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Radiation damage in NaCl. I. Optical-absorption experiments on heavily irradiated samples

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Results of optical-absorption experiments on heavily irradiated NaCl single crystals are presented. The dose rates were between 4 and 250 Mrad/h; the doses between 1 and 7 Grad. The irradiation temperatures were in the range of 20–150 °C. Because of the intense optical bands, the thickness of the samples had to be reduced to values between 2 and 100 μm using a thinning device. With this device we are able to investigate samples containing about 1 mol % Na and Cl_2. The optical spectra of the samples, irradiated at low temperatures, show intense *F*, *M*, *R*, and *N* bands. The positions of the optical bands of the electron excess centers are in agreement with the literature. With increasing irradiation temperature, the contribution of these centers to the total amount of radiation damage decreases due to coagulation to colloidal Na particles. The colloid band, however, is much wider than the literature values; in addition, it is located at longer wavelengths. These observations can be explained by assuming that we are dealing with extremely small colloids, showing appreciable quantum size effects.

I. INTRODUCTION

This paper is the first one of a series of four dealing with research on radiation damage products in heavily irradiated pure or doped NaCl samples, which has been carried out in connection with the eventual disposal/storage of high-level fission waste in rocksalt formations. The radiation field associated with the presence of the fission waste gives rise to the production of defects (such as *F* and *F*-aggregate centers, various hole centers, Na colloids, and chlorine inclusions) in the rocksalt crystals in the vicinity of the irradiation source. It appears that, depending upon the irradiation conditions, more than 10 mol % of the molecules in the NaCl crystal can be transformed into colloidal Na and chlorine inclusions. The transformation of these amounts of NaCl in the immediate vicinity of the high-level waste is highly undesirable from a safety point of view. For this reason it was found necessary to find information about the amounts of radiation damage and the physical properties of the above-mentioned defects.

Although significant efforts have been invested in the research on radiation damage in NaCl, the formation of Na colloids and Cl_2 inclusions is not yet completely understood. In particular, the effects of the dose, dose rate, and the irradiation temperature should be investigated closely. In this laboratory we are carrying out an extensive program to investigate radiation damage. Large numbers of synthetic crystals (pure and doped with for example KCl, LiCl, NaF, $BaCl_2$, or $MnCl_2$) are irradiated simultaneously at many different radiation temperatures between 20 and 150 °C by means of a van de Graaff electron accelerator.

Radiation damage in the above-mentioned materials is studied by means of several techniques, such as: optical-absorption spectroscopy (some results will be presented in this paper, paper I, and in a second one, paper II), differential scanning calorimetry (for stored energy measurements and latent heat effects; results of these experiments will be presented in paper III), thermoluminescence, conduction-electron-spin resonance (CESR), Raman scattering (results of these experiments will be presented in paper IV), scanning electron microscopy and transmission electron microscopy as a function of the irradiation temperature, the dose, dose rate, and the composition.

In this paper (paper I) and in paper II we will present the results of optical-absorption measurements, which allow us to draw conclusions about the amounts and sizes of the colloidal particles. We will show, that in some of the heavily irradiated samples relatively simple *F*-aggregate centers are formed in addition to Na colloids. In paper III we will present information revealing that the Na colloids in irradiated NaCl crystals often show a rather complex melting behavior with different melting temperatures. The latent heat due to melting of colloidal Na is correlated with the amount of stored energy which is released during an annealing experiment. Finally, in paper IV we will present results of Raman-scattering experiments showing that the surface of the colloids can be described in terms of a fractal.

Reviews on optical-absorption measurements of radiation damage in NaCl have been reported 20–30 years ago.[1–4] Depending upon the purity of the samples, different color centers have been investigated. First, we have the atomically dispersed electron excess centers, such as *F*, *M*, *R*, and *N* centers, with optical bands located in the visible or near infrared. Secondly, we have atomically dispersed hole excess centers such as *H* and V_K centers. In addition, many different coagulated hole centers have been described in the literature. Thirdly, we have colloidal aggregates of atomically dispersed centers. The optical band of Na colloids (plasmon absorption) depends on the shape and size of the particles, but it is usually located at approximately 560 nm. Finally, there are chlorine inclusions, formed by aggregation of atomically

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dispersed hole centers. We have established the presence of Cl_2 inclusions in our samples by their odor after crushing them in a mortar, grinding them using emery paper, or dissolving them in water.

