(iii) Blatt[13] has shown that Eq. (1.1) is not a good approximation and one cannot neglect the velocity dependence of B_1 to obtain the correct temperature dependence of $(\mu_{T,1})_0$.

(iv) The validity of the Maxwellian distribution, even at low fields has not been proved, and hence the expressions for β may not be quantitatively correct.

The author is highly grateful to Dr. G. M. Shrum for kind encouragement during this investigation and to Professor J. B. Gunn for communicating reference 12 before publication, valuable suggestions and helpful discussion. Thanks are also due to Professor R. E. Burgess for numerous suggestions to improve the paper. The work was carried out under a program of research supported by the Defence Research Board, Canada.

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[13] F. J. Blatt, J. Phys. Chem. Solids 1, 262 (1957).

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Production of Colloidal Sodium in NaCl by Ionizing Radiation*

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A study has been made of the coloration of synthetic and natural sodium chloride crystals with Co^{60} gamma-ray and 1.3-Mev electron irradiations. These irradiations produced the colloid band, at 565 mμ, in the synthetic crystals but not in untreated natural crystals. Various thermal treatments were given the natural crystals prior to their coloration. It was found that either type of irradiation would produce colloids in crystals that had been heated at 700°C for at least 24 hours in an atmosphere containing hydroxyl ions. Colloids were produced in the untreated natural crystals by additive coloration. It was found that the characteristics of the colloids were the same whether they were produced by ionizing radiation or by additive coloration, with the exception of the role played by hydroxyl ions in the crystals colored by ionizing radiation.

INTRODUCTION

ALKALI-HALIDE crystals that have been heated in a vapor of their alkali metal and then cooled to room temperature contain a stoichiometric excess of the metal. This metal is atomically dispersed if the crystal is quenched. These crystals can then be given certain thermal and optical treatments that will result in a coagulation of this excess metal to form colloidal alkali-metal particles.

A large volume of experimental results is available on the properties of these particles. Some of the topics that have been specifically studied are the following: (1) the wavelength at which the extinction coefficient is a maximum for colloids in various alkali-halide crystals; (2) the dependence of the extinction coefficient upon temperature; (3) the conversion of *F* centers into colloids; (4) the thermal conversion of colloids into *F* centers; and (5) the photoconductivity resulting from absorption of light by the colloids. Theoretical calculations of the extinction coefficients for absorption and scattering of light of various wavelengths have been made using the Mie theory of the scattering of light by spherical particles. A survey of these and other properties of the colloids is given by Seitz.[1]

A large amount of experimentation has also been done on natural alkali-halide crystals—both halite and sylvine—that contain colloidal metal particles. This work is summarized by Przibram.[2]

Silver chloride and bromide are known to develop a colloidal silver band when they are irradiated with light lying in the fundamental absorption of the material. A recent paper by Brown and Wainfan[3] summarizes these phenomena in silver chloride.

Westervelt[4] and McLennan[5] have reported that colloidal metal particles can be formed in synthetic alkali halides by bombarding these materials with ionizing radiation. There was no appreciable stoichiometric excess of metal in these crystals after the irradiation.

The three following tests can be used to establish the existence of colloidal particles and to distinguish these from absorbing centers that are atomically dispersed: (1) There is a wavelength dependence of light scattered at right angles to the direction of the incident light beam. The wavelength at which maximum scattering occurs is dependent upon the size of the particle. (2) The absorption peak is insensitive to temperature. Neither the half-width nor peak position are appreciably changed by cooling from 300°K to 77°K. (3) Absorption of monochromatic light by the colloids bleaches the absorption band selectively at that wavelength and leaves the remainder of the band unaltered. Although

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* This work was presented in part at the Color Center Symposium, Argonne National Laboratory, October, 1956.

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

[2] K. Przibram, *Irradiation Colours and Luminescence* (Pergamon Press, Ltd., London, 1956).

[3] F. Brown and N. Wainfan, Phys. Rev. 105, 93 (1957).

[4] D. R. Westervelt, Phys. Rev. 92, 531 (1953).

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

this is observed in the silver halides, the colloids in the alkali halides are not bleached by light absorbed by the particles.

