PHYSICAL REVIEW B VOLUME 50, NUMBER 14 1 OCTOBER 1994-II

Radiation damage in NaCl. II. The early stage of F-center aggregation

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(Received 3 September 1993; revised manuscript received 2 March 1994)

We study the early stage of aggregation of F centers into colloids in pure NaCl under irradiation. The crystals have been electron irradiated with a dose rate of 2 Mrad/h up to doses of 1500 Mrad and measured by optical-absorption spectroscopy. The major bands, the F, M, and the colloid band, are analyzed qualitatively as well as quantitatively. We have observed a relationship between the concentrations of the F and the M centers, which changes from quadratic to linear. The colloid band appears to peak at two distinct wavelengths, indicating that two types of colloids are formed during the nucleation stage. The defect concentrations are determined as a function of the dose and the irradiation temperature and are discussed in terms of models which describe the kinetics of defect formation.

I. INTRODUCTION

The coloring of alkali halides under irradiation has been investigated extensively, in connection with the purpose of storing radioactive waste in salt domes.[1-3] Optical-absorption spectroscopy is a technique which provides a detailed and extensive knowledge about the development of the defect concentrations under irradiation. However, the technique is limited to moderate defect concentrations, such that most of the early investigations concern irradiations with doses lower than 500 Mrad. For higher doses the measurement becomes complicated, since the crystal has to be thinned to thicknesses of less than 10 μm.[4,5] In this paper we report our measurements of pure crystals irradiated with doses in the region 20–1500 Mrad and at temperatures in the range of 20–150 °C. In this region the defect structure changes from mainly F and M centers to mainly colloidal centers. Therefore, this region is of particular interest in the investigation of the nucleation stage in the formation of colloids.

II. EXPERIMENTAL TECHNIQUES

The crystals have been irradiated with a 1.3-MeV electron beam scanned over a multisample target with a total area of 303 cm^2.[6] The crystals were of high purity, typically 1 ppm contamination with a maximum of 5 ppm potassium. The irradiation doses were 20 Mrad (0.2 MGy), 40, 80, 100, 160, 430, 1000, and 1500 Mrad, realized with a dose rate of 2 Mrad/h. To reach this low dose rate the Van de Graaff generator had to be operated at a very small beam current of 1.14-μA. The accuracy in adjusting these small current values is limited, therefore, it is possible that the effective doses deviate systematically from the given values by at most 30%. The irradiation temperatures have been chosen in the range of 20–150 °C, the region in which the F centers become mobile and may eventually coagulate to larger aggregates.

In order to perform the measurement the crystals were glued onto an optically flat glass plate. Thereafter, they were thinned by a special grinding device, which made measurement of samples with thicknesses less than 2 μm possible, with an accuracy of 0.5 μm (see paper I).[4] The optical-absorption spectra were measured with a Perkin Elmer Lambda-9 spectrophotometer. The calculation of the band areas has been carried out by choosing a base line from the minimum at about 350 nm to the minimum at 850 nm. The height and width were calculated in cm^{-1} and eV, respectively.

The irradiation produces mainly F, M, and colloidal centers. To determine the number of electronic centers we have used Smakula's equation:[7]

$$Nf=\frac{mc}{\pi e^2 h}\left[\frac{3}{n^2+2}\right]^2 n\cdot\frac{1}{2}\pi k_m W_{1/2} \ , \tag{1}$$

where N is the number of centers per unit volume in cm^{-3}, n is the index of refraction of the host crystal at the center of the absorption band, k_m is the maximum absorption constant in cm^{-1}, $W_{1/2}$ is the full width of the absorption band at half-maximum in eV, and f is the oscillator strength. The assumed line shape is Lorentzian with a bandshape factor of $\frac{1}{2}\pi$. The term between brackets is the Lorentz local-field correction. The oscillator strength is 0.86, evaluated by many authors,[8] using Smakula's equation. In the case of sodium chloride the following numerical values can be substituted (cgs units): $n=1.54$, $e=4.8\times10^{-10}$ esu, $h=4.14\times10^{-15}$ eV s, $c=3\times10^{10}$ cm/s and $m=9.11\times10^{-28}$ g. This leads to the following relation between peak height and width and the concentration of centers:

$$N=1.18\times10^{16} k_m W_{1/2} \ . \tag{2}$$

Since the integrated absorption under transformation (e.g., by bleaching or annealing a crystal with F centers) is constant we can apply the general sum rule, i.e., $\sum f$ is constant for all electron centers.[9,10] If we assume that the other bands are also Lorentzian we can use Eq. (2) also to calculate the number of M and colloid centers. In the Appendix the errors involved in these assumptions are reconsidered in more detail.

