Radiation damage in NaCl: the annealing behaviour of heavily damaged KBF_4 doped crystals

Radiation damage in NaCl: the annealing behaviour of heavily damaged KBF$_4$ doped crystals

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Abstract. In this paper the annealing of Na colloids in heavily irradiated NaCl with damage levels up to 10 mol% is discussed. Recently the melting properties of Na colloids in heavily irradiated NaCl have been studied using differential scanning calorimetry. The observation of three endothermal latent heat peaks, numbered 1, 2 and 3, as a function of the dose, has been reported. Here we discuss the annealing behaviour of heavily irradiated crystals doped with KBF$_4$, which show a large melting peak 3. The changes in the appearance of the latent heat peak provide us with information about the properties of the sodium colloids.

The annealing of the colloids in two different temperature ranges is described. At moderate annealing temperatures between 160 and 210 °C the peak shifts with annealing time to lower melting temperatures very rapidly. The shift of the peak is activated by an energy of 1–1.4 eV and strongly depends on the initial amount of latent heat. At high temperatures between 250 and 320 °C a decrease of the latent heat is measured, due to the back reaction between Na colloids and molecular Cl$_2$. After continued annealing at high temperatures the melting behaviour becomes very anomalous. The melting peak splits into two peaks, the main peak and a new, sharp one arising at 92 °C. After the splitting of the peak the back reaction slows down significantly, activated by an energy of 1.2 ± 0.3 eV.

Both the moderate- and high-temperature annealing behaviour indicate that the processes are very local, with a short length scale of the order of 1 nm. This implies that the morphology of this type of colloid is highly irregular, with a dense and fine nanostructure.

1. Introduction

The investigation of the production of radiation damage in NaCl is highly interesting from a fundamental point of view (the physics of small clusters and structures) and from a practical point of view (the storage of nuclear waste). Much research, using a variety of experimental methods, has been done in this field during the last decades. Recently a very appropriate method to analyse Na colloids in NaCl produced by high-dose irradiations has been described [1]. By means of differential scanning calorimetry (DSC) the melting transition of the Na colloids is measured. The melting of the colloids appears as an endothermal peak pattern in the DSC scan, in which up to three different latent heat peaks can be distinguished. Two peaks are already observed in crystals irradiated with relatively low doses; a third peak is only observed at high doses (> 20 Grad). The melting peaks 1 and 2 are found at characteristic positions (at about 80 and 92 °C), which do not change after annealing. The third peak is found at temperatures between 95 and 130 °C and is very sensitive to an annealing treatment, as we will discuss below.

In this paper we will focus our attention on the properties of this third peak. If this third peak starts to develop and the irradiation proceeds, the third peak increases, while the first

two peaks observed at low doses slowly vanish. No saturation of the colloid production connected to this third melting peak is observed for the applied dose range (up to 150 Grad). Based on the latent heat measurements it has been found that the amount of metallic Na in doped NaCl crystals can easily exceed the level of 10 mol%.

This third peak is particularly interesting, because the unlimited growth of peak 3 leads to instabilities in the crystal. In our laboratory we have frequently observed a sudden and violent fragmentation of heavily irradiated crystals that showed a large peak 3. In this paper we will study this peak extensively by monitoring changes in the appearance of the peak as a result of annealing treatments at moderate and high temperatures. Both the position and shape of the peak and the amount of latent heat as a function of both the annealing time and the annealing temperature provide us with important information about the properties of the colloids.

The paper has been organized as follows. First the annealing experiments, using the DSC set-up, will be explained. The next two sections describe the annealing experiments at moderate temperatures between 160 and 210 °C (section 3) and the annealing experiments at high temperatures between 250 and 320 °C (section 4). Finally, the results obtained for the two temperature ranges are connected by the conclusions presented in section 5.

2. Experimental method

The latent heat peak pattern is obtained by measuring the heat flow required to increase the temperature of the crystal containing the Na colloids at a constant rate. A rate of $10\,°C\ min^{-1}$ has been found to be the most appropriate choice, since it does not affect the actual peak shape [1]. Directly afterwards the crystal is heated to and kept at the required annealing temperature for some time. This procedure has been repeated as many times as necessary to obtain a complete picture of the annealing behaviour as a function of time. A survey of the isothermal annealing experiment at the annealing temperature T_{ann} for a variable time Δt_{ann} is given below:

melting scan	40–150 °C	$10\,°C\ min^{-1}$
heating to	T_{ann}	$250\,°C\ min^{-1}$
annealing at	T_{ann}	Δt_{ann}
cooling to	40 °C	$250\,°C\ min^{-1}$
next run.		