This paper gives the results of a study of the production of colloids by gamma rays and fast electrons in synthetic and natural crystals of sodium chloride. The presence of the colloids was established by applying the second criterion listed above; that is, the insensitivity of the absorption peak to temperature. The peak position of the band identified as arising from colloids agreed with the colloidal band obtained by slowly cooling a sodium chloride crystal containing excess sodium.

EXPERIMENTAL PROCEDURE

Natural and synthetic crystals of sodium chloride were irradiated in air at room temperature with Co^{60} gamma rays—1.1 and 1.3 Mev. The radiation flux averaged about 4.5×10^5 roentgens/hr. Similar samples were irradiated with 1.3-Mev electrons from a Van de Graaff generator. A beam current of 130 microamperes was used. The irradiation times varied between 2 days and 90 days for the gamma irradiation and between 5 minutes and 45 minutes for the fast-electron irradiation. The high beam currents utilized in the Van de Graaff irradiation resulted in an appreciable heating of the crystals. Thus the results obtained with electron irradiation can only be considered as qualitative.

Synthetic crystals were obtained from Harshaw Chemical Company and Optovac Company. Crystals were grown in this laboratory in air by the Kyropolous method. Natural crystals came from near Salina, Utah, Baden, Germany,[6] and Wielitschka, Poland. The crystals were cleaved into plates about 5 mm square by 0.15 mm thick prior to the irradiation. They were handled in red light after the irradiation.

In addition to the comparison among samples from various sources, a comparison was made among samples that had been annealed in various atmospheres. The crystals were heat-treated in the following atmospheres: (1) In air. The samples were placed in a platinum dish that was covered with a loose-fitting platinum lid. (2) In vacuum. Samples were sealed in a quartz tube in a vacuum of between 10^{-5} and 10^{-6} mm of Hg. (3) In dry oxygen. Quartz tubes containing the samples were evacuated to better than 10^{-5} mm of Hg and then filled with oxygen to a pressure of about 320 mm of Hg at room temperature. The oxygen was passed through a trap cooled with dry ice and acetone. (4) In dry helium. Samples were heated in an open-ended quartz tube through which a stream of helium was passed. (5) In wet helium. Samples were heated in an open-ended quartz tube. A stream of helium that had bubbled through boiling water was passed over the crystals while they were at the high temperatures. All the heat treatments were made at about 700°C for at least 24 hours. The crystals were then slowly cooled to room temperature over a period of about 2 days. The results were not affected by minor variations in the rate of cooling.

Optical absorption was measured with a Beckman Model DU spectrophotometer with the sample at room temperature or liquid-nitrogen temperature. The low-

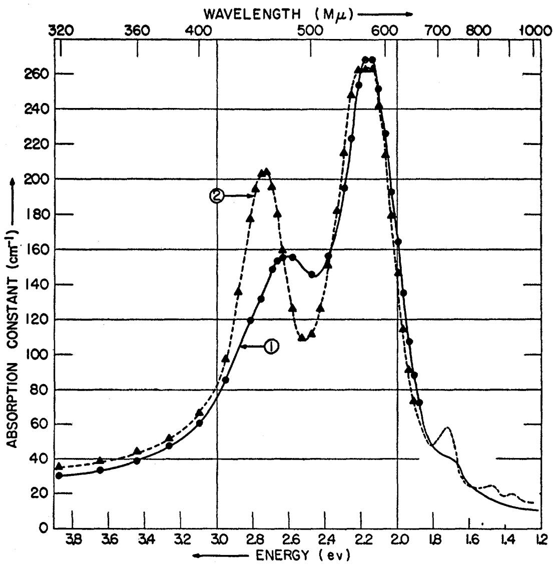

Fig. 1. Spectral absorption of a synthetic NaCl crystal grown in this laboratory after irradiation with 2.9×10^8 roentgens of Co^{60} gamma rays. Curve 1—measured at room temperature. Curve 2—measured at liquid-nitrogen temperature. The points at low energies were omitted from these curves and the curves of the subsequent figures for the sake of clarity.

