

Zeitschrift: Helvetica Physica Acta

Band: 46 (1973)

Heft: 6

Artikel: The optical absorption produced by small sodium metal particles in sodium chloride

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DOI: <https://doi.org/10.5169/seals-114515>

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The Optical Absorption Produced by Small Sodium Metal Particles in Sodium Chloride¹⁾

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(21. IX. 73)

Abstract. The optical absorption band due to small sodium particles (10 to 1000 Å diameter) in a sodium chloride matrix has been calculated using the theory of Mie and allowing for the scattering of the sodium conduction electrons by the metal particle surface. Various experiments have been done in order to verify the theory. Optical absorption spectra of small sodium particles were measured as a function of the size in additively coloured sodium chloride crystals which were UV irradiated and heat treated. Reasonable good agreement has been obtained between the calculations and the experimental results, for particles of sizes of order of 100 Å, whereas a discrepancy has been obtained for sizes of order of 10 Å. The evolution of the absorption suggests that the particles grow via a diffusing species and according to a ripening process. (Helv. Phys. Acta March 1974.)

1. Introduction

Alkali halide crystals which have been doped with an excess of metal have been the subject of extensive research for many years. In particular, if such doped crystals are irradiated with X-rays or with ultra-violet light (UV) they exhibit a number of optical absorption bands due to various 'colour centres' produced in the crystal matrix [1]. In sodium chloride which has been doped with an excess of sodium, UV irradiation produces an absorption at about 4600 Å due to *F* centres. The model for this centre is an electron localized on an anion vacancy. It is well known that heating a crystal which has been irradiated to produce such *F* centres can result in the formation of a new absorption band at about 5600 Å and a corresponding decrease in the *F* band absorption. This new band is variously known as the *X*, *C* or Δ band and the nature of the centre which gives rise to this band has been the subject of a great deal of research. The band is thought to be due to centres which result from a thermal agglomeration of *F* centres during the heating of the crystal. The exact nature of the centres is not established for certain. Many studies have led to the conclusion that the centres are colloidal sodium particles in the NaCl matrix [1, 2]. Other results, however, have suggested that the band is not due to colloidal centres but to atomically dispersed centres [1, 3, 4]. Some workers have suggested that the band might be due to 'quasi-colloidal' sodium, i.e. sodium centres which are too small to have metallic properties and which are an intermediate between the *F* centres and normal colloidal sodium [5-7]. In some cases [7] more than one absorption band or peak has been observed,

¹⁾ This work was supported by the Swiss National Fund for Scientific Research No. 2.666.72.

and the different peak positions ascribed to different quasi-colloidal sites within the NaCl matrix.

According to the literature, the centres responsible for the X band absorption do not scatter light. Metal particles whose size is comparable to the wavelength of light (say 500 Å diameter and above) scatter light (Tyndall scattering), and such particles of sodium have been identified in NaCl as a result of this scattering. They cause the NaCl to appear blue in transmitted light and red in scattered light. Also larger sodium particles (of size about 5 μ) have often been seen, with the optical microscope, to precipitate along dislocations and irregularities in NaCl crystals. Very small metal particles however do not scatter light but give only an absorption. Such particles might be responsible for the observed X band absorption, but are more difficult to positively identify, because, since they do not scatter light, they may be confused with other colour centres.

In this work we have applied the theory of Mie [8] to calculate in detail the optical absorption due to sodium particles in NaCl. The calculations were made as a function of the particle diameter, covering the size range 10 to 1000 Å. We have measured the X band in a large number of doped NaCl samples studying the formation of the X band from the F band and its subsequent evolution with various annealing conditions. We have then compared the measured X band properties with the calculated colloid absorption properties in an attempt to see if the X band is colloidal or not. This identification is important if the agglomeration process of colour centres in alkali halide crystals is to be understood.

2. The Theory of the Optical Absorption Produced by a Dispersion of Small Metal Particles

2.1. Description of the model used

The theory of the absorption produced by small metal particles in an insulating matrix is due to Mie [8]. The transverse vectors of the incident light produce a polarization of the electron gas cloud of the metal particles. This polarization oscillates with the frequency of the incident light and can interact with the plasma resonance of the electron gas to produce a resonant absorption of the incident light. This absorption may be thought of as the loss mechanism associated with the polarization of the particles by the incident light. The frequency at which the absorption occurs is determined mainly by the plasma frequency of the metal ω_p and the refractive index n_0 of the matrix.

If the particles are very small compared to the wavelength of the incident light λ (say less than 200 Å diameter), then only electric dipole terms contribute to the absorption and no light scattering takes place. For this special case the Mie theory reduces to a very simple form giving the following size independent expression for the absorption coefficient γ :

$$\gamma = \frac{18\pi NVn_0^3}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2n_0^2)^2 + \epsilon_2^2}. \quad (1)$$

This is the equation most often used in the literature to calculate colloidal band positions. $\epsilon(\lambda) = \epsilon_1 - i\epsilon_2$ is the complex dielectric constant of the metal and NV is the volume fraction of metal particles present in the matrix. According to the Drude free

electron theory ϵ_1 and ϵ_2 can be written

$$\epsilon_1 = \epsilon_0 - \frac{\omega_p^2}{\omega^2 + \omega_0^2} \quad (2)$$

and

$$\epsilon_2 = \frac{\omega_p^2 \omega_0}{\omega(\omega^2 + \omega_0^2)}, \quad (3)$$

where $\omega/2\pi$ is the frequency of the incident light, ω_0 is the collision frequency of conduction electrons which is simply the inverse of the resistivity relaxation time τ_R . ϵ_0 is the value of ϵ_1 at infinite frequency (which should be close to one for light metals). If equations (2) and (3) are substituted into equation (1) it is easy to show that an absorption maximum occurs at wavelength λ_p where

$$\lambda_p = \frac{2\pi c}{\omega_p} (\epsilon_0 + 2n_0^2)^{1/2} \quad (4)$$

and the width $\Delta\lambda$ of this absorption peak at half height is given by

$$\Delta\lambda = \frac{c}{2\sigma} (\epsilon_0 + 2n_0^2) = \frac{4\pi c \omega_0}{2\omega_p^2} (\epsilon_0 + 2n_0^2) \quad (5)$$

where c is the velocity of light and σ is the bulk conductivity of the metal. The product of the peak height γ_p and width can be used to measure the particle concentration, since

$$\gamma_p \Delta\lambda = \frac{18\pi N V n_0^3}{(\epsilon_0 + 2n_0^2)} \quad (6)$$

or

$$NV = \frac{A_p \Delta\lambda}{t \log_{10} e} \frac{(\epsilon_0 + 2n_0^2)}{18\pi n_0^3} = \frac{A_p \Delta\lambda}{t \log_{10} e} K \quad (7)$$

where A_p is the measured peak absorbance of a sample of thickness ' t '. As we have said, the absorption calculated using this dipole approximation formula appears to be independent of the particle size. However, the approximation is valid only for particles whose diameter is less than about 200 Å. This is smaller than the mean free path of conduction electrons in the bulk metal. Therefore conduction electrons in such particles will be scattered by the particle surface as well as by resistivity collisions, and hence the electron collision frequency ω_0 will become higher than for the bulk metal. Using the model of Kreibig and Frangstein [9] we write

$$\omega_0(R) = \omega_0(\alpha) + v_{F/R} \quad (8)$$

where $\omega_0(\alpha)$ is the collision frequency of the bulk metal and is given as we have said by the inverse of the resistivity relaxation time τ_R , $\omega_0(R)$ is the collision frequency

for a particle of radius R and v_F is the Fermi velocity of conduction electrons in the metal.