During heating and cooling at a rate of $250\,°C\ min^{-1}$ the crystal is in fact annealed for a short time, which we have estimated to be effectively 0.1 min, i.e. during the last 25 °C of the heating ramp (or the first 25 °C cooling). Since the annealing time is 1 min or longer this effect can be neglected.

The crystal system used for this investigation is NaCl doped with 300 ppm KBF_4. This type of crystal shows a relatively high tendency to form radiation damage, which is observable by a large peak 3 in the melting pattern. Often, particularly at high damage levels, peaks 1 and 2 have vanished in these crystals. The crystals were irradiated with 1.3 MeV electrons from a van de Graaff accelerator [2] with doses up to 150 Grad and a dose rate of 100 or 250 Mrad h^{-1} at various temperatures between 20 and 150 °C. The weight of a crystal varied between 5 and 20 mg. For crystals containing less than 1 J g^{-1} latent heat the weight had to be about 10 mg or more to obtain a good latent heat signal.
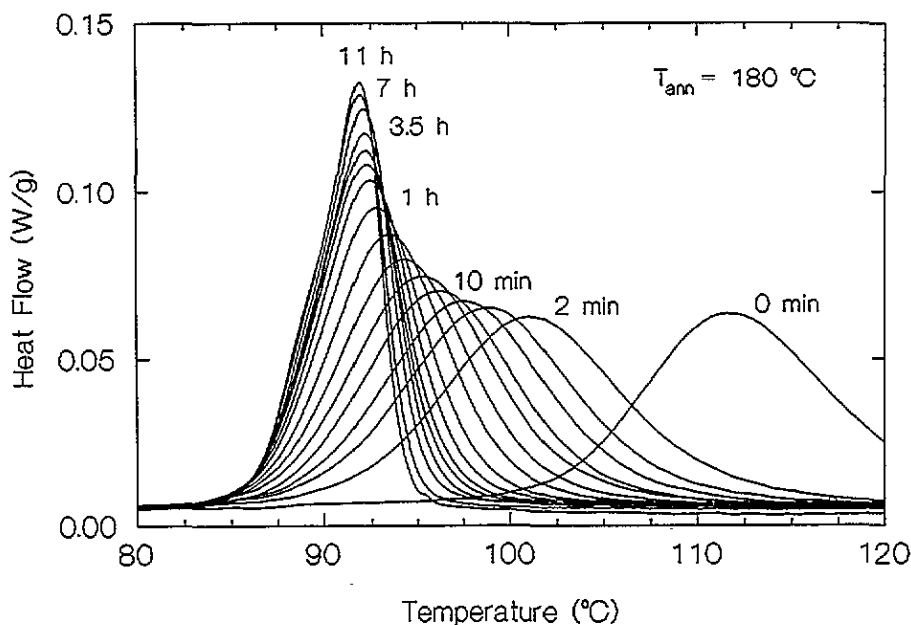
Figure 1. The position and shape of latent heat peak 3 after successive annealing runs at 180 °C. The labels denote the cumulative annealing times. Sample: 150 Grad, 250 Mrad h^{-1}, $T_{irr} = 75$ °C, 300 ppm KBF$_4$, weight = 22.35 mg, initial latent heat = 4.4 J g^{-1}.
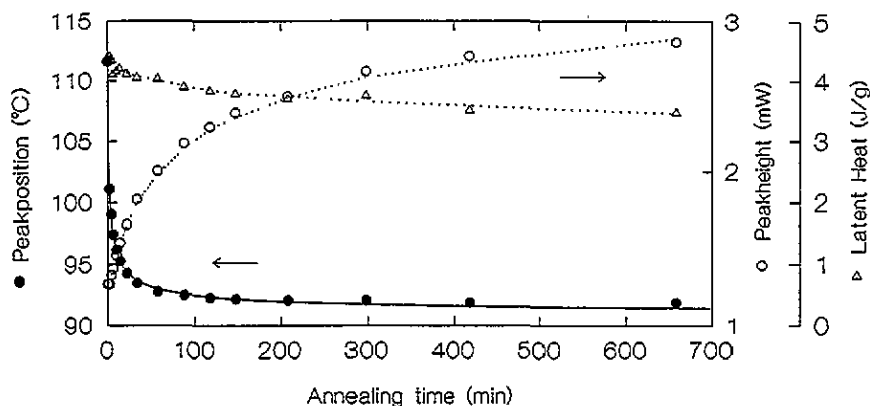

Figure 2. DSC data for the annealing experiment presented in figure 1. The solid line is a fit to a function $\sim (at + 1)^{-1/2}$.