The existing literature deals with the properties of lightly colored materials. The concentration of color centers is well below 100 ppm. In the present investigation we have studied samples with concentrations of about 1 mol % produced during irradiation of pure and doped synthetic samples. Because the samples used in this investigation are colored very heavily, we have to reduce the thickness drastically in order to perform reliable optical-absorption measurements. In this paper a description is given of a thinning device constructed for this purpose.

At low irradiation temperatures (<65 °C) the F band is the dominant one, with concentrations up to 10^{18} cm^{-3}. In these samples the total number of electrons trapped in M, R, and N centers is of the same order of magnitude as the number of F centers. With increasing irradiation temperature (>75 °C), the colloid band, which is usually located between 550 and 600 nm, increases in intensity. At temperatures higher than 90 °C, the colloid band is the dominant one, and the F, M, R, and N bands are absent.

The colloid band, as observed in this investigation, is located at longer wavelengths than those reported in the literature. This is probably due to size effects, which will be discussed in this paper. It is assumed that the position of the plasmon band is shifted to longer wavelengths due to spillout of the conduction electrons. The width of the plasmon band is also much larger than usual. This is caused by collisions of the conduction electrons with the colloid-host matrix interface. Our results suggest that we are dealing with colloids with diameters 2 nm and larger.

II. EXPERIMENTAL PROCEDURES

The samples used here have been grown by means of a modified Bridgman technique.[5,6] It is possible to grow 18 cylindrical NaCl single crystals, with a diameter of 6 mm and a length of 60 mm, simultaneously. After crystal growth the resulting materials are cut and polished in order to obtain cylindrical samples with a thickness of about 0.6 mm.

The irradiation experiments have been carried out at constant does rates between 4 and 250 Mrad/h, as described elsewhere.[7] In our irradiation facility more than 300 samples are irradiated simultaneously at 15 different temperatures between 20 and 175 °C. With this setup the temperature dependence of the radiation damage formation can be investigated.

As mentioned above, the irradiated samples are colored very strongly, and it is not possible to measure the optical-absorption spectra using conventional methods. The irradiated samples are first glued on an optically flat glass plate employing wax; a flat surface is obtained by polishing the samples on a flat polishing bench using a specially designed tool, which can be adjusted accurately to polish away parallel sections of the samples. After a flat surface is obtained, the samples are removed from the glass plate. Subsequently, the flat sample surface is glued, with low viscosity cyanoacrylate cement, to another optically flat glass plate. Finally, the samples are thinned carefully to a thickness of 2 to 100 μm, depending on the optical density. For a 2-μm sample with a typical absorption constant of 2, the concentration of colloidal Na is about 1%.

The thickness of the samples was measured with a Tesatronic TTD20 setup, capable of determining the sample thickness plus the thickness of the cement layer with an accuracy of 0.2 μm. The thickness of the cement layer has been determined separately. This is done by grinding the sample away completely or dissolving it in water, and detecting accurately the point where the sample thickness is zero. Especially for strongly colored materials, where very thin layers are employed this is not very difficult. Close to the point of zero sample thickness the change in color as a function of the thickness is very rapid. This implies, that after the experiment there is no sample left. The spectra are corrected for the background due to the glass substrate.

III. EXPERIMENTAL RESULTS

During the thinning and polishing procedures one can already distinguish between the two different types of samples. Samples containing predominantly F centers and small aggregates form a brown powder, whereas the powder obtained form the samples with colloids is dark blue.

A. Samples with F centers

Samples irradiated at low temperatures contain primarily F centers [Fig. 1(a)]. The positions of the F, M, R, and N bands are in agreement with those reported in the literature.[1-4] These results show that the experimental method including the thinning technique works quite well. From the intensity $A_{\max}$ (cm^{-1}) of the F band and the thickness of the sample we calculate, using the Smakula relation,[8,9] the F-center concentration N_F in the sample

$$N_F=\frac{10^{16}*A_{\max}}{2.06*f}\ . \tag{1}$$

In Eq. (1) f is the oscillator strength of the F center (0.9). For a more extensive discussion of the Smakula relation we refer to paper II. In heavily colored samples N_F is typically 10^{18} per cm^3, i.e., one F center per 10000 Na ions.