If this modified value for ω_0 is now put into equations (1) to (5) it is clear that the optical absorption becomes size dependent. The position of the absorption peak λ_p will not be greatly changed except for extremely small particles, but the width of the absorption $\Delta\lambda$ will increase rapidly with decreasing particle size. From equation (5) it can be seen that this 'surface' contribution to the absorption width will vary approximately as $1/R$ once the particle size is less than the bulk mean free path.

For particles larger than about 200 Å the surface effect will become less and less important. However the simplified dipole expression for the absorption given in equation (1) is no longer valid. As the particle size becomes appreciable compared to the wavelength of light, the Mie theory equation for the absorption becomes complicated and inherently size dependent. Both the peak position and the width increase with increasing particle size, and light scattering becomes appreciable. In fact the particle size range where the absorption is size dependent because of the surface effect and the size range where it is inherently size dependent overlap somewhat and so detailed calculations are required.

2.2. Calculation of the optical absorption spectra

The first three terms of the total extinction coefficient (i.e. absorption plus scattering) calculated by Mie can be written as

$$\gamma = \frac{N\lambda^2}{2\pi n_0^2} \text{Im}\{-a_1 + a_2 + p_1 + \dots\} \quad (9)$$

where each of the terms in the bracket is a power series in α where $\alpha = (2\pi R n_0)/\lambda$ is the ratio of the particle size to the wavelength of light. In this equation a_1 corresponds to an electric dipole term, a_2 to an electric quadrupole term and p_1 to a magnetic dipole term. In the limit of small R this reduces to equation (1). We have taken experimentally measured values of ϵ_1 and ϵ_2 for sodium, modified them for each particle size to allow for the surface effect and then substituted them into equation (9). We have then numerically calculated γ as a function of wavelength for each particle size to obtain the theoretical absorption curves. The calculation was made without approximating the high power terms in α . This sort of calculation was first done by Kreibig and Fragstein [9] for silver particles in a glass matrix.

For a real metal the dielectric constant can be expressed as the Drude terms plus interband terms, thus

$$\epsilon_1 = \epsilon_0 - \frac{\omega_p^2}{\omega^2 + \omega_0^2} + B_1(\omega) \quad (10)$$

$$\epsilon_2 = \frac{\omega_p^2 \omega_0}{\omega(\omega^2 + \omega_0^2)} + B_2(\omega). \quad (11)$$

We can compare such expressions with the measured bulk dielectric constant. For instance in Figure 1 the values of ϵ_1 measured by Smith [10] are shown as a function of λ^2 . From this straight line, using equation (10), we deduced that $\omega_p = 8.42 \cdot 10^{15} \text{ s}^{-1}$,

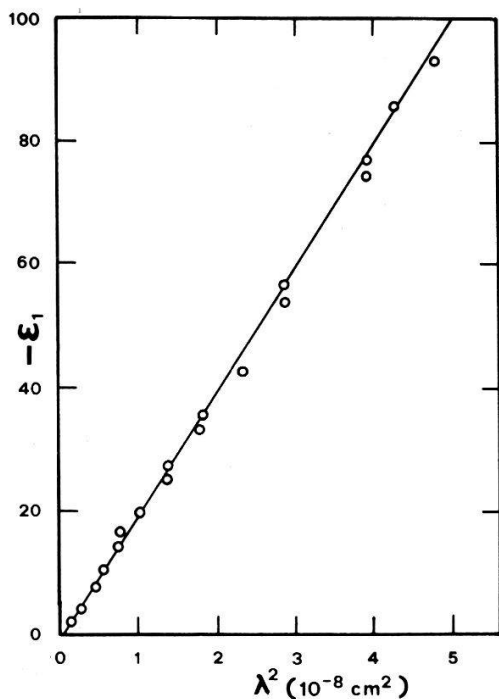


Figure 1

The real part ϵ_1 of the dielectric constant of sodium metal plotted against the square of the wavelength. These are the experimental values obtained by Smith. Using Drude theory, the plasma frequency ω_p can be obtained from the slope of this line, whilst the intercept gives ϵ_0 .

$\epsilon_0 = 1.25$ and that $B_1(\omega)$ was negligible in the frequency range of interest. Figure 2 shows the corresponding measured values of ϵ_2 multiplied by $\omega/4\pi$ and plotted as a function of $\hbar\omega$. The second curve shown is that obtained from equation (11) with the bulk value of ω_0 and using the theory of Animalu [11] for the interband term $B_2(\omega)$

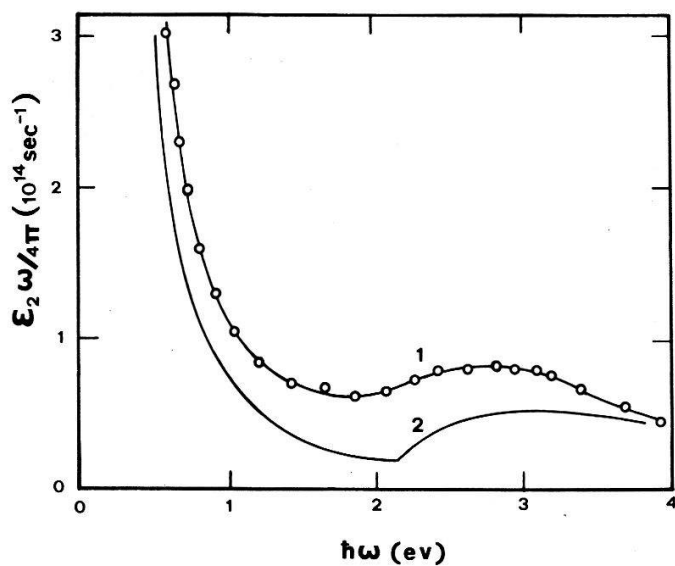


Figure 2

The imaginary part of the dielectric constant ϵ_2 , multiplied by $\omega/4\pi$ and plotted against the frequency in eV. Curve 1 is the experimental curve of Smith, curve 2 is obtained from the Drude theory together with the theory of Animalu for interband transitions which become important above 2 eV.

which becomes appreciable at high frequency. The reason for the discrepancy between these two curves, especially in the low frequency region, is not clear. It might be a sample surface effect in the measurement, or it might be due to electron-electron interaction effects. We have calculated the absorption using both of these curves. We used the bulk parameters $\omega_0(\alpha) = 2.98 \cdot 10^{13} \text{ s}^{-1}$ and $v_F = 1.03 \cdot 10^8 \text{ cm s}^{-1}$ to calculate $\omega_0(R)$. Then using equations (10) and (11) the surface modified values of ϵ_1 and ϵ_2 were obtained as a function of particle size and as a function of frequency. These values were fed into the Mie theory, equation (9), to obtain the absorption spectra for a series of particle sizes. The value of n_0 , the refractive index of NaCl, was taken to be 1.544.