3. Moderate-temperature annealing

3.1. The shift of melting peak 3

After annealing at moderate temperatures, between 160 and 210 °C, some striking features can be observed. Directly after the irradiation the so-called third peak is found at temperatures up to 126 °C, which is far above the melting temperature of bulk Na (98.7 °C). Due to the annealing treatment the peak shifts rapidly to lower temperatures. A typical

example is shown in figure 1. The crystal was kept at an annealing temperature of $T_{ann} = 180\,°C$ for a cumulative annealing time of 11 h.

In figure 2 the characteristic features of the measurements presented in figure 1 are shown. During the first few minutes the shift of the peak is very rapid. Only a very small amount of latent heat is lost, probably as a result of the back reaction of Na and Cl_2. The peak width decreases and the height increases. At times longer than 2 h the peak position stabilizes at the equilibrium value of about 92 °C, whereas the width still decreases. Finally, the peak becomes more and more triangular shaped, probably as a result of the continued narrowing of the distribution of melting temperatures (in the case of one melting temperature, e.g., for bulk Na, the DSC scan shows a sharp right-angled triangular peak shape).

Many samples doped with KBF_4 (300 ppm) were annealed as described above. The initial peak position T_0 varied from 126 °C to 102 °C. In general, T_0 is lower for higher irradiation temperatures and lower for larger amounts of latent heat. The final peak position T_∞ varies between 86 and 93 °C. T_∞ slightly decreases for increasing annealing temperatures, which indicates that the final equilibrium situation depends on the annealing temperature. If the annealing temperature is increased after previous annealing at a lower temperature, the peak shifts again to lower melting temperatures. This clearly demonstrates that the nature of the equilibrium depends on the annealing temperature. T_∞ increases slightly ($< 2\,°C$) with increasing amounts of latent heat, which is caused by the triangular shape of the peak: a larger peak will have a maximum at a higher temperature.

In order to analyse the shift of the peak we have fitted the curves of the peak position T_p against the time with different functions, in particular $\exp(-at)$ and $(at + 1)^{-x}$. It appears that the curves can be fitted very well with $(at + 1)^{-1/2}$, for crystals irradiated under different conditions, containing different amounts of latent heat and annealed at different temperatures. The empirical equation describing the shift of the peak has the following form:

$$T_p = T_\infty + (T_0 - T_\infty)/(at + 1)^{1/2} \tag{1}$$

where T_0 and T_∞ are the initial and final peak maximum melting temperatures, and

$$a = \alpha(T_0 - T_\infty)^2. \tag{2}$$

The parameter $\alpha = A \exp(-E/kT_{ann})$ is independent of the initial peak position and allows a direct comparison of crystals with different amounts of latent heat or annealed at different temperatures.

The temperature dependence of the shift has been measured by breaking a crystal into two or more pieces and annealing these pieces at different temperatures. The amount of latent heat for different pieces of the same crystal varied by an amount of about 0.1 J g^{-1}. The results for a series of crystals with different amounts of latent heat are presented in figure 3. The figure shows that the peak shift is activated by an energy of about 1–1.4 eV, slightly increasing for increasing amounts of latent heat. Figure 4 shows that the rate parameter α increases strongly if the amount of latent heat exceeds the value of 2 J g^{-1}. This indicates that the diffusion and dissociation processes depend upon the amount of damage in the crystal (see section 5).