0163-1829/94/50(14)/9787(6)/$06.00

III. MEASUREMENTS AND DISCUSSION

A. The spectra

Figures 1(a) and 1(b) show the development of the bands at a different irradiation temperatures. At low temperatures the main bands are the *F* and *M* band, which are located at 460 and 723 nm, respectively. The *N* band is only very small and has not been studied here. Possibly, the shoulder in the tail of the *F* band at 580 nm represents the colloid band, however it is indistinguishable from the *R* band, which grows at about the same position. The width of the *F* band varied between 0.50 and 0.55 eV. With increasing doses the crossover from a spectrum with a dominant *F* band to a spectrum with a dominant colloid band occurs at a lower irradiation temperature. At this temperature the number of absorbing centers reaches a minimum. The rise in absorption in the ultraviolet is due to the glass plate on which the samples were mounted.

The colloid band starts to grow at a wavelength of 580 nm and has a line width of about 120 nm (0.4–0.5 eV). At doses of 430 Mrad and higher a second peak starts to grow, at first at high temperatures. This peak is located at 680–690 nm and has a linewidth of approximately 100 nm (0.3 eV). In order to interpret this position and linewidth in terms of particle sizes we can use Mie's theory for the optical absorption of small metallic particles.[9,11–13] In this theory the electron is treated as a free electron and a size effect occurs if the particle diameter becomes smaller than the mean free path of the electrons (about 350 Å), due to scattering of the electron at the particle surface. A refinement of the theory is based on the effect that the density of electrons decreases with decreasing particle size (spillout of electrons).[4,5,14]

A relatively large linewidth of 0.4–0.5 eV located near the minimum wavelength where a colloid band is found (580 nm) suggests that we are dealing with the size effect due to surface collisions. This results in a particle diameter in the range of 30–100 Å. The relatively high wavelength of 680–690 nm of the second peak in combination with a large width of 0.3 eV indicates that we are dealing either with particles with a diameter smaller than 20 Å (where the spillout causes a shift to long wavelengths, $\omega_p^2 \sim n$), or with particles with a diameter larger than 700 Å. Since the instantaneous formation of a large particle of 700 Å is hardly to be expected and since at larger doses the colloid peak is found at 580 nm we assume that this peak is due to extremely small particles (< 20 Å).

The calculations show that the position of the plasmon peak is very sensitive to the particle radius. Therefore, it should be noted that the estimates given above will be quite rough. It cannot be excluded that we are dealing with a distribution of particle sizes resulting in a superposition of overlapping bands. If so, it is difficult to understand why this distribution is partitioned into two size classes, with the larger colloids appearing at first. We could also be dealing with nonspherically shaped colloids, e.g., ellipsoidal shapes,[15–17] with different plasma resonances for each axial direction. The change in the ratio of the two band maxima would then be caused by a varying particle shape.

In order to investigate the development of the different bands we have calculated the number of *F* and colloidal centers in the dose range from 20 to 1500 Mrad. The growth of the *F* band is shown in Fig. 2. It is clear that at higher temperatures the *F*-center concentration stabi-

