Radiation induced color center and colloid formation in synthetic NaCl and natural rock salt

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Résumé. — On étudie la formation de centres F et de particules colloïdales dans des cristaux naturels et synthétiques de NaCl avec un appareil permettant la mesure de l'absorption optique pendant l'irradiation. La formation des centres F et des particules colloïdales dépend, entre autres, de la température, due au taux d'irradiation et de la dose totale, ainsi que des contraintes appliquées avant irradiation. Beaucoup de propriétés observées répondent à la théorie de Jain-Lidiard pour la croissance des centres F et des particules colloïdales induites par irradiation au-dessus de la température ordinaire.

Abstract. — F-center and colloid particle formation have been studied in synthetic NaCl and natural rock salt crystals with apparatus for making optical absorption measurements during irradiation. F-center and colloid formation are functions of temperature, dose, dose rate, strain applied prior to irradiation and numerous other factors. Many of the observed properties are in accord with the Jain-Lidiard theory for radiation induced F-center and colloid growth above room temperature.

1. **Introduction.** — Radiation induced color center formation in the alkali halides have been studied extensively at or below room temperature but not, in comparative detail, above room temperature. Coloring studies on natural and synthetic rock salt (NaCl) at elevated temperatures are of interest for purely basic reasons and for practical radioactive waste disposal considerations. However, basic radiation effect aspects will be emphasized in this paper.

For three decades or more references to colloid formation have been scattered throughout the color center literature. Space is not available to describe them here. Most of the recent work on radiation effects in natural and synthetic rock salt was undertaken by groups at Oak Ridge National Laboratory and Harwell. Much of the Oak Ridge work, particularly that on stored energy, is described in a widely distributed report [1]. Chemical properties of irradiated NaCl have also been investigated [2]. The Harwell efforts, which included numerous electron microscope studies, are described in numerous reports and papers [3-6]. These studies established many of the general features of radiation induced color center and colloid formation in synthetic NaCl above room temperature. They will be described below, but in the context of the measurements to be described in this paper. The experimental studies, particularly those at Harwell, are the basis of a general theory of color center and colloid particle formation in sodium chloride above room temperature formulated by U. Jain and A. B. Lidiard [7].

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2. **Experimental techniques.** — All of the measurements outlined below were made with equipment at Brookhaven National Laboratory for making optical measurements on samples during irradiation with 0.5-3.0 MeV electrons (Fig. 1), at dose rates in the 10^4-10^9 rad per hour range. The optical absorption of the sample, and any radioluminescence, can be recorded as often as every 40 s in the 200-400 or 400-800 nm range. Only absorption measurements in the 400-800 nm region are described here. Luminescence has been observed during irradiation from both natural and synthetic salt samples but has not been studied in detail. The samples are located in a temperature controlled chamber containing inert gas. Even at the highest dose rates, the sample temperature is never more than a few degrees above the chamber temperature. Numerous measurements have been made on both synthetic NaCl crystals and on natural rock salt samples from a variety of geological locations.

3. **Measurements.** — The measurements described here were chosen to emphasize the most general features of radiation induced defects formation in NaCl which can be compared to the Jain-Lidiard Theory. Additional details are contained in published or soon to be published papers [8, 9].

Measurements made on *synthetic* NaCl at room temperature are in accord with the results reported

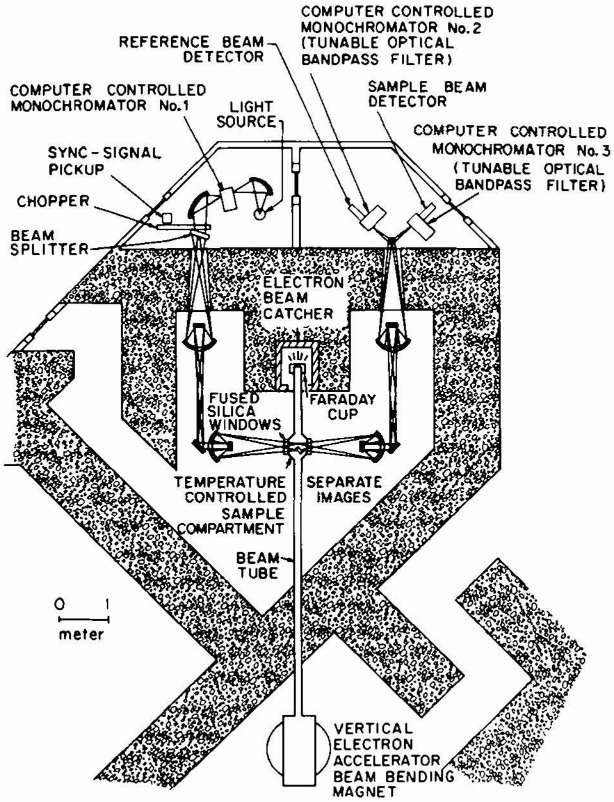

Fig. 1. — Experimental equipment used to study radiation damage in synthetic and natural rock salt samples.