3.2. Theoretical concepts

Changes in the melting temperature of the colloids associated with peak 3 due to an annealing treatment will be caused by changes in the local structure, the size and shape of the colloids
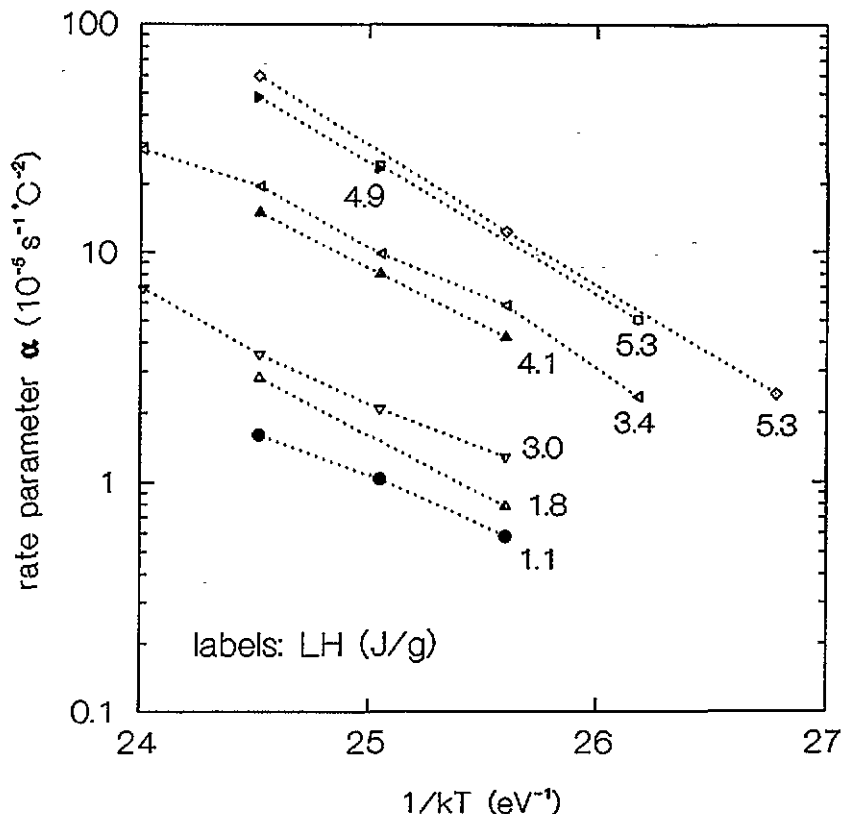
Figure 3. An Arrhenius plot of the rate parameter α, representing the rate of the shift of peak 3 for various heavily irradiated crystals with different initial amounts of latent heat. The labels denote the average amount of latent heat for the different pieces of one crystal.

and the interface between the colloids and the matrix. In the recently published paper about the melting properties of sodium colloids as a function of irradiation dose [1], we have already discussed the size dependence of the melting temperature, based on a refinement of the classical thermodynamical treatment of Pawlow [3–6]. According to this theory the high melting temperature of peak 3 can be associated with relatively small particles in the range of 50–200 atoms. Such a small size scale explains the sensitivity of the peak position to an annealing treatment at moderate temperatures: small changes in the number or position of atoms result in a relatively large change of the thermodynamical properties of the particle.

On the other hand the crystal structure of the Na particles inside the matrix will strongly affect the melting temperature. It is not unlikely that the interactions with the NaCl matrix (with an FCC Na substructure) will force the relatively small Na particles into an FCC structure, while the large Na particles attain predominantly the normal BCC Na metal structure. The actual structure of the particle will strongly affect its melting temperature. The occurrence of two crystal structures is in agreement with x-ray diffraction studies of irradiated LiF, carried out by Lambert *et al* [7,8], which show the existence of BCC and FCC Li clusters.

Since there is little knowledge available about the properties of small metallic particles in a matrix, we cannot be very precise about the relation between the melting temperature and the size, shape and structure of the particles. Therefore, it is not possible to analyse

the initially Gaussian shape of the melting peak and the shift to lower temperatures during annealing very thoroughly. Obviously, the change of the melting peak can be associated with a change in the distribution of the number of Na atoms, which are part of a colloidal particle of a specific size, shape or structure. In this section we will discuss some theoretical concepts briefly, in order to give some ideas about the processes leading to the changes in the melting peak.

A possible process leading to a change in the distribution is Ostwald ripening: the growth of the larger particles at the expense of the smaller ones. This process has been analysed extensively by Jain and Hughes [9], based on the theory of Lifshitz, Slezov and Wagner (LSW theory). The colloid is subject to growth by diffusion of F centres towards and shrinkage by evaporation of F centres from the colloid. If the melting temperature is proportional to the curvature ($T_m \sim 1/R$), as can be derived from the thermodynamical considerations, mentioned above [4, 5], the growth of larger particles would correctly describe the shift to lower melting temperatures.

Unfortunately, the LSW theory is only valid for relatively low colloid concentrations and consequently leads to very low rates of ripening, with characteristic times τ of the order of magnitude 10^6–10^9 s [5, 10]. For comparison, the annealing experiment at $T_{ann} = 180\,°C$ presented in figure 1 (where $T_0 = 112\,°C$, $T_0 - T = 20\,°C$ and $\alpha = 5.9 \times 10^{-5}$ s^{-1} $°C^{-2}$) leads to a characteristic time of $\tau = a^{-1} = 40$ s for the shift of the melting peak.