Some calculated spectra are shown in Figure 3. From these spectra we measured the absorption peak widths $\Delta\lambda$ and positions λ_p and plotted them as a function of particle diameter as shown in Figures 4 and 5. These curves show the size dependence

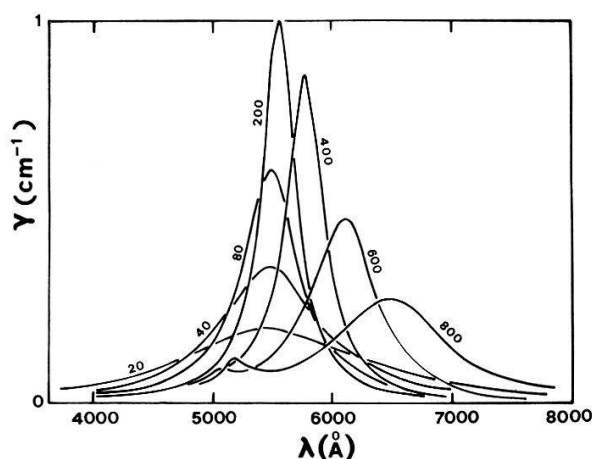


Figure 3

Showing the calculated absorption spectra for several different size spherical sodium particles. The absorption $\gamma \text{ cm}^{-1}$ is shown for a volume concentration of particles of 10^{-7} . The numbers marked alongside the curves are the appropriate particle diameters in Ångstrom units. As the particle size increases from 20 Å, the width of the absorption peak at half height, $\Delta\lambda$, decreases, passes through a minimum for particles of about 250 Å and then increases again for larger particles. With increasing particle size the peak position λ_p at first does not change markedly but then moves to longer wavelength for sizes greater than about 100 Å.

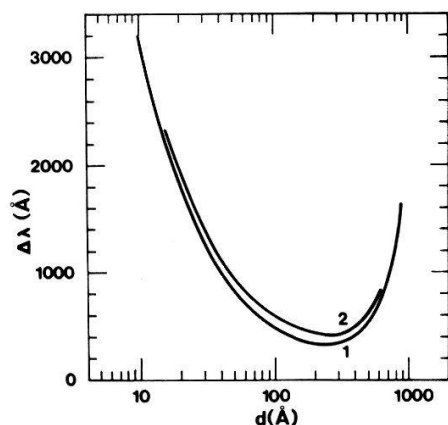


Figure 4

Showing the variation of the absorption peak width as a function of the particle diameter (both in Ångstrom units). Curve 1 was deduced using the theoretical values of ϵ_2 shown in Figure 2. Curve 2 was obtained using the experimental values.

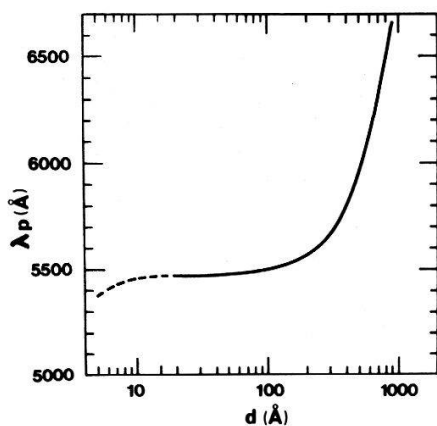


Figure 5

Showing the variation of the peak position λ_p of the absorption as a function of the particle diameter. Below about 20 Å the results are not very reliable. The peak position was the same for experimental or theoretical values of ϵ_2 .

which we expect from the model used. As the particle size increases from 10 Å the absorption width decreases rapidly, as the surface effect becomes less important, and reaches a minimum of about 330 Å for a particle diameter of about 250 Å. As the size increases above this value the peak widens again as the diameter becomes finite compared to the wavelength of light. The position of the peak is at first approximately constant with increasing size and occurs at 5470 Å. As the particle size gets larger than about 100 Å the peak moves to longer wavelength. For particles less than 20 Å diameter the peak position calculated was critically dependent on the bulk parameters used and was therefore unreliable.

The peak position calculated was the same using either the theoretical or the experimental values of ϵ_2 . The width was found to be slightly larger if the experimental values were used, as shown in Figure 4.

The area under the absorption curves was found to be roughly independent of the particle size, for instance by measuring the product of the calculated peak height and width the numerical factor K in equation (7) was found to be 0.029 for particles of 20 Å diameter and 0.032 for 600 Å diameter.

3. The Measured Optical Spectra and their Interpretation

3.1. Sample preparation

High purity monocrystals of NaCl were obtained from Korth Laboratories Kristalloptik oHG, Kiel, Germany. They were initially of size $20 \times 20 \times 20$ mm. These crystals were cleaved into pieces of size approximately $20 \times 20 \times 5$ mm and were additively coloured with an excess of sodium by heating them in a sodium metal vapour. This was done in two ways. Some samples were placed in a nickel bomb with a piece of sodium metal and heated for several hours at 700°C. Others were doped in a Van Doorn [12] apparatus for several hours at 700°C using nitrogen pressures of 100 to 1000 mm Hg. In both cases, after the doping process, the apparatus was cooled to room temperature by plunging it into cold water. The NaCl crystals in the interior undoubtedly took some finite time to reach room temperature however.

After doping, the samples were found to have the appearance shown in Figure 6 with

- 1) a transparent surface layer which did not scatter light,
- 2) a blue layer which scattered red light,
- 3) the interior region of the crystal which was usually like region 2) but absorbed and scattered less intensely.

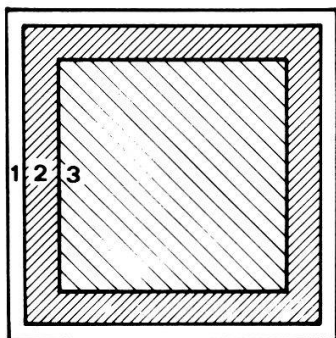


Figure 6

Showing the cross-section of a typical crystal after doping. 1) Transparent surface region, 2) blue layer which scattered red light, 3) interior region which was similar to region 2) but absorbed and scattered less intensely. Samples prepared in a nickel bomb had a surface region 1) which was coloured blue and which was wider than in the Van Doorn samples.

The blue coloration and Tyndall scattering were attributed to the presence of large sodium colloidal particles which precipitated as the NaCl crystals cooled down from the doping temperature. Samples prepared in the nickel bomb tended to be more intensely coloured. The surface layer was also wider and less transparent than in the Van Doorn samples. Frequently the bomb samples contained colloids of size 1 to 10 μ which could be seen, with an optical microscope, do 'decorate' irregularities in the crystal matrix. This effect was seen less often in the Van Doorn samples. In the experiments to be described below, samples prepared in the bomb and samples prepared in the Van Doorn apparatus showed essentially the same behaviour and the results presented will be a mixture from both types of sample. However, it was noticed that samples cleaved from the surface 1) region showed very different behaviour to those cleaved from the interior regions 2) and 3). The results are therefore presented in two different sub-sections.