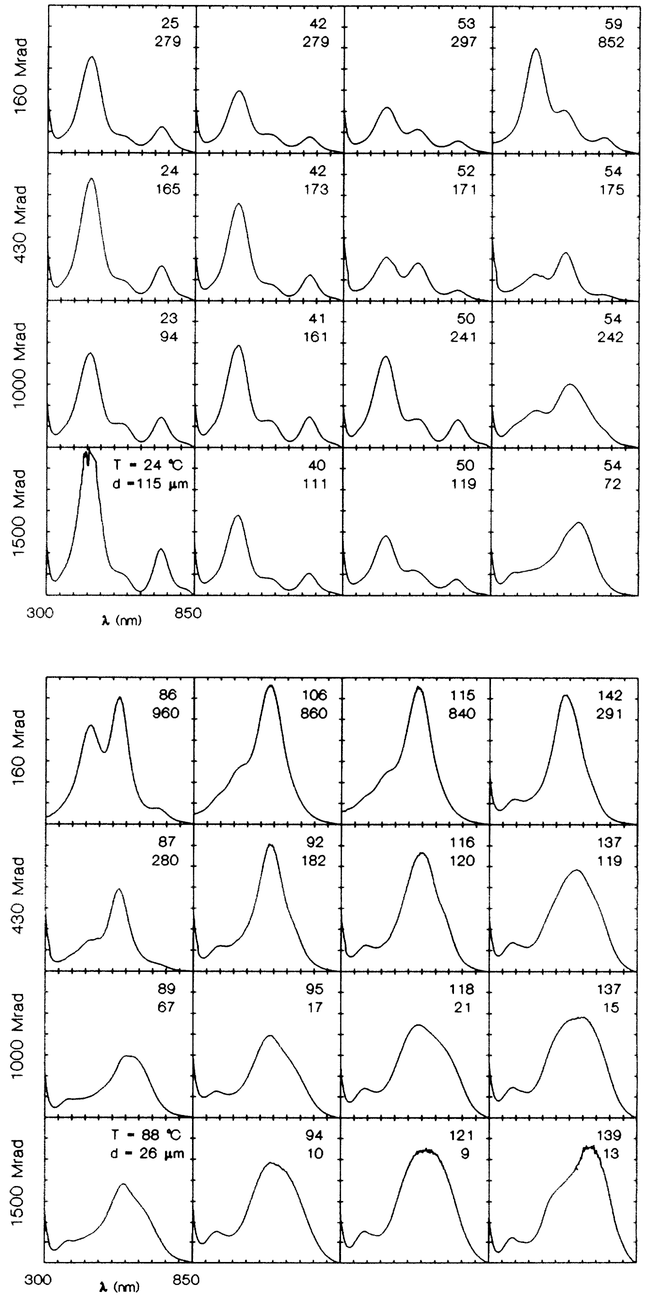

FIG. 1. (a) Optical-absorption spectra of pure NaCl irradiated at low temperatures with a dose rate of 2 Mrad/h. The irradiation temperatures and sample thicknesses are denoted in the upper right corners in °C and μm, respectively. The absorption axis has a full scale of 3.5. (b) Optical-absorption spectra of pure NaCl irradiated at high temperatures with a dose rate of 2 Mrad/h. The irradiation temperatures and sample thicknesses are denoted in the upper right corners in °C and μm, respectively. The absorption axis has a full scale of 3.5.

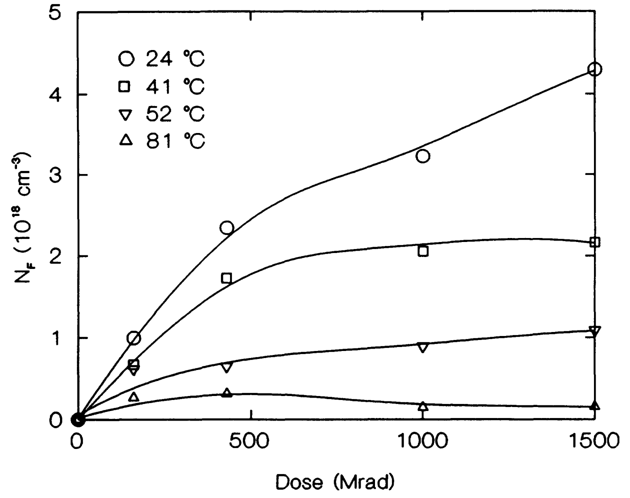

FIG. 2. The development of the number of F centers versus dose for different irradiation temperatures (dose rate = 2 Mrad/h).

lizes, while at low temperatures it continues to grow. In the dose range under study the production of colloids becomes very fast, at first at high temperatures. For doses below 1 Grad the maximum production efficiency is obtained at a temperature higher than 135 °C. From Fig. 3 it can be seen that with increasing dose the growth curve bends down for high temperatures, resulting in the observation that the maximum amount of colloidal centers is reached at lower irradiation temperatures.

The results of calculations based on the model of Jain and Lidiard,[18,19] agree qualitatively with these features. This model describes the kinetics of defect formation, and is developed further by several workers, to describe the effect of a backreaction in more detail[20,21] and the effect of impurities on the nucleation of F and H centers.[22] According to these models the bending down of the growth curve at high temperatures is due to the increased evaporation of F centers from the colloid at high temperatures.