The intensities of the M, R, and N bands are lower than the F-band intensity, but if we employ the sum rule of Doyle,[10] we estimate that the number of absorbing electrons in the coagulated centers divided by the total number of absorbing electrons is 0.50 to 0.60. According to the sum rule the total area under the absorption bands per absorbing electron does not depend on the type of electron excess centers involved. The large numbers of complex centers are due to the high-defect concentrations, because it is energetically favorable for the F centers to form coagulates. We note that the color centers have sufficient time during the irradiation run to form coagulates. This is also suggested by the results obtained from samples irradiated at higher temperatures.

In Fig. 1(b) we show the optical-absorption spectrum of pure NaCl, irradiated at 75 °C. As compared to Fig. 1(a) the *F* band relative to the *F*-aggregate bands is weaker. The major difference between Figs. 1(a) and 1(b) is the presence of the colloid band at 578 nm. The latter band almost coincides with the *R* band.

B. Samples with colloids

Samples irradiated at higher temperatures contain mostly colloidal particles. The colloid concentration, and the particle size and shape, depend on the irradiation conditions: the temperature, dose and dose rate. Also the dopant plays an essential role. In pure NaCl the formation of colloids is difficult. Samples with Br^- or Li^+ behave similarly. Doping with K^+, F^-, Mn^{2+}, Ba^{2+}, or Fe^{3+} ions enhances the formation of colloids. The enhancement effects of the impurities are already observable at concentrations of 100 ppm. Above this value the variations as a function of the concentration of the dopant are less important.

In Fig. 1(c) we show an optical-absorption spectrum of irradiated, pure NaCl (T_{irr}=93 °C). The colloid band is located between 500 and 650 nm. At the high-energy side of the plasmon band we always find a weak band at 380 nm. This band has also been observed in the literature.[11-14] Different models were proposed,[13,14] but none of these models is accepted. In Fig. 2 we have shown some plasmon peaks in pure NaCl irradiated at various temperatures. In agreement with theory we observe a pronounced maximum for the colloid concentration at T_{irr} = 100 °C (see also Refs. 15-17). The widths of these colloid bands are much larger then for additively colored NaCl. After short annealing at 450-500 °C a weak colloid band is left at 550-560 nm; the width has decreased to the literature value (see Fig. 3). According to