However, since we are dealing with very high colloid concentrations, the short time of 40 s can still very well be understood in terms of some kind of ripening process. High colloid concentrations of more than 10 mol% lead to distances between the colloids that are relatively small as compared to the size of the colloids, such that the migration of F centres from peripheral parts of the colloids to more stable parts can occur very rapidly. During the time $\tau = 40$ s an F centre diffuses only over a distance $\sqrt{\langle x^2 \rangle} = \sqrt{(D\tau)} = 1$ nm at $180\,°C$ (calculated with the bulk diffusion constant $D = 0.01 \exp(-0.88/kT)$ [11, 12]), which indicates that we are dealing with a nanostructure.

If the rearrangement of the colloidal centres occurs on a length scale of 1 nm, the transformation will depend strongly on the local morphology of the colloids and its surroundings. This requires a more probabilistic model, which deals with the processes on an atomic level. Such a model would have to describe the evaporation of F centres and diffusion of colloidal centres along the surface of the colloid. We recently started to develop such a model for the growth of colloids, using a two-dimensional Monte Carlo simulation of the growth kinetics [13]. Such a model can easily be adjusted to provide us with information about the annealing behaviour of colloids.

4. The high-temperature annealing behaviour of melting peak 3

At high temperatures, above $250\,°C$, the amount of latent heat contained in peak 3 decreases strongly, due to the back reaction between the colloids and molecular Cl_2. The annealing experiments offer us the possibility to study the back reaction as a function of the annealing time. An example of the high-temperature annealing behaviour is shown in figure 5. In the beginning of the annealing experiment we observe the (very rapid) shift of the melting peak to low melting temperatures. After some time the peak splits into two peaks, the original peak, which continues to shift down to temperatures of about $80\,°C$, and a new peak arising at a fixed temperature of about $92\,°C$. (Note that the correspondence between the position of the new peak at $92\,°C$ and the position of the peak described in subsection 3.1, which stabilizes also at about $92\,°C$, is accidental. For annealing temperatures higher than $180\,°C$
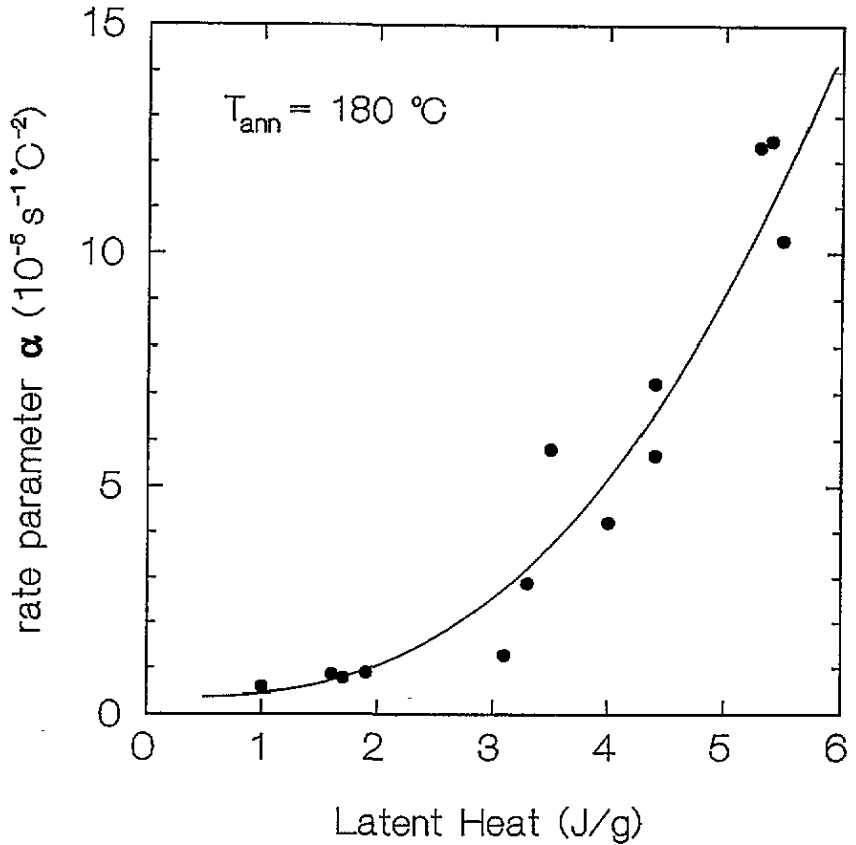
Figure 4. The rate parameter α versus the initial amount of latent heat for various heavily irradiated crystals annealed at 180 °C. The solid line serves to guide the eye.

the value at which the position of the peak described in subsection 3.1 stabilizes is lower than 92 °C.)