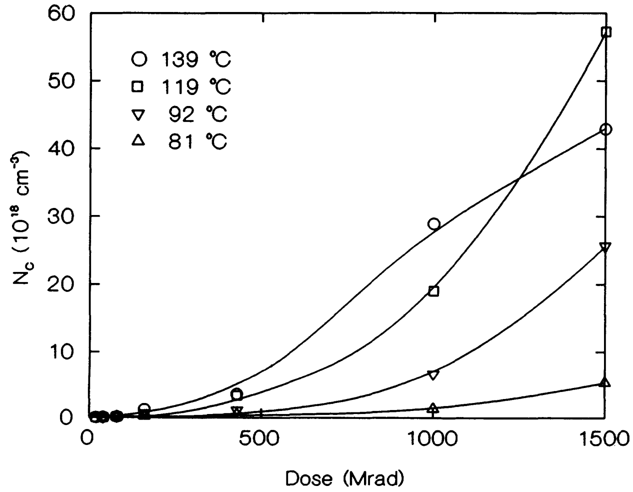

FIG. 3. The development of the number of colloid centers versus dose for different irradiation temperatures (dose rate = 2 Mrad/h).

B. The relationship between F and M centers

If we take a closer look at the F- and M-center concentration we find that for low doses (40–80 Mrad) the relationship is quadratic, independent of dose or irradiation temperature (Fig. 4). The ratio between N_F^2 and N_M is 2.2×10^{19} cm^{-3}, or about 2×10^{-3} cm/optical density (OD) which is of the same order of magnitude as the values reported by Hodgson, Delgado, and Alvarez Rivas.[23-25] These authors also found a quadratic relationship, in the low-dose (< 10 Mrad) and low-dose-rate regime, and observed a clear dependence on the impurity content (8×10^{-4}–7×10^{-3} cm/OD, decreasing with increasing impurity content). Hodgson, Delgado, and Alvarez Rivas explained the quadratic relationship by the statistical production of M centers. It can also be explained solely by the diffusion of F and the dissociation of M centers. This concept has been introduced into the model for the nucleation kinetics.[22] Under the assumption that the dissociation of M centers is the dominant reaction involving the M centers, it can be derived that

$$c_{F_2}=\frac{K_F}{K_{F_2}^{(e)}}C_F^2 . \qquad (3)$$

Here c_F and c_{F_2} are the fractional number of F and M

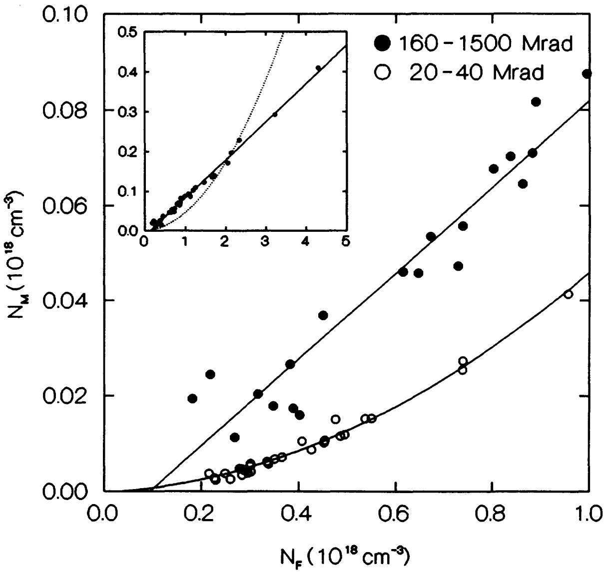

FIG. 4. The relation between F and M centers for different dose regimes. For the low-dose regime (20–40 Mrad) $T_{\mathrm{irr}}=20$–$130\,^{\circ}$C. For the high-dose regime (160–1500) the temperature range is smaller, $T_{\mathrm{irr}}=20$–$100\,^{\circ}$C, since at temperatures higher than 100 °C the growth of the colloid band dominates the spectrum. The inset shows the full set of high-dose data points, together with the quadratic relationship (dotted line).

centers (one F_2 represents two electronic centers) and K_F and $K_{F_2}^{(e)}$ are the rate constants for formation and dissociation of the M centers, respectively.