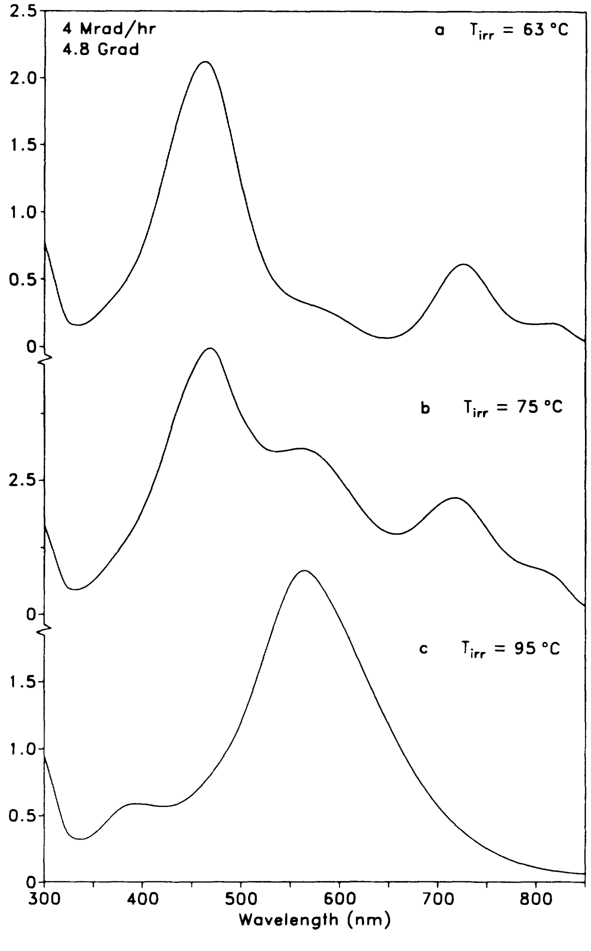

FIG. 1. Curve a—Optical-absorption spectrum of pure NaCl, irradiated at 63 °C, showing only the *F* and *F*-aggregate bands; the dose rate used was 4 Mrad/h and the total dose was 4.8 Grad, Curve b—The spectrum of pure NaCl, irradiated at 75 °C, showing the *F* and *F*-aggregate bands and the colloid band; the dose rate was 4 Mrad/h, the total dose was 4.8 Grad, Curve c—The spectrum of pure NaCl, irradiated at 95 °C, showing an intense plasmon band; the dose rate was 4 Mrad/h and the total dose was 4.8 Grad.

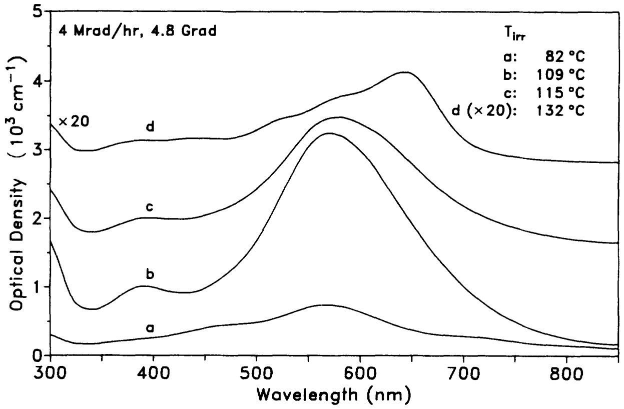

FIG. 2. The spectra of pure NaCl, irradiated at different temperatures (as indicated) at a dose rate of 4 Mrad/h, the total dose was 4.8 Grad.

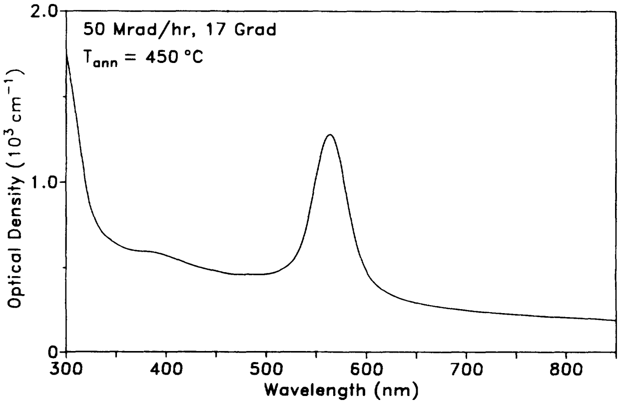

FIG. 3. The spectrum of pure NaCl, irradiated at elevated temperatures and annealed subsequently. From a comparison of this spectrum and the one shown in Fig. 3, it is clear that the width of the plasmon band in this figure is much smaller.

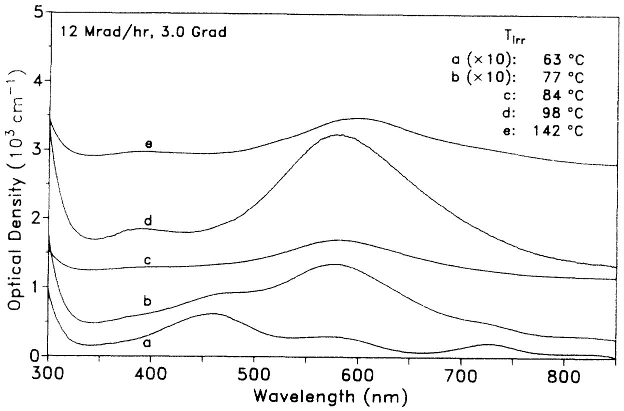

FIG. 4. The optical-absorption bands of NaCl, doped with 0.02 mol. % NaF, irradiated at different temperatures (as indicated) at 12 Mrad/h; the total dose was 3 Grad. Note lower scale for curves a and b.

Smithard and Tran[18] the colloids associated with the plasmon peak at 550 nm and width of 50 nm have a diameter of 10–20 nm.