3.2. *Samples cleaved from the interior regions of the doped crystals*

The samples were cleaved to sizes of typically $5 \times 5 \times 0.5$ mm. All the samples were then heated for about 3 minutes at a temperature of 650 to 700°C and then quenched between two copper plates. After this treatment the coloration due to large colloidal sodium particles was no longer present, but the crystals were coloured yellow due to an absorption band at approximately 4600 Å. This band was attributed to the presence of *F* centres. It was noted however that a part of this absorption was localized at the surface of the sample and could be removed by wiping away the surface of the crystal to a depth of several microns with a damp tissue (see for example Fig. 7). After quenching, all the samples were wiped in this way, because it was found that this surface localized *F* centre was stable and could not be converted into the *X* band

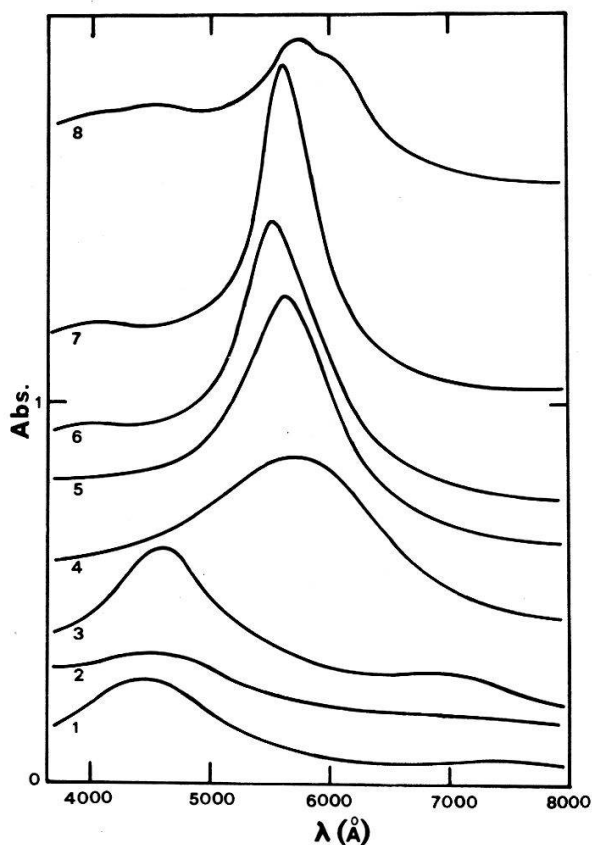


Figure 7

Showing the formation of the *F* and then the *X* band in an interior sample. Spectrum 1) sample heated for 3 minutes at 650°C then quenched to room temperature. This was the standard treatment used to put the samples in a defined state. An *F*-type absorption is present after this treatment. 2) After wiping away a thin surface layer of the sample with a wet tissue part of this absorption disappeared, hence part of this absorption was probably due to *F* centres localized in the sample surface. 3) Irradiation with UV for 30 minutes at room temperature generated the normal *F* centre in the volume of the sample. 4) Heating at 250°C for 10 minutes caused the *F* band to disappear and a wide *X* band to appear. 5) to 8) Heating for 10 minutes at 300, 350, 400 and 450°C caused the *X* band to narrow then to widen and become asymmetric.

Sometimes this surface localized absorption came at a slightly shorter wavelength than normal *F* centre absorption.

After the samples had been quenched and wiped to remove the surface layer, they were UV irradiated by placing them a few centimetres away from a 125 W high pressure mercury lamp for a period of 30 minutes. After this treatment the samples showed a more intense *F* centre resonance which was not localized near the sample surface. The *X* band was subsequently developed by heating the samples at temperatures between 150 and 450°C. These anneals were carried out by placing the samples on a light silver tray which slid into a slot in a copper metal block which was maintained at the selected temperature inside a small furnace. In this way the samples were heated more or less in darkness and reached the furnace temperature very quickly. Figure 7 shows the formation of the *F* band and the subsequent development of the *X* band by annealing a sample for 10 minutes at temperatures from 250 to 450°C. These spectra show that the *F* band disappears completely in the early stages as the wide *X* band appears. Figure 8 shows a sample which was annealed at 200°C for 180 minutes to produce a wide *X* band. Also shown are the spectra from another sample which was heated 5 minutes at 300°C and then for longer times at 400°C. These spectra

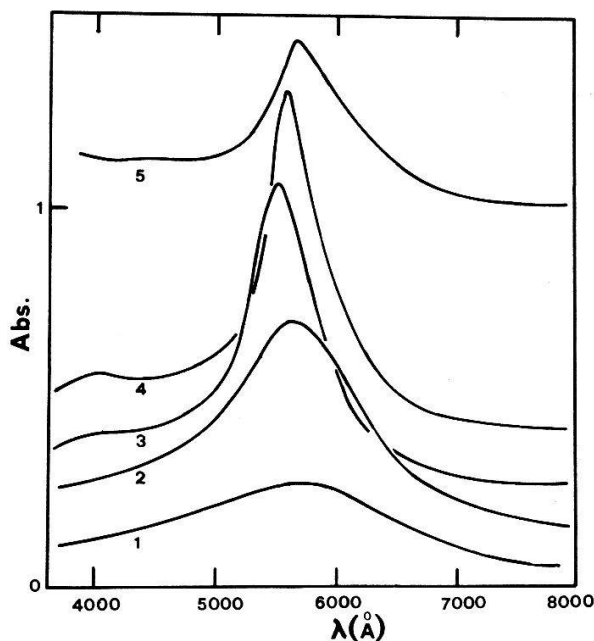


Figure 8

1) Sample treated with UV then heated 180 minutes at 200°C. 2) Another sample exposed to UV then heated 5 minutes at 300°C, then 3) 1 minute at 400°C, 4) 10 minutes at 400°C, 5) 140 minutes at 400°C. The *X* band shows a progressive narrowing then a broadening and shift to longer wavelength. These curves resemble the calculated spectra of Figure 3 and suggest a progressive growth of particle size.

show that the band tends to narrow with increasing anneal time or temperature and then finally broaden again or become asymmetric with a component of the absorption at longer wavelength. Preliminary comparison with the calculated spectra suggest that the *X* band is due to the formation of small sodium particles which grow larger with annealing. The measured position of the *X* band peak was 5500 Å (this was the minimum value observed) and this is very close to the value 5470 Å calculated for sodium particles with a diameter less than about 100 Å.

In order to obtain more detailed results we annealed a large number of samples at each of the temperatures 200, 250, 320, 400 and 450°C and studied the evolution of the *X* band as a function of the anneal. We measured the width and the position of the *X* band peak and plotted it as a function of anneal time. The results were found to be very reproducible from one sample to another. In Figures 9 to 13 the results are shown for three samples at each of the temperatures. The samples were a mixture of bomb and Van Doorn samples and they indicated the following evolution:

- 1) The width of the band absorption peak decreased with increasing anneal time, passed through a minimum value of about 500 Å and then increased with further annealing. Samples annealed at the lower temperatures did not attain the minimum width for the anneal times given. The absorption peak at first moved to shorter wavelength with increasing anneal time, reached a minimum wavelength of 5500 Å and then moved to longer wavelength with further annealing. The *X* band evolution was more rapid at the higher temperatures.
- 2) The rate at which the *X* band evolved from the *F* band was higher at higher temperature. The *F* band always disappeared before the *X* band narrowed and moved to longer wavelength.