The two peaks are closely connected. Immediately after the annealing run the main peak is much larger than the new one at 92 °C. However, during storage at room temperature the new peak grows at the expense of the other one. For instance, the upper measurement in figure 6 shows the peak pattern immediately after 5 h annealing at 250 °C. The lower measurement shows the peak pattern after storage at room temperature for 2 d. The peak at 92 °C has grown much larger after the storage at room temperature, whereas the total integrated peak area has remained the same. Immediately after the next annealing run, the situation is reversed again. It appears that two states are possible for the colloid, with different melting temperatures. If the annealing is continued without intermediate relaxation, the area of the main peak (at about 83 °C) decreases, while the area of the peak at 92 °C remains constant.

Up to the moment of splitting of the peak the amount of latent heat decreases very rapidly. After the splitting the back reaction becomes relatively slow. This can be seen from the decrease of the amount of latent heat as shown in figure 7 for the annealing experiment at 270 °C (shown in figure 5). We have analysed the decrease of the latent heat in many samples annealed at different temperatures by means of curve fitting. The analysis of these annealing curves is complicated, since probably two or more processes
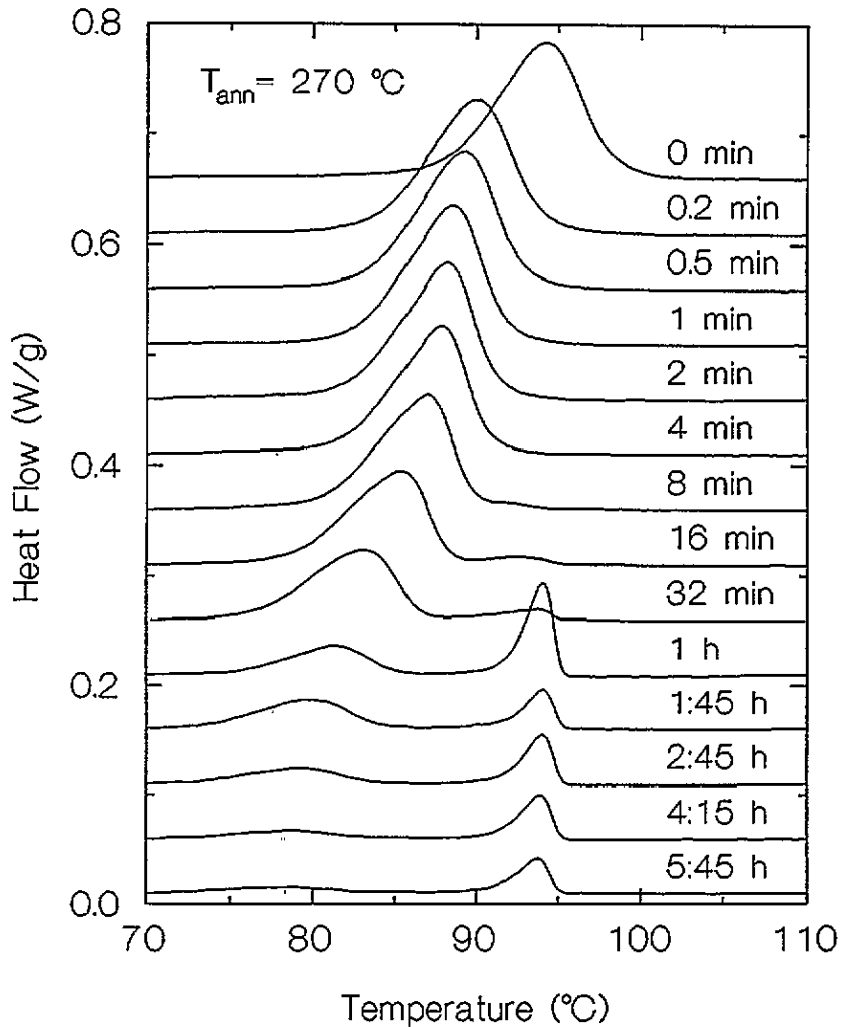
Figure 5. The vanishing of latent heat peak 3 due to annealing at 270 °C. The labels denote the cumulative annealing times. Sample: 150 Grad, 250 Mrad h^{-1}, $T_{irr} = 90$ °C, 300 ppm KBF$_4$, weight = 12.90 mg, initial latent heat = 4.8 J g^{-1}.