In Fig. 4 we present the results on NaCl:0.02 mol. % NaF. For $T_{irr}=63\,°C$ (curve a) the F band is dominant. For $T_{irr}=77\,°C$ the colloid band (570 nm) is more intense than the F and F-aggregate bands (curve b). For $T_{irr}=84\,°C$, the colloid band (582 nm) is dominant (curve c). In this temperature region the intensity of the colloid band increases very rapidly with increasing irradiation temperature until a maximum is reached at $T_{irr}=100\,°C$. In curve d, the colloid band and extra band at 380 nm can be observed. If the irradiation temperature is increased further, the colloid band and the 380-nm band decrease with increasing temperature. In curve e a very weak extra band is observed higher than 400 nm plus a weak shoulder at about 700 nm.

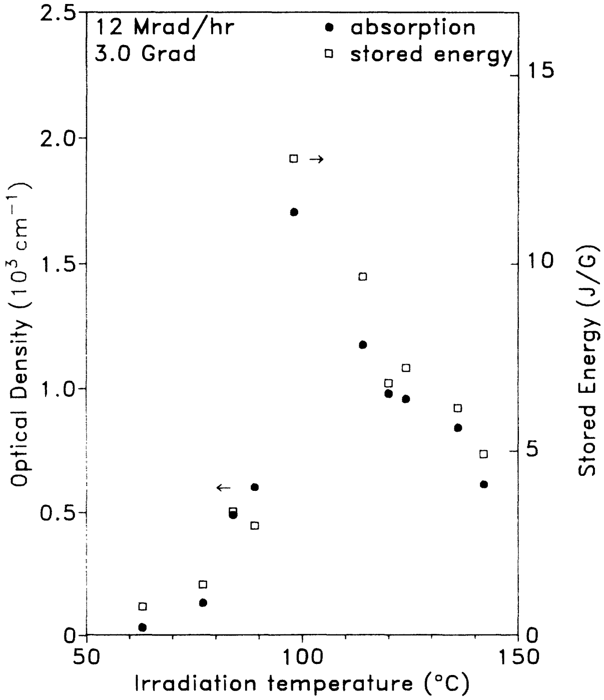

FIG. 5. Survey of intensities of the colloid band in irradiated NaCl (doped with 0.02 mol. % NaF) as a function of the irradiation temperature. The results of the optical experiments have been presented together with the stored energy results.

The optical results are correlated with the stored energy measurements (Fig. 5, for a description of the stored energy results we refer to paper III). In almost all cases both the stored energy and the intensity of the colloid band show a pronounced maximum as a function of the irradiation temperature. The position of the colloid band varies between 550 and 700 nm, depending on the irradiation conditions and the dopant. Initially it was assumed, that we were dealing with large colloids, which show a colloid band at long wavelengths. This idea could not be maintained, because of information from CESR, Raman scattering, and latent heat experiments, showing that we are dealing with very small colloids.

IV. DISCUSSION

We have shown, that colloid concentrations up to 1 mol % can be detected with optical-absorption spectrometry if the thinning technique is employed. F, M, R, and N centers, which are formed at irradiation temperatures of 65 °C and below, have been detected for sample thicknesses of typically 100 μm. With increasing irradiation temperature higher aggregates and some colloids are formed [Figs. 1(a) and 1(b)]. The transition to the colloid-formation regime is made with only the formation of the above-mentioned aggregate bands. In Fig. 2, curve a the F and F-aggregate bands are no longer observable. This suggests, that either the optical bands associated with higher F aggregates are hidden by the colloid band or these higher aggregates have optical properties, which are quite similar to those of colloids. We note, that the plasmon band of extremely small colloids is very wide due to surface scattering, implying that the intensity will be small.

The production of radiation damage in NaCl:F proceeds much faster than for pure NaCl. This is remarkable, because the properties of chloride and fluoride ions are quite similar. For high irradiation temperatures the deviations between the pure and undoped materials are very large (see Figs. 2 and 4). The spectrum shown in Fig. 2(d) is similar to those observed by Gyulai[11,12] for irradiated natural rocksalt samples.