- 3) Once the X band had formed, the concentration of the centres which caused it (measured by the product of the height and the width of the absorption) decreased with further annealing. The rate at which this decrease occurred was linked to the rate at which the band evolved, i.e. to the rate at which it narrowed and shifted to longer wavelength, being higher for higher anneal temperatures.
- 4) Only samples which had been annealed for a long time at the higher anneal temperatures showed appreciable light scattering.

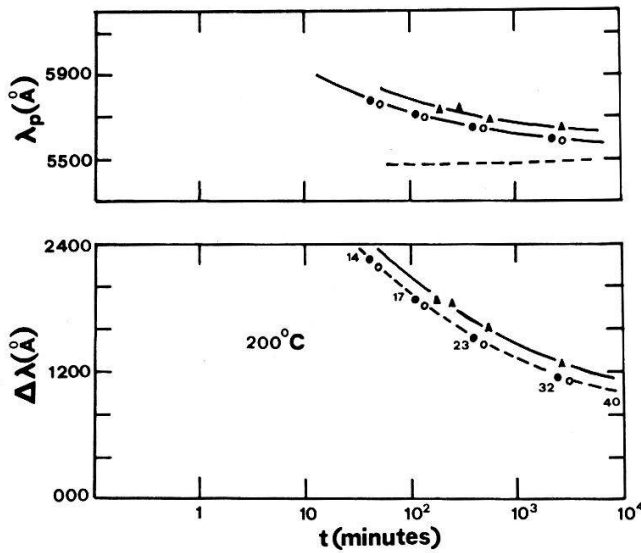


Figure 9

Evolution of the X band absorption with progressive annealing time at 200°C . The width of the absorption peak $\Delta\lambda$ and its position λ_p are shown as a function of the annealing time. The triangle and circles are the experimental points obtained for three different samples, and the solid lines are drawn through these points to show the evolution more clearly. In order to see if this X band is in fact due to Mie absorption from sodium particles which grow with annealing time, we have constructed (using Figs. 4 and 5) the theoretical curves for sodium particles whose size increases with annealing time. These are the broken lines. Then the particle diameters (in Angstrom units) which have to be assumed in order to construct these theoretical curves are marked alongside the broken line for several anneal times.

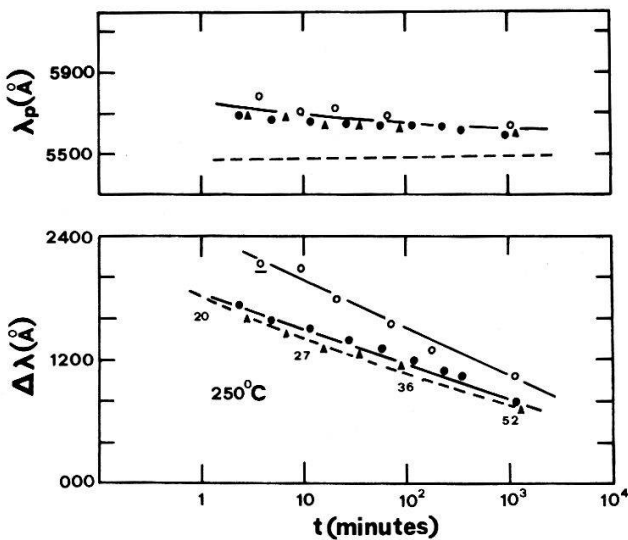


Figure 10

Evolution of the X band absorption at 250°C with the same notation.

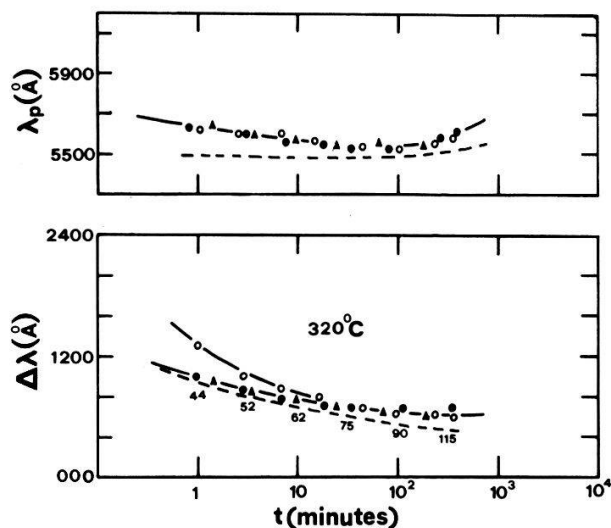


Figure 11
Evolution of the X band absorption at 320°C .

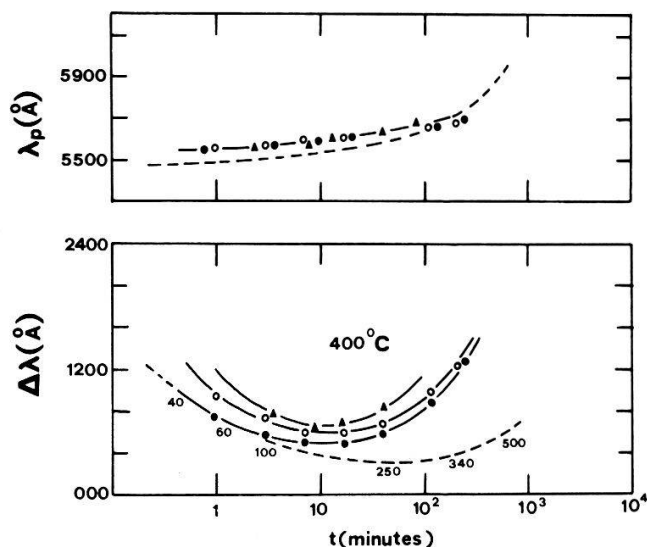


Figure 12
Evolution of the X band absorption at 400°C . There is now a discrepancy between the theoretical curves and the experimental points in the later stages of the anneal. The measured widths are too large and this is attributed to the existence of a large range of particle sizes.

These results suggest the following interpretation: The X band is due to colloidal sodium particles. These particles are formed by the thermal coagulation of F centres. All the F centres become converted into sodium particles which are initially very small. For instance, when the deduced particle diameter is only 20 \AA nearly all the F centres have been already converted. When all the F centres have been converted the deduced volume concentration NV of metal particles formed is typically $0.7 \cdot 10^{-5}$ for the Van Doorn samples and $1.5 \cdot 10^{-5}$ for the bomb samples. As the thermal annealing continues the average particle size increases and the total concentration of metal present decreases. This particle growth is deduced from the fact that the absorption linewidths decreased, passed through a minimum and then increased again as the anneal progressed. In the later stages of the annealing the particles were sometimes large enough to scatter light. The temperature dependence of the X band evolution

