the three-dimensional model. Thus, in either schematization, the variation of vacancy-production efficiency with electron energy is roughly the same.

It has been pointed out by Klick and Patterson[6] that the results for 50-kV unfiltered x rays yield vacancy-production efficiencies of 450 and 240 eV/vacancy for KCl and KBr, respectively. These efficiencies were obtained by dividing the *F*- plus alpha-center concentration by the total amount of energy absorbed by the crystal. If one weights these efficiencies by the electron stopping powers of the halide ions to reflect the energy actually dissipated on the halide ions, efficiencies of 215 and 160 eV/vacancy are obtained for KCl and KBr, respectively.[62] This means that about 10% of the ionizations on the halide ions in these materials lead to vacancy formation. It is interesting to note that these efficiencies approach the first-stage coloration efficiencies for *F*-center production at room temperature, so that the possibility of the generation of vacancies at room temperature by the same processes operative at low temperature cannot be excluded solely on the basis of the efficiencies involved.

The electrons generated by an Auger cascade have rather low energies and dissipate most of their energy near the point of their creation. Thus, they may have a high probability for ionizing adjacent halide ions and generating vacancies by the mechanisms of group C. The energy dependence of such an effect would be expected to follow the predictions of Durup and Platzman for the initial inner-shell ionizations. The subsequent Auger cascades, while unpredictable in nature, should not change in character as long as the coloration is being examined in region I; i.e., well above the absorption edges. Changes in the Auger-electron spectrum would be expected in region II as the various edges are crossed. The expected energy dependence would then be essentially energy-independent in region I with some possible changes occurring in region II as changes in the Auger cascades modify the probability that the ejected Auger electrons will interact at a nearby halide ion site. The experimental results of Fig. 9 indicate that this sort of process is not a dominant factor in the coloration. It is possible, however, that this process is opera-

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[59] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[60] P. E. Best, Proc. Phys. Soc. (London) **79**, 133 (1962).

[61] The decreased colorability exhibited by NaCl is attributed to the explanation proposed by Rabin and Klick (Ref. 3) and is not included in the model forming the basis for Eq. (3) and (4).

[62] Note that as little as 50 eV/vacancy is required in the initial nonlinear portion of the KCl growth curves.

tive as well as the energy-dependent process described by Eq. (3) or (4) and produces a fairly efficient energy-independent contribution to the vacancy-generation rate.

Another possible source of pairs of singly ionized halide ions might be the fast secondary electrons generated in "knock-on" events. In such a process a fast electron could ionize a halide ion and produce another fast electron which might interact with an adjacent halide ion if its stopping power were sufficiently high. An energy dependence would be expected for this process in region I as the character of the degradation spectrum changed, but the estimates of Compton and Arnold[33] would seem to indicate that too few low-energy secondary electrons are generated to account for the high vacancy-production efficiencies ($\approx 10\%$) observed experimentally.

D. Mechanisms of Group A: The Single Ionization of One Halide Ion

The yield of vacancy production from mechanisms involving the single ionization of isolated halide ions would be expected to be quite high, approaching the energy needed to simply ionize the outer-shell electrons. If *all* of the single ionizations lead to vacancies, irrespective of whether or not they are formed in clusters, then the yields would be expected to follow the predictions of Durup and Platzman in Tables III and IV. This would indicate an energy-independent response in region I with a decreased yield near the absorption edges in region II as discussed previously. Another possibility would be that only isolated single ionizations produce vacancies, i.e., clusters of two or more ions do not contribute to the coloration process. In that case the vacancy-production yield should decrease steadily in regions I and II as the electron energy decreases and more clusters of singly ionized halide ions are formed. Thus the predicted energy dependence of vacancy production would be for either a constant or decreasing yield in region I with decreasing electron energy.[63] This behavior does not seem to be compatible with the experimental results presented here.

E. Summary of the Discussion

The arguments presented in the discussion are now summarized briefly and some additional possible situations are considered. The mechanisms are discussed in the order in which they were grouped in the Introduction.

1. Group A: The Single Ionization of One Halide Ion

The yield for this process would probably be great enough in the outer shells to account for the observed vacancy-production rates. The predicted energy dependence in region I is for either a constant yield or a decreasing yield as the electron spectrum present in the sample decreases in energy. This is at variance with the experimental results of Fig. 9 which show an increase in yield with decreasing electron energy. The formation of singly ionized halide ions by a double ionization (either directly or through an inner-shell ionization followed by an Auger event) and subsequent electron capture would appear to have a constant yield in region I, under the assumption that the capture process is energy-independent.[64] The same arguments would seem to apply to single ionizations generated by Auger electrons in region I where the spectral distribution of the Auger electrons is relatively independent of electron energy.