are involved. It appears that the long-time behaviour can be fitted reasonably well with an inverse linear time dependence, $n = n_0(at + 1)^{-1}$, but it is difficult to decide when this behaviour dominates the process. However, from the analysis we can roughly estimate the activation energy. In figure 8 an Arrhenius plot of the normalized rate parameter $\alpha = a/n_0$ is shown. We obtain for the activation energy of the process a value of 1.2 ± 0.3 eV, which is close to the activation energy for the peak shift at moderate annealing temperatures. However, it is considerably lower than the activation energy of 1.7 eV, as obtained by stored energy (SE) measurements [14, 15] for crystals containing relatively small amounts of damage (less than 1 mol% in Na colloid, showing only the latent heat peaks 1 and 2).

At 270 °C $\alpha = 6 \times 10^{-5}$ (J g^{-1}) s^{-1}, which leads to an absolute rate of decrease of the latent heat of about 2×10^{-3} J g^{-1} s^{-1} for an amount of latent heat of 3 J g^{-1} and 1.5×10^{-5} J g^{-1} s^{-1} for an amount of latent heat of 0.5 J g^{-1}. It is interesting to compare

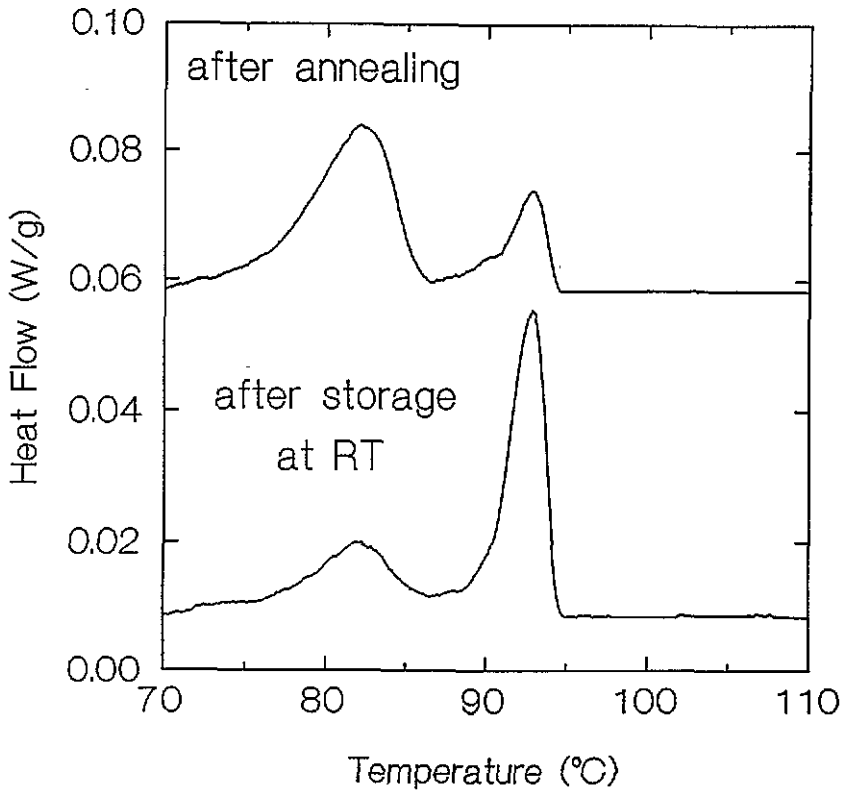**Figure 6.** The change of the peak pattern after storage at room temperature. Sample: 105 Grad, 100 Mrad h^{-1}, $T_{irr} = 90\,°C$, 300 ppm KBF$_4$, weight $= 8.80$ mg. The sample has been annealed at 250 °C for 5 h.

the latter value with the value for the type of crystal that only shows melting peaks 1 and 2 and, therefore, can be expected to have an entirely different colloid morphology. The rate of decrease of latent heat for this type of crystal, with an equal amount of latent heat of 0.5 J g^{-1}, is about 0.5×10^{-3} J g^{-1} s^{-1} [5], which is almost two orders of magnitude larger than the corresponding value of the crystal described above (the value 0.5×10^{-3} J g^{-1} s^{-1} can also be obtained from the SE measurements [14, 15, 5], using the fact that 0.5 J g^{-1} latent heat $\cong 100$ J g^{-1} SE [1]: the rate of release of SE at 270 °C is about 8×10^{-2} J g^{-1} s^{-1}, calculated with $dn/dt = n^{1/3} \times 10^{14} \exp(-1.7/kT)$, i.e. 4×10^{-4} J g^{-1} s^{-1} latent heat).