In the dose regime around 100 Mrad the relationship between the F- and M-center concentration changes from a quadratic to a linear relationship. This crossover occurs at first at low temperatures, the region in which the production of F centers is the highest. After 160 Mrad the linear relationship has set in (Fig. 4), $N_M = 0.10\ N_F$, independent of the irradiation temperature. Hodgson, Delgado, and Alvarez Rivas also observed deviations from the quadratic relationship at higher doses, which were ascribed to a radiation-induced short-range diffusion. The model calculations based on the nucleation kinetics give a quadratic relationship without any deviations due to other reactions (such as the capture of other F centers by M centers or the recombination of M and H centers), and the result is not affected by the impurity content. It is clear that the model requires improvements at this point.

C. The temperature dependence of defect formation

Since in the temperature and dose region under study the aggregation is completely governed by the increase of the mobility of the F centers for increasing temperatures, it may be expected that the concentration of absorbing centers can be related to the migration energy for the F centers, E_F. In Fig. 5 the F-, M-, and colloid-center concentrations are plotted against $1/kT$ for a dose of 160 Mrad. It can be seen that the respective concentrations are proportional to $\exp(\pm A/kT)$. In Table I we have compiled the slope A_i with $i = F$, M or C, for the F, M and the colloid band for increasing doses. The temperature dependence of the M band at high doses is not given since the M band is relatively weak at high temperatures and therefore difficult to measure. The same argument applies to the colloid band at low doses. According to the kinetic models[18,19,22] the F-center fraction stabilizes at a value of

$$c_F^{\text{sat}} = \left[\frac{KD_H}{K_2 D_F}\right]^{1/2}, \tag{4}$$

where K is the rate of production of F and H centers, K_2 is the rate constant for direct recombination, and D_F and D_H are the diffusion constants of the F and H centers. Since K_2 is determined by the diffusion of the H centers and therefore proportional to D_H, c_F^{sat} is expected to depend on temperature only by $\sqrt{(1/D_F)}$, thus the slope should finally become $\frac{1}{2}E_F$. From the measurements it is found that the slope A_F reaches a maximum of 0.42 ± 0.05 eV for doses higher than 160 Mrad, which results in a migration energy E_F of 0.84 ± 0.1 eV. The increase of A_F from 0.10 eV at 20 Mrad up to this maximum can be explained from the fact that the F-center concentration has not stabilized yet (see also Fig. 2). At low doses A_M is twice A_F, which reflects the quadratic relationship as described above.

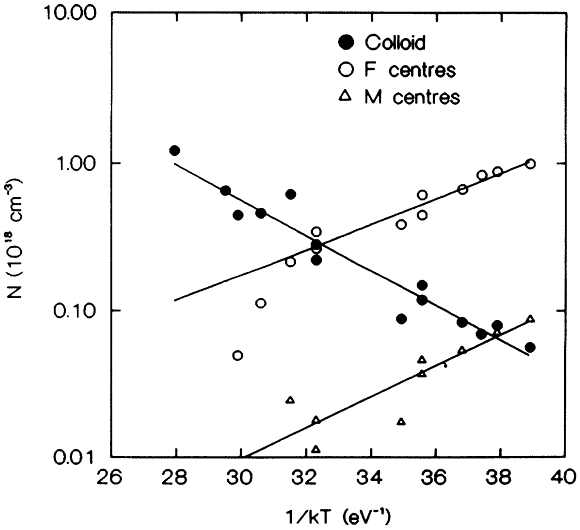

FIG. 5. The number of electron centers plotted against 1/kT for a dose of 160 Mrad.

TABLE I. The temperature dependence of the growth of the F, M, and colloid band, $N_{F,M} \sim \exp(A_{F,M}/kT)$ and $N_C \sim \exp(-A_C/kT)$.