2. Group B: The Multiple Ionization of One Isolated Halide Ion

The formation of multiply charged halide ions by K-shell ionization[20] and a subsequent Auger cascade would appear to be orders of magnitude less efficient than the experimentally observed results. In addition, in region I, the prediction is for a slight decrease in yield as the electron spectrum present in the material decreases in energy. In region II the experimental yields appear to decrease at higher electron energies than would be expected for the K shell. The ionization of L-shell electrons would appear to be approximately efficient enough to account for the experimental F-center-production efficiencies, but the inclusion of alpha centers in the vacancy-production efficiency would appear to require use of the M shells in KBr and KCl and the L shell in LiF to produce agreement with the experimental yields. However, the energy dependence predicted for these outer shells is very flat in region I so that this sort of process would seem to be incompatible with the experimental results.

The production of a doubly charged halide ion by a direct double ionization is roughly efficient enough[16] to account for the observed vacancy-production rates. The predicted energy independence of this process, which is not observed experimentally, would seem to eliminate it as a dominant factor in the coloration process. The probability that two successive ionizations would occur on the same halide ion has been estimated by Mitchell *et al.*[65] and found to be orders of magnitude too small to

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[63] W. D. Compton (private communication, 1963) has pointed out that a decreased yield in region I might also be expected with decreasing electron energy if back reactions were an important factor in the coloration process at helium temperature. Presumably the back reaction would be more severe for the high stopping powers characteristic of low-energy electrons.

[64] It has been tacitly assumed in this paper that the probability for electron capture by a multiply ionized halide ion is independent of the degree of ionization of the ion or its neighbors. This assumption obviates an additional possible energy dependence in the coloration process. The estimation of such effects would appear to be rather difficult in the absence of a detailed knowledge of the way in which energy is dissipated along the electron tracks.

[65] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **121**, 484 (1961).

account for the coloration process. In addition, such a process should exhibit a squared dependence upon intensity instead of the direct proportionality observed here.

The generation of doubly ionized halide ions through capture after an Auger cascade or through the electrons from an Auger cascade would appear to be subject to the arguments discussed previously; i.e., in the absence of an energy-dependent capture process or radical changes in the nature of the Auger cascades, the yield should be constant in region I.

3. *Group C: The Single Ionization of Two Adjacent Halide Ions*

The generation of vacancies by the single ionization of two adjacent halide ions appears to be the only class of mechanisms which is in good agreement with the results of Fig. 9. The probability for the production of vacancies calculated in the simple model presented here yields reasonable agreement with experiment. A more decisive consideration is the fact that this class of mechanisms is the only one which exhibits the proper variation in efficiency in region I as the electron-degradation spectrum decreases in energy. The generation of pairs of singly ionized halide ions by the electrons from an Auger cascade would appear to be an equally probable process, but a comparison of the expected energy-independent coloration in region I with Fig. 9 indicates that such a process is not the dominant one. The formation of pairs by the ionization of two adjacent ions by two different intersecting electron tracks would seem to be quite improbable in view of the calculations of Mitchell[65] and the lack of a squared dependence upon intensity.

The simple model calculated here is in only fair quantitative agreement with experiment in region II where a rapid decrease in yield is observed. The onset of this decline occurs at higher electron energies than one would expect if the effect were caused by more energy proportionately going into excitation than into ionization at low energies. The annealing of vacancies by subsequent ionizations generated by fast photoelectrons other than those which created the vacancies would appear to be too small an effect to account for the decreased yield in region II. The annealing of vacancies by the high rate of energy deposition along the track of the electron which created them appears to be a reasonably possible explanation for this behavior, although the calculation of the magnitude of such an effect would be rather difficult.

V. CONCLUSIONS

The *F*-center-production efficiency in alkali halides is a strong function of the spectral energy distribution of the electrons generated by irradiation. All of the alkali halides investigated here exhibit the same variation in coloration efficiency with energy. They are fairly difficult to color with 2.0-MeV electrons, become easier to color at moderate x-ray energies, and then rapidly become more difficult to color again at low x-ray energies. The coloration efficiency is independent of the intensity of the radiation.