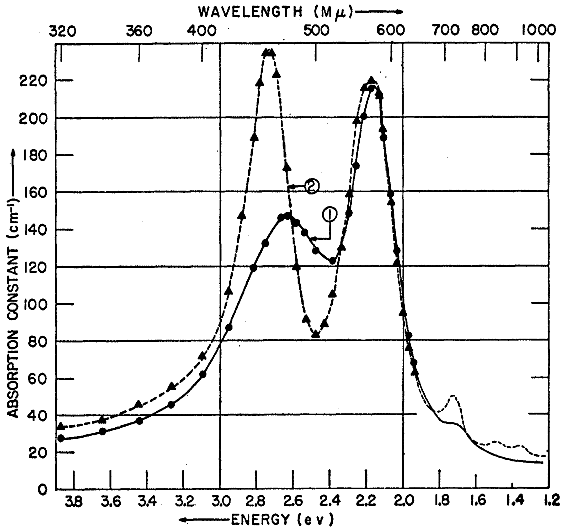

Fig. 2. Spectral absorption of a synthetic NaCl crystal grown in this laboratory after irradiation with 1.3-Mev electrons. Curve 1—measured at room temperature. Curve 2—measured at liquid-nitrogen temperature.

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[6] Halite crystals from Salina, Utah (Catalog No. 105044) and Baden, Germany (Catalog No. 62946) were made available by the Smithsonian Institution, Washington 25, D. C.

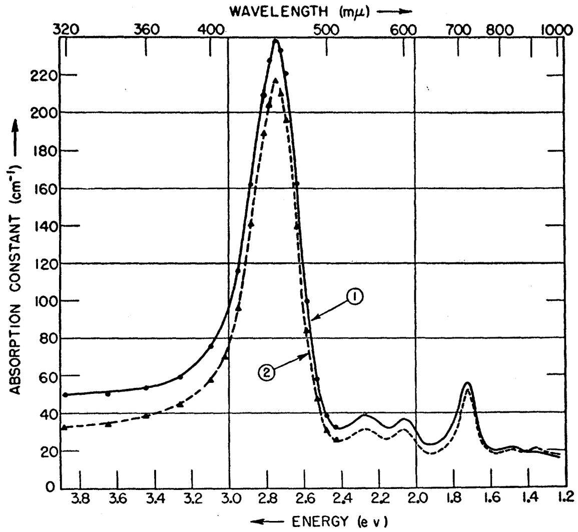

FIG. 3. Spectral absorption of natural NaCl crystals after irradiation with 3.9×10^8 roentgens of Co^{60} gamma rays. Curve 1—crystal from near Salina, Utah. Curve 2—crystal from near Baden, Germany. All measurements were made at liquid-nitrogen temperature.

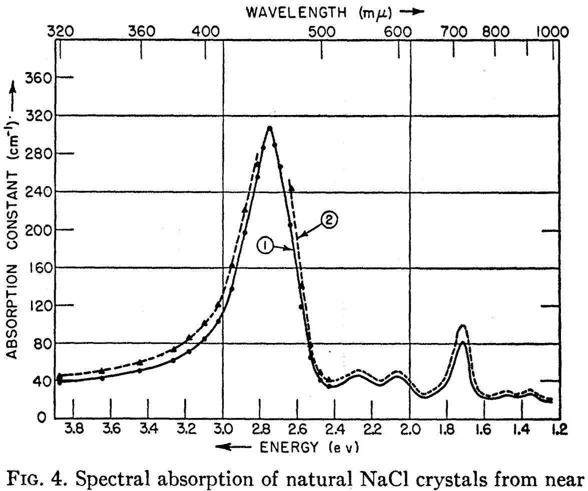

FIG. 4. Spectral absorption of natural NaCl crystals from near Baden, Germany, after irradiation with 9.7×10^8 roentgens of Co^{60} gamma rays. Curve 1—crystal was heated in vacuum prior to the irradiation. Curve 2—crystal was heated in a dry oxygen atmosphere prior to the irradiation. All measurements were made at liquid-nitrogen temperature.

temperature measurements were made with the Dewar described by Russell and Klick.[7]

RESULTS

For gamma-ray doses of less than 5×10^7 roentgens, only *F*, *M*, and a few *R* centers were formed in all of the various crystals. Gamma irradiations of greater than 10^8 roentgens developed the colloid band in the synthetic crystals grown in this laboratory. The spectral absorption of these crystals after heavy gamma irradiation and fast-electron bombardment are shown in Figs. 1 and 2 respectively. The peak at 2.18 ev is associated with the colloids. The same qualitative results were found for Harshaw crystals. However, the tendency to form colloids varied greatly between two groups of Harshaw crystals. One group of crystals showed a considerably stronger tendency to develop the colloids than did the crystals grown in the laboratory, while the other group showed a much lower tendency. The sample of Optovac sodium chloride did not develop colloids even after 8.8×10^8 roentgens. This difference in synthetic crystals will be discussed further.