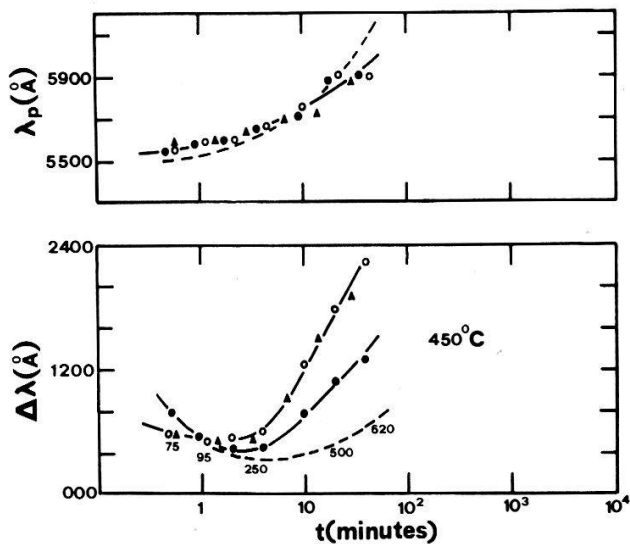


Figure 13
Evolution of the X band absorption at 450°C .

suggests that the particle growth is a diffusion limited process. If we assume that the colloid is in equilibrium with a diffusing species in the NaCl then the average particle size might increase by an Ostwald ripening process. The nature of the diffusing species is not known. It might be perhaps a sodium atom or ion or it might be an F centre. If it is an F centre then the concentration must be very low since, as we have already said, no F centre optical absorption was left once the X band had been formed. The higher surface tension pressure on the smaller particles would mean that they effectively evaporate sodium preferentially, via the diffusing species, onto the larger particles and hence the larger particles grow larger at the expense of the smaller ones. This process would result in an increase in the average particle size but could also lead to a wide distribution of particle sizes or even distinct groups of particle sizes which might explain the asymmetric or doublet type of spectra sometimes seen after annealing at 400 or 450°C .

We have compared the measured width and position of the X band as a function of annealing with those which might be expected from a sodium colloid. In Figures 9 to 13 the broken lines represent the calculated width and position of the absorption from a colloid whose size evolution was chosen so as to have a good fit with the measured curves. In other words the widths and position of the absorption were obtained from Figures 4 and 5 using the particle size as an adjustable parameter to have the best fit with the measured curves. The numbers written alongside the broken line are examples of the particle diameter, in \AA , which was used to deduce the values for that particular stage of the anneal. The correspondence between the measured curves and the synthesized colloid curves is quite good. In Figure 14 we show the deduced colloid diameter as a function of the anneal time for each of the anneal temperatures used. In the later stages of the annealing process, when the particle size becomes large, Figures 11, 12 and 13 show that the measured absorption width was too large compared to the calculated width (which was a compromise fit to both the width and the position of the peak). This difference was attributed to the presence of a wide range of particle sizes at this stage of the anneal. This is plausible enough if the growth proceeds by a ripening process. Clearly this size range means that the corresponding particle sizes shown in Figure 14 may be subject to considerable error. Nevertheless the sizes deduced

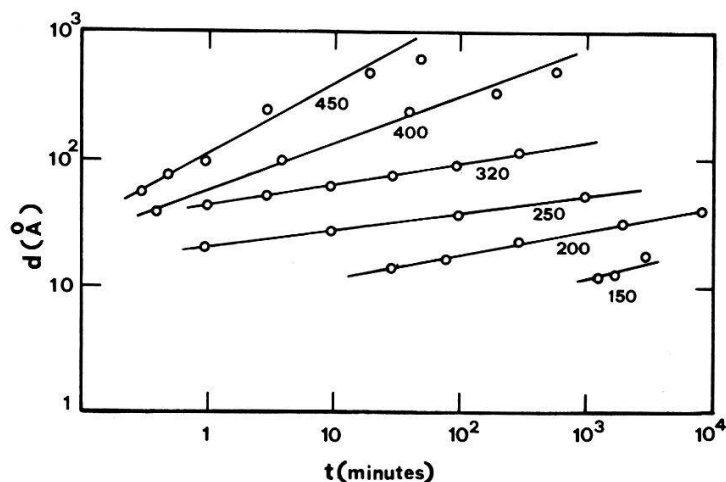


Figure 14

If we assume the *X* band to be due to colloidal sodium particles then we deduce these curves for the evolution of the particle size as a function of the anneal time. The diameters (in Ångstrom units) shown here for each anneal temperature are those which had to be used in order to construct the broken line curves in Figures 9 to 13.

for the earlier stages should be fairly reliable. It should be noticed that a curve like those shown in Figure 14 was obtained earlier by electron microscope and optical absorption measurements of silver particles in a glass matrix [13]. From the anneal curves (Figs. 9, 10, 11) it is clear that the measured peak wavelength λ_p for the smallest particles was always longer than the calculated value, and the discrepancy became greater as the particle size decreased. Taking the particle sizes used to plot the broken line, we have compared in Figure 15 the measured and calculated peak position as a function of the particle size. The form of the discrepancy is strikingly similar to that found for the silver particles in glass [13] and hence it seems that the theory may not be sufficiently good to predict peak positions for the smallest particle sizes, i.e. in the 'surface' region.

Using the above model for the evolution of the observed spectra we can interpret

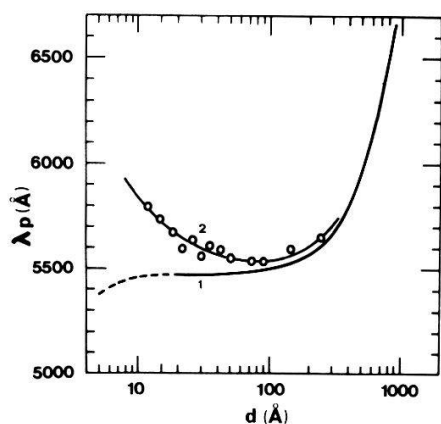


Figure 15

For several different samples we have plotted the experimentally measured peak position against the particle size deduced from the broken lines in Figures 9 to 13. The experimentally measured peak position is seen to be at longer wavelength than the calculated one, especially for the smallest particles. A very similar curve was obtained earlier for silver particles in a glass matrix.

the effect of the initial heat treatment and quench from 650°C. During such a high temperature annealing there would be a very rapid growth of particle size but at the same time the diffusing centres would tend to be recaptured by competing sites and tend to revert to their state before irradiation took place. We observed that the samples could in fact be recycled but the intensity of the X band decreased each time. This decrease occurred because while the samples were being heated at 650°C some of the diffusing species became localized F centres on the sample surface and these, as we have said, could not be converted to the X band. Presumably some centres were also 'lost' by forming large stable particles, but this was not investigated in detail.