Formation of colloids occurs in a narrow temperature range. With decreasing doses, the transition temperature, where the production of damage is enhanced, increases. Due to the increasing coagulation the damage formation is very efficient. The sum of the numbers of electrons in the electron excess centers and colloids, which is equal to the numbers of holes in the hole excess centers and in the Cl_2 inclusions, increases rapidly if the formation of colloids starts. This conclusion is drawn form the rapid increase of the optical density of the plasmon band with increasing irradiation for temperatures below 100 °C. A similar observation has been made in our stored energy measurements.[19]

The increased rate of formation of higher aggregates and colloids at moderate temperatures is accounted for by the increasing rate of formation of *F* centers and the increased diffusion constant of *F* centers. According to the Jain-Lidiard model there are many reactions contributing to the production of radiation damage.[15–17] If $T_{\mathrm{irr}} > 100\,^{\circ}\mathrm{C}$ the intensity of the plasmon band decreases with increasing irradiation temperature. This is due to increased annihilation of damage and it can be understood in terms of a modified Jain-Lidiard model (Refs. 15–17, see also Fig. 5).

Smithard and Tran[18] found a minimum width of the plasmon peak of 35 nm, which is obtained for colloids with a diameter of about 20 nm. In our experiments we have observed plasmon peaks 150 to 200 nm wide. According to Smithard and Tran this means, that the diameter of the smallest Na particles is about 2 nm. This value is in line with our CESR results[20] for the same samples. We estimate that the colloids contain about 100 Na atoms.

Let us assume, that we are dealing with extremely small spherical particles. The position of the peak depends on the density of the conduction electrons. The average electron density decreases with decreasing diameter, because the conduction electrons are not localized exclusively inside the colloid. They spend a fraction of their time outside the particle, leading to an appreciable shift of the plasmon peak.

The conduction electrons behave as free particles in a potential well with a depth *W* (in eV), which depends upon the difference between the Fermi level in Na and the bottom of the conduction band of NaCl and the work function of Na metal. The wave function outside the potential well is $\Phi = C\exp[-2\pi x\sqrt{2\,mW/h}]$, which can be approximated by $\Phi = C\exp[-0.5x\sqrt{W}]$, with $h =$ Planck's constant, *W* the energy difference inside and outside the potential well in eV, and *x* is the distance in Å. This implies, that the electron density outside the potential well is $C^2\exp[x\sqrt{W}]$. In accordance with this, we find for the probability (*P*) for each electron to be found outside a (one-dimensional) particle

$$P = \frac{1}{RW^{1/2}+1} \; . \tag{2}$$

In (2) *R* is the size of the particle in Å. The density of the conduction electrons inside a three-dimensional cubic particle should be modified by a factor of

$$1-3P = \frac{RW^{1/2}-2}{RW^{1/2}+1} \; . \tag{3}$$

For a large spherical particle the plasmon peak occurs at

$$\Omega_s = \frac{\Omega_p}{(2\epsilon+1)^{1/2}} \; , \tag{4}$$

where Ω_p is the plasma frequency and ϵ is the dielectric constant of NaCl. For the plasmon peak frequency Ω_c, corrected for the above-mentioned size effects, we obtain

$$\Omega_c = (1-3P)^{1/2}\Omega_s \; . \tag{5}$$

As expected, the calculated electron density as a function of the diameter decreases. For the position of the colloid band vs the particle diameter we find the plot presented in Fig. 6, in which we have shown our results together with those of Snider and Sorbello[21] and Smithard and Tran.[18]

We have produced large colloids in irradiated samples after annealing at high temperatures (narrow plasmon peak at 550 nm, see Fig. 3). With CESR we observed for these samples a weak and narrow CESR line with a *g* value of 2 and a linewidth close to the bulk Na value. Another way to produce large colloids is to irradiate the samples at high temperatures [see Fig. 2(d)]. Comparing this spectrum with the one shown in Fig. 3 we see, that the optical spectra are completely different. The colloids corresponding with the plasmon peak in Fig. 3 are compact, probably with a fractal surface structure, whereas the particles associated with the plasmon peak(s) in Fig. 2(d) have a highly irregular structure.