No evidence of a colloid band was found in natural crystals that were irradiated prior to an annealing treatment. Figure 3 shows the spectral absorption of samples of crystals from Salina, Utah, and Baden, Germany, after 3.9×10^8 roentgens of gamma rays. The crystal from Wielitschka, Poland, showed no colloids after 8.8×10^8 roentgens. Thus, a distinct difference existed between the natural and synthetic crystals.

The natural crystals were now annealed. It was hoped that a treatment would be found that would result in the production of colloids in these crystals.

A sample of the Salina, Utah, natural crystal was annealed in air. It was found that all surfaces of this crystal showed a strong tendency to develop colloids while the interior did not. This surface layer containing the colloids was only about one mm thick. Only *F*, *M*, and *R* centers were found in the interior of the crystal after irradiation. Thus, it is assumed that some impurity diffused into the crystal from the atmosphere.

The results of irradiation of natural crystals that had been annealed in vacuum or oxygen are shown in Fig. 4. The surface of the oxygen-annealed sample was used for this measurement. The absence of the colloid band in these samples after the strong gamma irradiation implies that the atmospheric impurity was not oxygen.

Figure 5 shows the absorption spectra of irradiated crystals that had been annealed in wet and dry helium. The same results were obtained on samples from Salina, Utah, and Baden, Germany. No colloids were found in the natural crystals that had been annealed in dry helium even after 6.7×10^8 roentgens of gamma rays. Irradiation of successive layers of the crystal that had been annealed in wet helium indicated that the impurity had only penetrated a short distance—a result very similar to that found for the crystal annealed in air.

From these results, it is concluded that hydrolysis of the crystals at high temperatures is sufficient to make possible the production of colloids by ionizing irradiation. It is presumed that the hydroxyl ion was the impurity that diffused into the crystals.

The spectral absorption of an irradiated synthetic crystal that had been annealed in vacuum is shown in Fig. 6. The amount of colloid band that was produced by irradiation was radically reduced by the annealing. However, the ill-defined minimum between the R_1 and

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[7] G. Russell and C. Klick, Phys. Rev. **101**, 1473 (1956).

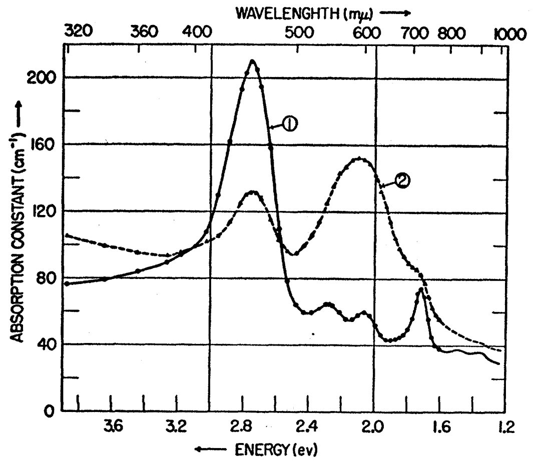

FIG. 5. Spectral absorption of natural NaCl crystals from near Baden, Germany, after irradiation with 3.3×10^8 roentgens of Co^{60} gamma rays. Curve 1—crystal was heated in dry helium prior to the irradiation. Curve 2—crystal was heated in wet helium prior to the irradiation. All measurements were made at liquid-nitrogen temperature.

R_2 bands indicates that a small colloid band was present. This is supported by the observation that further irradiation resulted in a very large colloid band. Thus, the vacuum annealing merely retarded the growth of the colloids.

Figure 7 gives the absorption coefficient at the peak of the F band and the colloid band as a function of irradiation for four crystals. It is noted that the F band approaches a saturation level while the colloid band is rapidly increasing. The only crystal that contained an appreciable number of colloids was the untreated synthetic crystal. Thus, it is concluded that the rate of production of F centers is essentially independent of the concentration of colloids. The natural crystals were all found to have slightly greater F, M, and R bands after annealing than before annealing. This is not unreasonable, since impurities occluded in the crystals are put into solution by the anneal. Thus, variations in the amounts of F, M, and R bands observed after annealing are not considered to be important. The data for the annealed Baden crystal are presented to show that after an initial rapid coloration the rate of production of the F centers is not altered appreciably by the anneal.