All the samples described so far were UV irradiated at room temperature. Some additional samples were irradiated at a temperature of approximately 180°C. In these samples the F centre absorption appeared in the usual way, but as the irradiation continued another band appeared at about 6800 Å. With continuing irradiation these two bands disappeared as a very wide X band appeared. The width of this band was 3500 to 4000 Å and the peak occurred at about 4700 Å. Comparison with the results obtained for the samples already described suggested that this band was also colloidal but with a particle diameter of only about 10 Å. When this sort of sample was annealed at 400°C the band narrowed and evolved in the same way as samples which had been treated with UV at room temperature. This apparently confirms that the band was due to very small colloidal particles and indicates then that particles as small as 10 Å

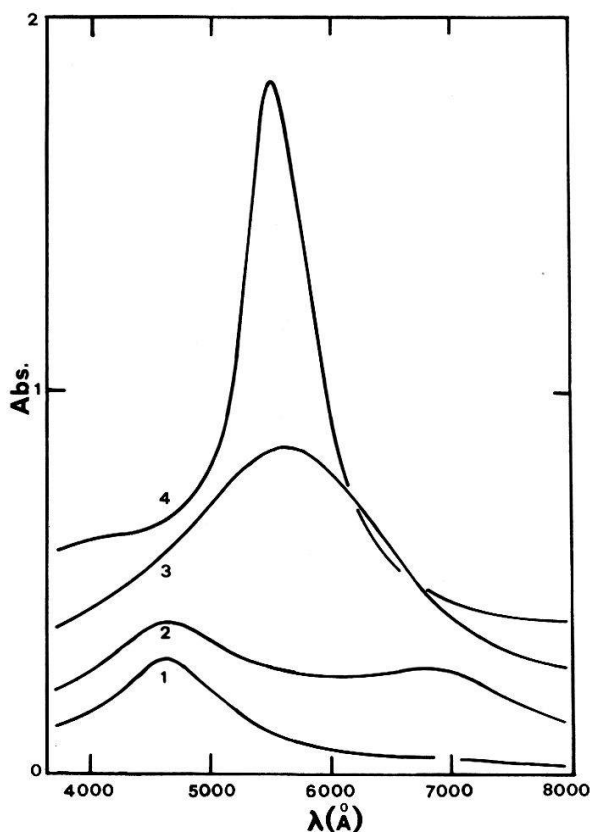


Figure 16

Showing the effect on the absorption spectrum of irradiating an interior sample with UV at a higher temperature than normal. 1) Normal UV irradiation for 30 minutes at room temperature, showing the F band 2) 1½ minutes UV irradiation at approximately 180°C showing an extra band around 7000 Å. 3) 30 minutes UV irradiation at 180°C showing a very wide X band. 4) 30 second anneal at 400°C showing a narrowing of the X band in the normal way.

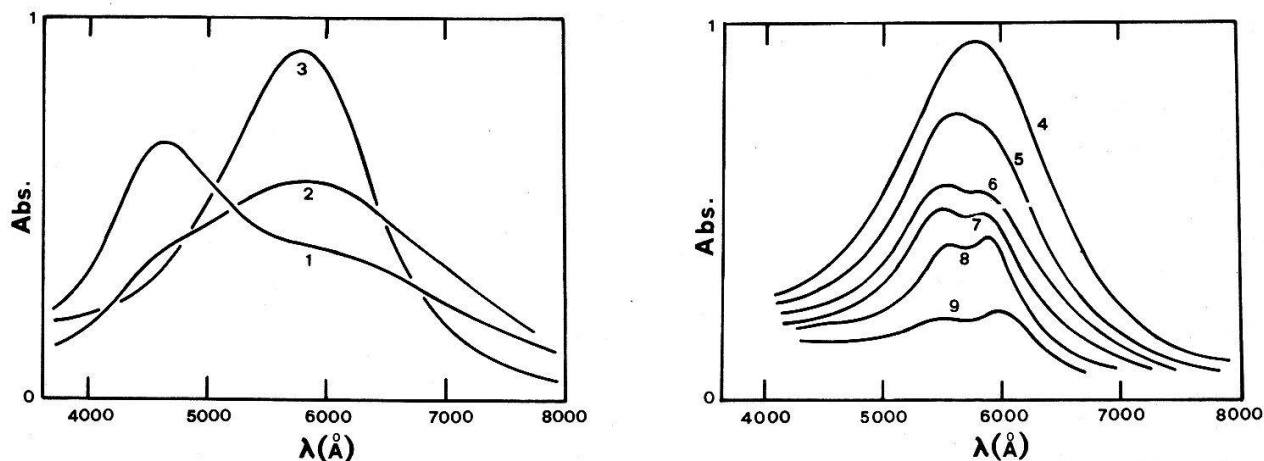
can be stable when formed. The band seen at 6800 Å was also seen in samples exposed to UV at room temperature. The peak wavelength of this band varied between 6800 and about 7300 Å from one measurement to another. This band was formed after the *F* band and always disappeared as the *X* band appeared. It seems likely then that it was an intermediate between the *F* band and small particles of diameter about 10 Å. We have not studied this band in detail. In the literature it is called the *M* band and is attributed to an agglomerate centre containing two *F* centres. The rather large variation in the peak wavelength is rather surprising for such a centre however, and it may be possible that the band we saw was composite, containing the *M* band plus a contribution from metallic agglomerates smaller than 10 Å diameter which contain very few atoms and which precede the formation of 'normal' colloidal particles.

We have attempted to confirm the deduction from the optical measurements by electron microscopy. Samples were thinned in alcohol, to which had been added a small concentration of water, and mounted on double grids. The technique was sufficiently good to provide extensive areas of sample which were transparent to the 80 keV electron beam. Usually an extensive microstructure was present in the samples. Micrographs were made using a low beam current since otherwise the electron beam itself caused extensive structure to appear in the samples during the measurement. We were unable to detect the presence of sodium particles in the micrographs obtained. We believe that this negative result can be attributed solely to the low concentration of particles present. With a magnification sufficiently high to observe the particles we can expect to see only about one particle per micrograph, and this is easily hidden in background microstructure.

3.3. *Samples cleaved from the surface region of the doped crystals*

Samples taken from the surface region were treated in the same way as samples from the crystal interior, i.e. they were heated at 650°C, quenched, wiped to remove the surface layer and then UV irradiated at room temperature for 30 minutes. However instead of gradually turning yellow due to the *F* centre absorption, these samples very quickly became a blackish blue colour during the UV irradiation. Some typical spectra are shown in Figure 17. The blackish colour was due to a composite absorption by an *F* band and a very wide *X* band. If the samples were left in the dark for about a week at room temperature, the *F* band almost completely disappeared and left a very wide *X* band only. This band resembled the wide *X* band obtained by irradiating interior samples above room temperature but it occurred at slightly longer wavelength, usually at about 5900 Å, and contained a higher concentration of centres than was usually obtained in interior samples, giving typically a volume fraction of $4 \cdot 10^{-5}$. This band was thought to be due to particles even smaller than those observed before, i.e. less than 10 Å diameter. In order to test this idea we annealed the samples to try and make the particles grow larger. Heating at 200 to 300°C for very short periods did narrow the band but more slowly than usual and the concentration decreased.