It is usually assumed that the colloids are spherical. In some papers, however, the effect of the shape of the particles has been investigated. We are probably dealing with fractally shaped colloids, where the surface area is much larger than for spherical colloids. This is in line with the conclusions of Duval *et al.*[22] from their Raman-scattering experiments on Na colloids in additively colored NaCl. Duval *et al.*[22] have interpreted their Raman results on the basis of the theory of Alexander and co-workers.[23–26] The colloids in additively colored crystals are formed under equilibrium conditions, whereas during radiolysis at low temperatures there is no equilibrium and the shape of the colloids is determined by statistical fluctuations. If the branches of the fractals are smaller than the mean free path for bulk Na, scattering of the conduction electrons at the Na-NaCl interface is the

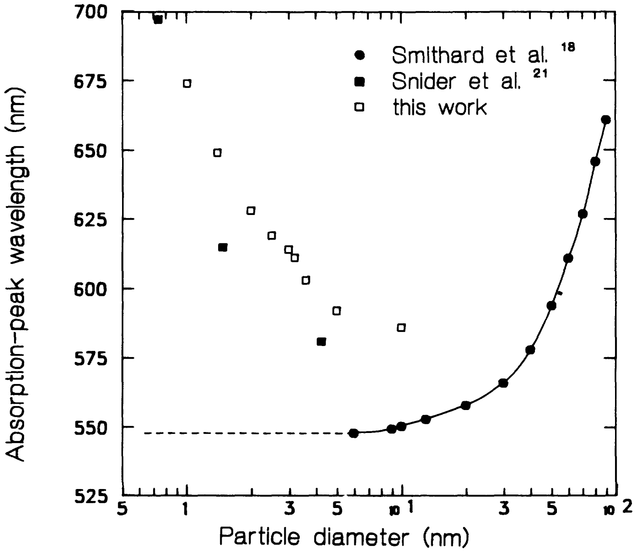

FIG. 6. The position of the plasmon band associated with small Na colloids in NaCl; the effect of the electron spillout has been taken into account. The drawn line, including the (broken) horizontal one is the theoretically expected behavior without spillout effects.

most important source of the broadening of the plasmon peak.

The results of Duval *et al.*[22] are in line with those obtained in our laboratory (see paper IV). The assumption that we are dealing with fractally shaped colloids implies that (a) the surface area of the colloids is much larger than expected for spherical particles and (b) the numbers of atoms in these colloids will be larger than those mentioned above. From the observed optical spectra we conclude that the detailed structure of the smallest branches of the fractal particles consist of at least 5 *F* centers (Na atoms). If these branches would contain 4 *F* centers or less, the optical-absorption spectra would show bands close to the *F*, *M*, *R*, and *N* bands. Fractal particles have, like very small spherical colloids, a large surface to volume ratio, suggesting that size effects will be important.

In *all* spectra where the plasmon band is present, we find a peak at about 380 nm. The 380-nm band is much weaker than the plasmon band, and scales roughly with the colloid band. Because the optical density of the 380-nm band is in some cases very large, the concentration of the centers which give rise to this band is very large [see Fig. 1(c)]. From the scaling behavior and the fact that we did not observe new ESR lines in the spectra of irradiated NaCl, we think that the 380-nm band, like the plasmon peak, is due to Na colloids. Perhaps the 380-nm band can be explained by the optical properties of the conduction electrons in the Na particles in NaCl. Another explanation could be that the additional band is due to surface plasmons. From the work of Selby *et al.*,[27] however, we deduce that this excitation should be located at the low-energy side of the plasmon peak. Finally, the explanation proposed by Creighton[28] should be mentioned. According to Creighton an additional band is expected in samples where colloids are very close to each other. We have also observed the 380-nm band in samples with low concentrations of colloids. It should be noted, that in the present study we are dealing with fractally shaped colloids. The 380-nm band associated with these colloids could be explained by the interactions between excitations in different parts of one particular colloidal particle. On the basis of the results presented in this paper we are not able to decide which one of the existing models for the 380-nm band is the correct one.

For some dopants the samples show, after irradiation at high temperatures, a main plasmon peak between 650 and 700 nm. In agreement with Gyulai[11,12] also some weak shoulders are observed. The origin of these shoulders is unknown. From the fact that these bands have now been observed in both pure (Fig. 2, curve d) and natural samples (Gyulai[11,12]), we conclude that the additional bands belong to intrinsic centers. The dominant peak in Fig. 2(d) is due to rather large colloids. This is confirmed by CESR experiments,[20] showing a weak and 6-G-wide line due to conduction electrons in large colloids. These results indicate that the nucleation stage, which is very important for the size and shape of the colloids in later stages of the radiolysis process, depends on the dopant.

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