Dose (Mrad)	A_F (eV)	A_M (eV)	A_c (eV)
20	0.10±0.04	0.22±0.03	
40	0.13±0.02	0.27±0.06	
80	0.12±0.01	0.26±0.08	
100	0.19±0.01	0.35±0.03	
120	0.21±0.005	0.34±0.03	
160	0.20±0.01	0.24±0.03	0.27±0.01
430	0.40±0.04		0.34±0.03
1000	0.48±0.04		0.58±0.15
1500	0.37±0.07		0.74±0.20

The results are comparable with those of other authors on the saturation levels of F centers. Based on the same analysis Levy and co-workers[1,26] found for E_F a value of 0.2 eV below 250 °C and 0.9 eV at higher irradiation temperatures. The relatively low value of 0.2 eV below 250 °C can be explained by an unsaturated F-center concentration, since the applied doses were less than 500 Mrad. Also Hodgson, Delgado, and Alvarez Rivas[23] and Jain and Lidiard[18] concluded on similar grounds that the migration energy for F centers lies in the range of 0.8–0.9 eV.

The slope A_C increases from a value of 0.27 eV at 160 Mrad up to 0.74 eV at 1500 Mrad. This slope can also be derived from the underlying kinetics of colloid growth. However, the actual value can only be estimated, since many secondary reactions are involved. Neglecting the evaporation of F centers the amount of colloid depends on temperature by (see Jain and Lidiard[18] for a detailed analysis):

$$c_A^{1/2} + \lambda c_A^{2/3} \sim C_l^{1/2}\left[K\frac{D_F D_H}{K_2}\right]^{1/2} t\ . \tag{5}$$

Here $\lambda \sim C_l^{1/2} C_c^{-2/3}$ and C_l and C_c are the number of dislocation loops and colloids per cm^{-3}, respectively. We conclude that after the nucleation stage the temperature dependence of Eq. (5) will not change with increasing dose. The slope A_C is then stable and will be characterized by the migration energy of the F centers, in such a way that A_C lies in the range of $\frac{3}{4} E_F - E_F$, i.e., 0.6–0.9 eV. From the calculations[22] it appears that C_l is nearly temperature independent, while C_c depends on the number of F centers, and therefore behaves as $\sqrt{(1/D_F)}$. If we incorporate the temperature dependence of the number of colloid nuclei C_c the slope A_C will be somewhat lower. Although the experimental values for the temperature dependence are in the range of these expected values, A_C still increases in this dose region. This indicates that the nucleation stage has not been completed yet.

From this point of view it is interesting to note that the temperature dependences for doped NaCl show significant differences. The experimental results, obtained until now, from a set of crystals irradiated with the same dose and doserate, show a higher slope for K, and Ba-doped crystals than for F-, Br-, Li-doped and pure crystals. Apparently the nucleation process is affected by the impurities. If we assume that the temperature dependence is a measure for the progress of the nucleation stage, it may be concluded that the nucleation proceeds more rapidly for K- and Ba-doped crystals than for F-, Br-, Li-doped and pure crystals.

IV. COMPARISON WITH DIFFERENTIAL SCANNING CALORIMETRY

The total number of electronic centers ($F,M,R,\ldots$, colloidal centers) is a measure for the damage produced by the irradiation. Differential scanning calorimetry provides us with two additional methods to obtain a measure of the damage contents in the crystal: (1) the measurement of the release of stored energy, and (2) the measurement of the latent heat of fusion of the melting colloids.

The stored energy experiment is performed by heating the crystal with a constant rate from 40 up to 500 °C. The release of stored energy is measured as an exothermal peak in the heat flow. The amount of stored energy is given by the total area of the peak. In order to make a direct comparison possible, the optical and stored energy measurements have been performed on different pieces of the same crystal. In Fig. 6 the stored energy is plotted against the total number of electronic centers (F, M, and colloid centers). Based on the optical-absorption experiments the stored energy per electronic center is 6.2±1 eV.

This value can be compared with the stored energy per sodium atom obtained from latent heat measurements on the melting of the sodium colloids in irradiated NaCl.[27] The crystals have been heated with a constant rate from 40 up to 15 °C. The melting transition of the colloids becomes visible as an endothermal peak in the heat flow. The total latent heat of melting of the sodium colloids divided by the specific heat of melting of sodium (0.113 J/mg), provides us with a measure of the number of sodium atoms contained in colloids in the crystal. The comparison with the stored energy gives the energy release per sodium atom. The stored energy per sodium atom is found to be 5.3±0.5 eV.