Attempts to anneal the band by heating at 400°C produced behaviour very different from in the interior samples. The concentration of centres decreases rapidly whilst the band stayed fairly broad then split into a doublet as shown in Figure 18. Some *F* centre absorption was sometimes regenerated during these anneals so that the spectrum consisted of two or three absorption peaks. These results are more difficult to interpret than those obtained from the interior samples. Apparently very small sodium particles (less than 10 Å) are precipitated by UV irradiation at room tempera-



Figures 17 and 18

Showing the spectra obtained from a typical surface sample. 1) 30 minutes UV at room temperature in the normal way; 2) left 1 week at room temperature in the dark; 3) annealed 30 seconds at 320°C; 4) further 2 weeks at room temperature; 5) annealed 30 seconds at 400°C; 6) 1½ minutes at 400°C; 7) 4 minutes at 400°C; 8) 20 minutes at 400°C; 9) 76 minutes at 400°C.

ture. This suggests that diffusion plays a less important role in these samples, i.e. perhaps the centres which precede the colloid in these samples are not regularly dispersed but already grouped to some extent making the colloid form more readily. Since the concentration of centres decreases more rapidly in these samples it might be that the diffusing species (which normally leads to particle growth) is more easily captured by competing centres and returned to its initial state before the irradiation took place. Hence some larger particles would be formed whilst others would become smaller and perhaps unstable. The resulting doublet spectrum might then be due to a mixture of particle sizes. Alternatively the doublet might be due to non-spherical particles or to the precipitation of an anomalous phase of sodium. In order to see if the first alternative was possible we rotated the samples whilst measuring the absorption in plane polarized light. Under these conditions the relative amplitude of the two peaks should have changed if the peaks were due to non-spherical particles aligned preferentially along one crystal direction. We observed, in fact, only very small changes, to which we were unable to give a definite interpretation. The existence of two size groups seems to be the most likely explanation of the doublet, however it is clear that further experimental work would be needed to clarify this point.

The reason for the difference between the surface and the interior samples is not clear. It is possible that some impurity diffused into the surface layer of the crystals during the doping process. Alternatively the difference might be due to the fact that the surface region cooled more quickly from the doping temperature and less or no colloid precipitated during this short cooling period. In order to try and understand the difference between the two groups of samples we examined their UV spectra. We examined the *U* band which is ascribed in the literature to the presence of H^- replacing Cl^- anions in the NaCl structure. According to the accepted model, UV irradiation causes the formation of H^0 atoms from these *U* centres. The H^0 can diffuse away leaving an electron localized on an anion vacancy, i.e. an *F* centre. The agglomeration of these *F* centres then forms the *X* band. In all the interior samples we observed the usual *U* centre at about 1920 Å. However, in the surface samples we observed a more intense absorption which overlapped with the *U* band, which peaked a slightly

longer wavelength and which had a tail extending towards longer wavelength. Hence the total absorption in the UV was wide and asymmetric. Aegerter [14] has noted similar UV bands and attributed them to *U* centre pairs. This interpretation is clearly very interesting in view of the fact that, as we have said, the colloid formation process in surface samples might be explained if the pre-colloidal centres were already partly grouped together. Further work is needed to better understand the behaviour of the surface samples. Such a study might be interesting in view of the marked similarities between the spectra formed in these samples and those observed during the formation of the latent image in the photographic effect. Optical bleaching of the 'print out' image has been shown [1] to produce doublets similar to those observed here by thermal annealing of the *X* band in surface samples.

4. Concluding Discussion

The optical absorption due to small sodium particles in a matrix of NaCl has been calculated using the theory of Mie with the modification of Kreibig and Frangstein, which allows for the scattering of conduction electrons by the surface of the metal particles. The resulting absorption spectra are very dependent on the particle size. As the size increases from, say, 10 Å the width of the absorption decreases rapidly, passes through a minimum for particles of about 250 Å diameter then increases with increasing particle size. The position of the peak, 5470 Å, was calculated to be almost size independent up to a size of about 100 Å and to shift towards longer wavelength for larger particles. The size dependence of the absorption was similar to that calculated earlier for silver particles in a glass matrix.

The *X* band absorption produced in NaCl doped with an excess of sodium has been studied experimentally. The doped crystals were irradiated with UV light to produce the *F* band absorption then thermally annealed to produce the *X* band. The width and position of the *X* band were measured as a function of the annealing time and temperature and the results compared with the values calculated for the absorption due to sodium particles. From this comparison we concluded that the *X* band is colloidal and we deduced the size and concentration of the colloidal particles as a function of the annealing time and temperature. The results suggest that the growth of the sodium particle size with annealing time is the result of a ripening process which occurs via a diffusing centre. The evolution of the *X* band from the *F* band and the evolution of the particle size both depended sharply on the annealing temperature, suggesting a diffusion limited mechanism. The *F* centres were almost completely converted to the colloid band by the time the average colloid diameter reached 20 Å. No measurable *F* centre contribution remained when the particles grew larger than this. Samples could be recycled after heating them a few minutes at 650°C and quenching them. However, the colloid concentration decreased each time a sample was recycled. This was partly due to the fact that stable *F* centres formed in a thin surface region of the sample. These *F* centres could not be converted into the colloid band. They were presumably formed when the diffusing species reached the sample surface during the thermal annealing. In our measurements we removed these surface centres after the quenching, hence the total concentration of centres in the sample decreased with each cycling. Possibly centres were also lost in forming large stable colloidal particle.

In most samples the deduced sodium particle sizes were in the range 10 to 600 Å diameter. At 150°C several days were needed to develop a colloid of 10 Å particles,

whilst at 450°C only a few minutes were required to produce 200 Å particles. The peak position of the absorption from particles smaller than about 100 Å diameter (i.e. in the 'surface' region) was found to be at longer wavelength than the calculated position and the discrepancy became larger as the particle size decreased, so that effectively the peak position went through a minimum value for particles of an intermediate size (like the width). The particle size in this range was therefore deduced from the width rather than the position of the peak. A similar discrepancy was noted for silver particles in a glass matrix and hence it seems that the absorption theory is not adequate to predict the peak position in this size range.

Samples which were prepared in the Van Doorn apparatus showed the same behaviour as those doped in the nickel bomb, and in both cases the results were very reproducible from one sample to another. However, samples cleaved from the surface region of the crystals showed very different behaviour from the normal samples cleaved from the sample interior. In these samples a very wide absorption was produced after UV irradiation at room temperature and was attributed to the formation of particles smaller than 10 Å diameter. This absorption was unstable during annealing at 400°C, the concentration decreased rapidly and a doublet was formed which may have been due to the presence of two distinct family size groups. The results suggest that this band formed from pre-colloidal centres which were already grouped together to some extent, and it is interesting to note that the anomalous *U* band seen in these samples may have been due to *U* pairs. The instability of this colloidal band may be explained if we assume that the diffusing centre, which normally leads to particle growth, in these samples is very easily recaptured by competing centres. For instance, a small particle might evaporate a sodium atom which converts to a diffusing centre but is absorbed by another centre before it reaches a second particle on which to condense. The absorbing centre might for instance be the hydrogen atoms formed from the *U* centres by UV irradiation. Further work is needed to understand the colloid evolution in these samples, and such work might be particularly interesting in view of the apparent similarities with the photographic process.

Attempts to observe the sodium particles with an electron microscope were unsuccessful, probably because the particle concentration was too low. A preliminary attempt was also made to observe the conduction electron spin resonance from the particles, again without success. This may also have been due to a concentration problem, however further work is needed to clarify this point.

These measurements show that the optical absorption can be a useful way of studying colloidal metal particles especially if the evolution of the colloid is followed. It is clear that this type of measurement can be extended to a range of other colloid-containing materials, and it would be interesting to see if the same sort of model for the optical absorption always applies.

Acknowledgments

We wish to acknowledge the helpful discussions which we have had with Professor J. P. Borel.

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