in the literature. F-center concentration *vs.* dose curves, i.e. the growth curves, increase monotonically and appear to be approaching a plateau or a nearly linear curve with pronounced slope. At room temperature, F-center growth in natural rock salt crystals is similar to that observed in synthetic crystals. However, in natural salt F-center growth is accurately described by a (irradiation time) $^{1/2}$ dependency not observed in synthetic crystals.

3.1 F-CENTER AND COLLOID FORMATION IN THE 100-300 °C TEMPERATURE RANGE. — Radiation induced F-center and colloid growth, in the temperature range where colloid growth is observed, is illustrated by figure 2. This figure shows absorption spectra obtained with synthetic NaCl crystals irradiated with electrons at approximately 1.2×10^8 rad per hour and at 150 °C. Successive recorded spectra are identified by scan numbers. Qualitative features illustrated by figure 2 apply to both synthetic and natural samples throughout the temperature range where colloid growth is observed. A typical F-center growth curve is obtained at low doses. At the dose corresponding approximately to F-center *saturation* the colloid formation rate increases from a low or negligible value to a rapidly increasing one. Thus colloid concentration *vs.* dose curves closely resemble classical *nucleation-and-growth* curves which can be specified by an arbitrarily defined

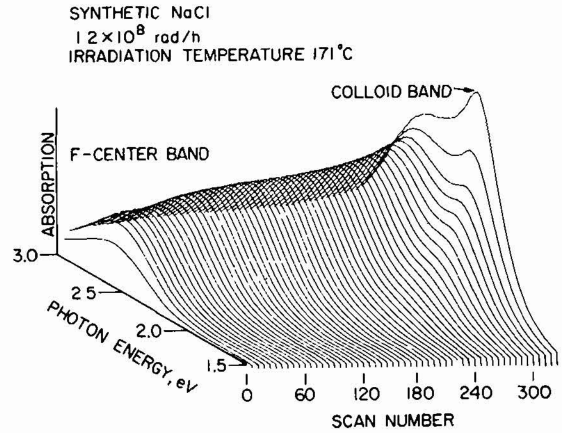

Fig. 2. — Radiation induced absorption spectra in NaCl recorded at four minute intervals during irradiation with 1.5 MeV electrons. The F-center growth is observed immediately after irradiation commences, but rapid colloid growth is proceeded by a pronounced induction period.

induction period and a rapidly increasing segment well approximated by a power law.

The measured absorption in synthetic NaCl near the peak of the F-band, illustrated in figure 3, shows three important features. First, as the irradiation temperature increases the *saturation* level

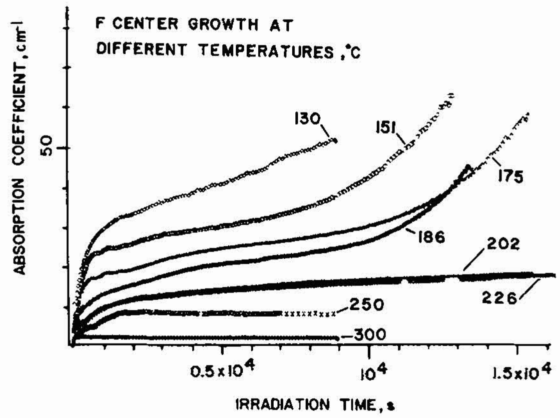

Fig. 3. — Growth of optical absorption, near the F-center peak, recorded during irradiation of synthetic NaCl. This data has not been corrected for the contribution from the overlapping colloid band.

decreases. Second, in natural rock salt and above 200 °C in synthetic NaCl, the rate at which the F-centers reach saturation increases as the temperature increases. Third, the activation energy for vacancy migration contributing to colloid particle growth, calculated from the measured saturation levels using the Jain-Lidiard theory, is 0.2 eV below 250 °C and 0.9 eV at higher temperatures. Comparisons between the data and the Jain-Lidiard theory are summarized in table I.