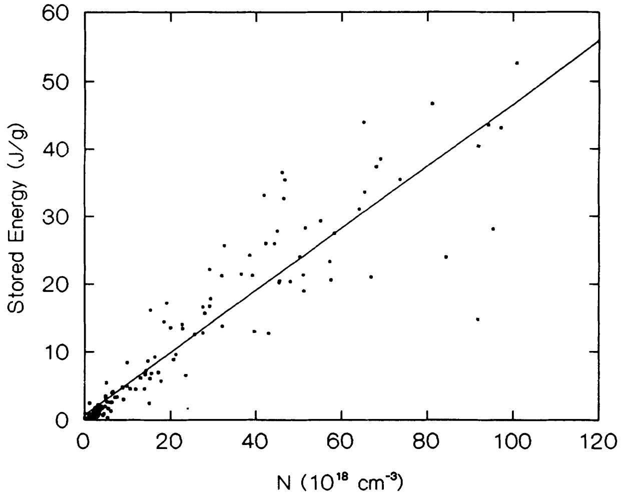

FIG. 6. The release of stored energy in irradiated NaCl versus the number of electron centers measured by optical-absorption spectroscopy. The data are fitted by linear regression.

The value obtained by latent heat measurements may be compared with the optical-absorption value of 6.2±1 eV. Both values agree very well and are near the theoretical (about 5 eV)[28,29] and experimental (4.25 eV)[30] values given by other authors. Unfortunately, a direct comparison of the latent heat measurements with the optical-absorption measurements performed on the same crystals is impossible since the detection limits are different (opt. abs. up to about 0.3 mol %, latent heat above 0.2 mol %). Consequently, both values are obtained from different sets of crystals, each set involving a different dose regime (latent heat: higher than 5 Grad, opt.abs: 3 Grad and less).

V. CONCLUSIONS

Many of the observed phenomena in the formation of radiation damage can be understood in the light of the underlying kinetics of formation of the primary defects, which eventually aggregate into sodium colloids and molecular halogen. The time development as well as the temperature dependence of the different optical bands is reasonably well understood. However, with respect to the nucleation stage there remain some fundamental aspects to be explained. The relation between the M and F centers can be partly understood in terms of a thermally unstable M center, however, other explanations are possible, and final conclusions cannot be drawn.

The two different colloid bands can be ascribed to two different size classes or to a nonspherical shape of the colloids. The order of appearance of the peaks is difficult to explain: if the second peak at 685 nm is due to smaller sizes, with a relatively larger spillout of the electrons, why does the nucleation stage begin with larger colloids, which show a peak at 580 nm? Possibly, one type of colloid is transformed into another type of colloid, or an entirely different nucleation mechanism becomes favorable.

Based on the kinetics of defect formation, the *F* center migration energy has been estimated to be 0.8–0.9 eV. A more detailed study of the temperature dependences of the *F*-center and colloid production will provide us with more information about the *F*-center diffusion and the role of impurities in the nucleation mechanism. To make an accurate prediction of the amounts of radiation damage in NaCl, the observed phenomena have to be understood and incorporated into the kinetic models. More detailed investigation of the nucleation of *F* centers will be necessary, in order to make further progress in the development of these models.

ACKNOWLEDGMENT

This work has been supported financially by the Dutch Ministry of Economic Affairs, as a part of the OPLA (OPberging te LAnd) research programme, in order to investigate the disposal of high level nuclear waste in salt domes.

APPENDIX

For the analysis of the spectra we used Smakula's equation based on a Lorentz local-field approximation and a Lorentz line shape. There is some evidence that the use of the Onsager local-field approximation gives better agreement with experiment.[9] This would also be consistent with Mie's theory for metallic particles (colloids) in which the Drude free-electron theory is applied. However, since the oscillator strength $f=0.86$ is determined for Smakula's formula by independent measurements of the number of *F* centers, an error in the local-field correction will be compensated by an error in the oscillator strength. The same argument holds for errors due to our baseline procedure, as described in Sec. II.

The consistency with Mie's theory implies that, if our assumption that the colloid peak(s) are Lorentzian is good enough, we can apply the same formula for the colloid band. We have analyzed a selected number of spectra to estimate the error in determining the peak area. We found that the result of fitting the spectra with Lorentz-shaped peaks depends strongly on the choice of the baseline. A Lorentz-shaped band seems to overestimate the long-wavelength tail of the colloid band, whereas it fits well to the short-wavelength tail. From this fitting analysis the error in the peak areas has been estimated to be about 10%.

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