The concentration of M centers is also nearly independent of the concentration of colloids. In fact, the ratio of the absorption at the peak of the F band to the absorption at the peak of the M band is independent of the colloid concentration. It is found that this ratio approaches a constant for large doses and that this constant is the same within about 5% for all samples except one for irradiations greater than 3×10^8 roentgens. That is,

$$\alpha_F/\alpha_M \rightarrow 4.5.$$

The exception was the halite sample from Poland. The lack of dependence of this ratio upon the concentration of colloids in the crystal is clearly shown in Fig. 6.

The half-width of the colloid band decreased about 25% with increasing irradiation. It is suggested that the colloids that are initially formed are of random sizes whereas those formed after long irradiations are more uniform in size. The wavelength of the peak position remained nearly constant, however.

As a result of the importance of the hydroxyl ion in the synthetic crystals, an attempt was made to determine its concentration by measuring the infrared absorption of the crystal at 2.7 μ. Only a weak absorption was found. The OH^- concentration in the crystal was estimated to be no greater than a few parts per million from this absorption.

Formation of colloidal particles of sodium was found to occur in natural crystals of sodium chloride that were additively colored at 730°C and then slowly cooled. The sodium was triply distilled under vacuum into a Pyrex tube containing the crystals and the tube was then sealed off under vacuum. The capsule was then sealed in quartz at a pressure that prevented collapse of the Pyrex at the high temperature. This procedure was designed to eliminate all hydroxyl ions from the container. Thus, hydroxyl ions do not seem to be necessary for the formation of colloids in additively colored crystals.

DISCUSSION

Hydroxyl ions are probably introduced into the synthetic crystals when they are grown in air. Evidence exists that potassium chloride that is melted in air contains hydroxyl ions, whereas material melted in HCl vapor does not.[8] It is suggested, then, that

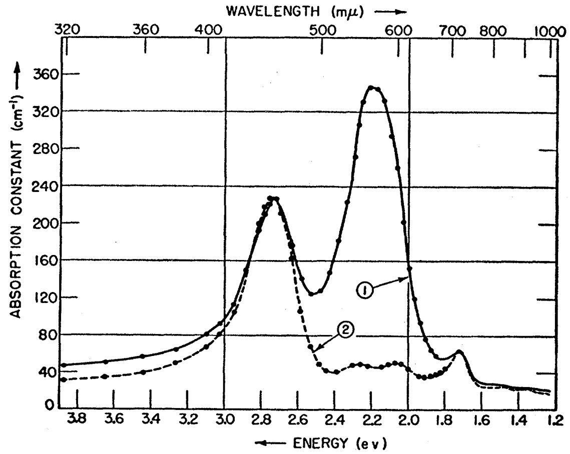

FIG. 6. Spectral absorption of a synthetic NaCl crystal grown in this laboratory. Curve 1—untreated prior to irradiation with 3.9×10^8 roentgens of Co^{60} gamma rays. Curve 2—heated in vacuum prior to irradiation with 4.2×10^8 roentgens of Co^{60} gamma rays. All measurements were made at liquid-nitrogen temperature.

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[8] Mr. Robert Ginther of this laboratory has observed that the visible luminescence excited by 2537 A light in uncolored synthetic KCl is destroyed if it has been melted in an HCl atmosphere.

hydroxyl-free synthetic crystals can be produced by growing the crystals in a dry inert atmosphere from material that has been purged of the OH^- by a prior melting in HCl vapor.

The hydroxyl-ion content of crystals may depend strongly upon the portion of the boule from which they come. This may account for the differences between the two batches of Harshaw crystals. It appears that the Optovac crystal contained no hydroxyl.

It is also concluded that the crystal must be at a high temperature if the hydroxyl ion is to substitute into the lattice. Otherwise, natural crystals, that are presumed to have grown from an aqueous solution, would also contain this impurity in a substituted form. The amount of occluded water in these natural samples was insufficient to produce an appreciable hydrolysis of the crystals when they were annealed.