A number of curves showing optical absorption *vs.* irradiation time, near the peak of the colloid

Table I. — *Selected comparisons with Jain-Lidiard theory.*

Theory	Synthetic NaCl	Natural rock salt
F-centers increase monotonically to a *saturation* level	observed	observed
F-saturation level independent of crystal source and strain	observed	observed
F-saturation level varies as (dose rate) $^{1/2}$	observed	observed
Activation energy obtained from F-center saturation single valued and ≈ 0.4 eV	0.2 eV observed below ≈ 250 °C and 0.9 eV above ≈ 250 °C	under study
Colloid formation in a restricted temp. range	observed	observed
Colloid formation not observed at low dose rate	not studied	not studied
Colloid induction period dependent on dislocation density	observed : induction period reduced by prior strain	observed : induction period reduced by prior strain
Colloid formation rate in the t^2 to $t^{3/2}$ range	t^4 to t^5 observed in unstrained crystals, $t^{2.1}$ to $t^{2.3}$ observed in highly strained crystals	$t^{2.1}$ to $t^{2.3}$ observed in crystals not additionally strained

band are shown in figure 4. Irrespective of the choice of nucleation and growth parameters, it is found that colloid growth is low at 100 °C, increases to a maximum in the 150-175 °C range and decreases to a negligible value at approximately 250 °C. In synthetic NaCl the rapidly increasing portions of the colloid growth curves are well approximated by a power law of the form t^4 to t^5, where t is irradiation time. In contrast, in natural rock salt colloid growth curves are well approximated by $t^{2.1}$ to $t^{2.3}$ dependencies. This is one of several results illustrating differences between natural and synthetic rock salt.

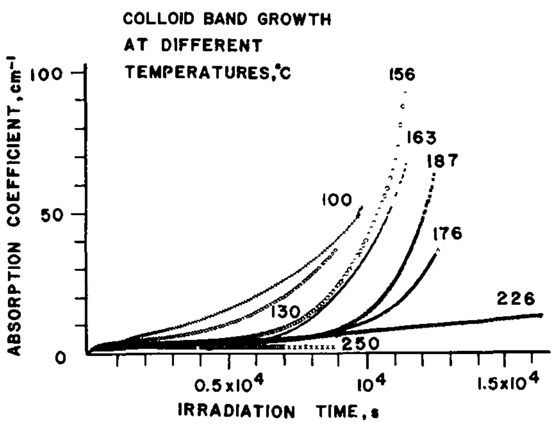

Fig. 4. — Growth of optical absorption, near the colloid band peak, recorded during irradiation of synthetic NaCl. This data has not been corrected for the contribution from the overlapping F-center band.

3.2 STRAIN OR PLASTIC DEFORMATION EFFECTS. — Only results obtained with synthetic crystals irradiated at a fixed temperature and dose rate will be described. Samples were slowly compressed to different strains ranging from zero to approximately 10 %, prior to irradiation. This increases the initial F-center coloring rate and decreases the colloid growth curve induction period dramatically, as shown in figure 5. This observation strongly suggests, but does not prove, that the nuclei for colloid formation are dislocation related. Natural samples, not strained prior to irradiation, exhibit shortened induction periods that can be explained by assuming the samples were strained by geological forces.

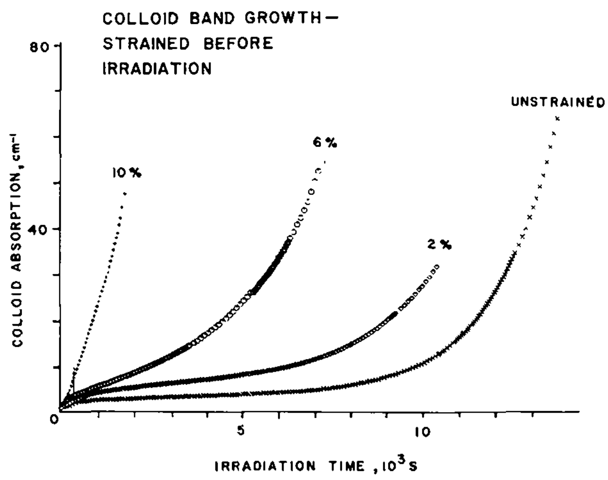

Fig. 5. — Colloid band growth curves for synthetic NaCl crystals both unstrained and strained the indicated amounts prior to irradiation.

4. **Comparison with Jain-Lidiard theory.** — The results outlined above are compared with selected elements of the Jain-Lidiard theory [7] in table I. It is apparent that many aspects of the theory are in accord with the observations. Also, there are points

of disagreement. Some may be experimental artifacts and others may be removed by slightly modifying the theory.

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