Various quantitative and qualitative arguments have been presented which indicate that inner-shell ionization does not adequately account for either the magnitude of the observed vacancy production or the direction of its energy dependence. A correlation has been made between the coloration efficiency and the ionization density along the tracks of the electrons generated by irradiation. The mechanisms of group C involving the single ionization of two adjacent halide ions appear to be the only group in which the spatial distribution of the ionized halide ions would influence the coloration efficiency. A calculation of the yield to be expected for this group of mechanisms is in reasonable agreement with experiment.

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APPENDIX

The vacancy-production efficiency for mechanisms of group C can be estimated by calculating the number of isolated pairs of singly ionized halide ions formed on a random statistical basis along the path of an electron traversing the lattice. In general, the probability p_p for the creation of an isolated pair in an infinite lattice is given by $p_p = ap^2(1-p)^m/2$, where p is the probability for any random ionization, a the number of nearest-neighbor halide ions around a halide ion in the lattice, and m the number of nearest neighbor halide ions around a pair of adjacent halide ions in the lattice.[53] In a one-dimensional lattice each halide ion has two nearest neighbors, as has each pair. In three dimensions each halide ion has twelve nearest neighbors while the pair has eighteen nearest-neighbor halide ions. Substitution of these conditions in the expression for p_p results in $p^2(1-p)^2$ and $6p^2(1-p)^{18}$ for the one- and three-dimensional cases, respectively. The corresponding ratios of pairs to any ionization are accordingly $p(1-p)^2$ and $6p(1-p)^{18}$. Under the assumption that each pair requires four times the band gap, b(eV), to ionize it, the yields (vacancies/eV) are

$$n_1=p(1-p)^2/4b\,, \tag{A1}$$

$$n_3=6p(1-p)^{18}/4b\,, \tag{A2}$$

where n_1 and n_3 are the one- and three-dimensional yields, respectively.

To estimate the probability p for any ionization along an electron track one considers a one-dimensional line of halide ions traversed by electron of energy E(eV). The electron loses energy at a rate proportional to the Bethe-Bloch stopping power $S(E)$ in eV-cm²/g, weighted for the halide ion interaction. In traversing a distance t(cm) along the line of atoms the electron will lose an energy $S(E)\rho t$, where ρ is the density of the alkali halide. If $2b$ is required for each halide ion ionization, then the number of ionization produced in the distance t is equal to $S(E)\rho t/2b$. The number of halide ions traversed in the distance t is equal to t/d where d is the halide ion spacing in the lattice. Dividing the number of ionizations in the distance t by the number of atoms one obtains the probability that any halide ion will be ionized:

$$p=S(E)\rho d/2b\,. \tag{A3}$$

Substitution of this expression for p into Eqs. (A1) and (A2) results in

$$n_1=\frac{S(E)\rho d}{8b^2}\left(1-\frac{S(E)\rho d}{2b}\right)^2, \tag{A4}$$

$$n_3=\frac{3S(E)\rho d}{4b^2}\left(1-\frac{S(E)\rho d}{2b}\right)^{18}. \tag{A5}$$

It is interesting to calculate the rate of vacancy generation N (vacancies/cm³-sec), produced by electrons traversing the lattice. The rate of energy absorption in such a situation is given by

$$w=IS(E)\rho/E\,, \tag{A6}$$

where w is the rate of energy absorption (eV/cm³-sec), I the electron intensity (eV/cm²-sec), $S(E)$ the electron stopping power (eV-cm²/g), ρ the density (g/cm³), and E the electron energy (eV). Multiplying Eq. (A5) by Eq. (A6) yields

$$N=\frac{3I\rho^2dS^2(E)}{4b^2E}\left(1-\frac{S(E)\rho d}{2b}\right)^{18}. \tag{A7}$$

The stopping power is small for energetic electrons with energies of a few MeV, so that Eq. (A7) can be approximated by

$$N\approx\frac{3I\rho^2d}{4b^2E}S^2(E)\,. \tag{A8}$$

Thus in this model the vacancy-generation rate depends upon the second or higher power of the stopping power. This may be contrasted with the behavior one might expect if the vacancy-generation rate depended only upon the rate of energy absorption w; in that case only the first power of $S(E)$ would appear. The model calculated here introduces the stopping power again through the probability functions for the creation of isolated pairs along the electron tracks. This result may be worth considering in studies of the kinetics of F-center formation at higher temperatures which have not, as yet, included any energy-dependent factors in their formulation.