If hydroxyl ions are not substituted into the lattice of the natural crystals, then one must look elsewhere for the source of colloids in the naturally occurring blue rocksalt crystals. There does not seem to be a uniformly accepted theory of the process of formation of these colloids. It is thought that they are produced by ionizing radiation from radioactive minerals. Przibram mentions that a blue rocksalt crystal that has been bleached by heating shows no tendency to re-form the colloid upon irradiation. One does not know how strongly it was irradiated, however. Przibram[9] presumes, then, that an impurity complex, some type of imperfection or the long duration of the irradiation process in nature is responsible for the colloid formation in blue rocksalt.

It is usually presumed that colloidal alkali-metal particles are formed by coagulation of *F* centers into sufficiently large groups that the alkali-metal ions can trap the electrons from the *F* centers and coalesce. Thus, *F* centers are annihilated during the formation of the colloid. The number of *F* centers used in this process can be estimated if the oscillator strength of an *F* center in a colloid is known. This has been estimated by Seitz[1] to be about four times that of the isolated *F* center. This value is given qualitative support by the observations of Scott and Smith who found that the total area under the *F* and colloid bands increased as the *F* centers were converted into colloids.[10] The colloid bands produced here by 3.8×10^8 roentgens have half-widths comparable to the *F* band. Noting that the absorption of the colloid band is somewhat larger than the *F* band for a dose of 3.8×10^8 roentgens (see Fig. 7), one concludes that the number of *F* centers used in forming the colloids in the crystal grown in this laboratory is roughly one-third of the number of isolated *F* centers at that dose.

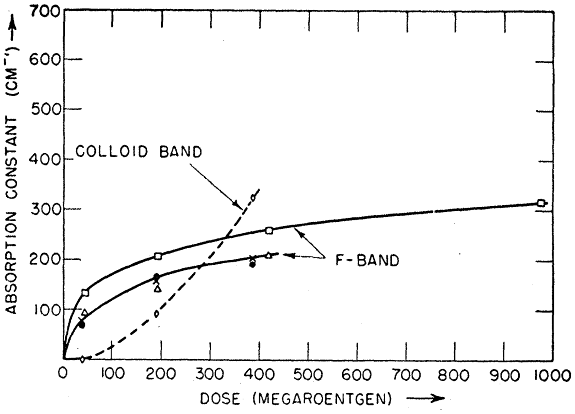

FIG. 7. Absorption constant *vs* Co^{60} gamma-ray dose as measured at liquid-nitrogen temperature. ●, □, △, and ×—measurements at the peak of the *F* band. ●—natural crystal from Baden, Germany. Crystal was untreated prior to irradiation. □—natural crystal from Baden, Germany. Crystal was heated in vacuum prior to irradiation. △—synthetic crystal grown in this laboratory. Crystal was heated in vacuum prior to irradiation. ×—synthetic crystal grown in this laboratory. Crystal was untreated prior to irradiation. ◇—measurements at the peak of the colloid band on the synthetic crystal grown in this laboratory that was untreated prior to irradiation.

The independence of the *F*-center concentration upon the concentration of colloids is in agreement with the results of a study by Scott and Smith[10] on additively colored KCl. They concluded that the interaction of the colloids and *F* centers is similar to that of a gas in equilibrium with its liquid phase.

Thus, in most respects, colloidal particles formed by ionizing radiation behave similarly to those formed in additively colored crystals. An important difference seems to be the role played by the impurity OH^- in sensitizing the growth of the particles in radiation-damaged crystals.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. W. F. Foshag and Mr. G. Switzer of the Smithsonian Institute for providing the samples of halite from Baden, Germany, and Salina, Utah, to Professor H. Pick of the Physikalisches Institute of Stuttgart, Germany, for the sample of halite from Wielitschka, Poland, and to Mr. J. Hon of Brown University for the Optovac crystal sample. I would like to thank Dr. James H. Schulman, Dr. C. C. Klick, and Mr. Robert Ginther for many helpful discussions, and Mr. James Allard and Mr. Peter Vrahiotes for carrying out the irradiations.

If this material is then fired with KOH, it is found that 2537 A light now excites the crystal and that the luminescence is the same as was observed prior to the melting in HCl. Natural halite crystals do not exhibit such a luminescence while the synthetic crystals of Harshaw and those grown in this laboratory do give such a luminescence when excited by ultraviolet radiation.

[9] See reference 2, p. 139.

[10] A. Scott and W. Smith, Phys. Rev. 83, 982 (1951).