5. Conclusions

Both the moderate- and high-temperature annealing behaviour support the idea that the colloids are rough and highly irregular with a morphology characterized by a short length scale. A rough interface explains the rapid shift of the latent heat peak at moderate temperatures. The annealing causes a rearrangement of atoms from peripheral sites of the colloids to more stable sites. The finest details will disappear first, leaving irregularities with a larger length scale, corresponding to a lower melting temperature. Ultimately some equilibrium structure is formed as a result of the competition between the build-up and a
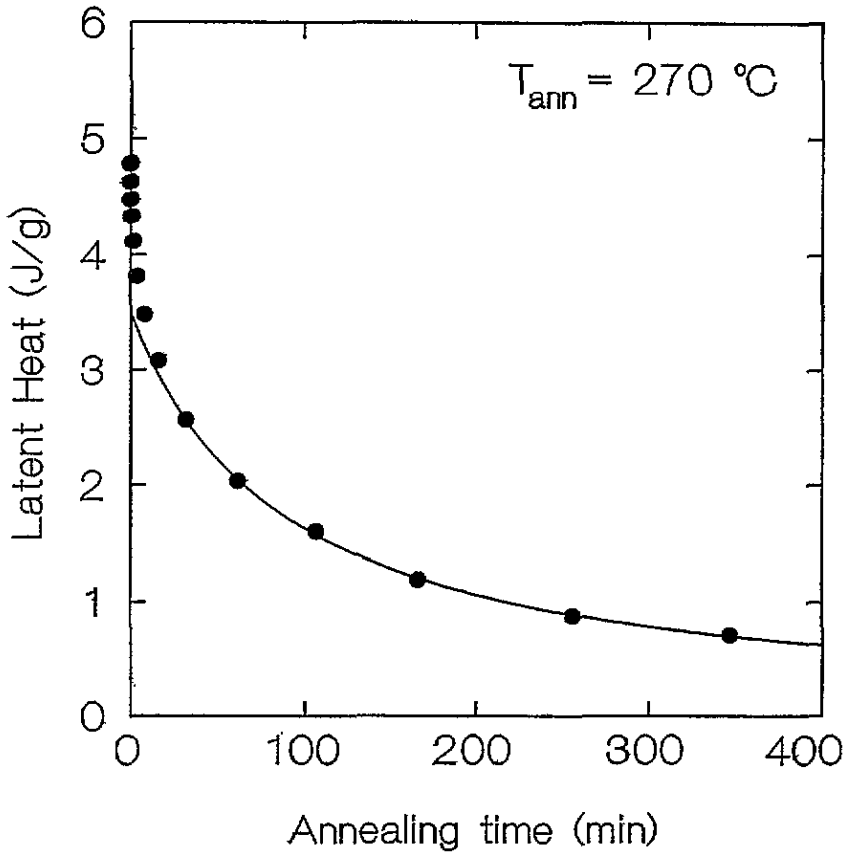
Figure 7. The decrease of the latent heat contained in peak 3 for the annealing experiment presented in figure 5. The solid line is an inverse linear fit to the data.

temperature dependent breakdown of a stable structure (e.g. the competition between surface diffusion to stable sites and evaporation and subsequent bulk diffusion to random sites).

On the other hand the rough morphology of the colloids explains the rapid decrease of the latent heat during the first minutes of annealing at high temperatures. F centres from peripheral sites evaporate easily, such that the rate of the back reaction is relatively high. If, after some time, the surface has become smooth, the F centres evaporate less easily, which explains the slowing down of the back reaction.

The rate of the shift of peak 3 at moderate annealing temperatures depends strongly upon the amount of latent heat, i.e. on the amount of damage in the crystal (figure 4). If the process is a short-distance rearrangement, the rate will be determined by local exchange processes between the irregularities of the colloid and not by the microstructure as a whole. Therefore, a rate that increases with increasing damage level indicates that the colloid morphology becomes finer and denser, having a decreasing length scale.

The splitting of the main melting peak into two peaks at high annealing temperatures is difficult to understand. Since the transition from one peak into the other is reversible, we conclude that both peaks belong to the same colloid. Possibly the colloidal Na can attain two structures. If the crystal is heated and cooled down again to room temperature the colloid solidifies in a chaotic structure, which is imposed on the Na precipitates by the
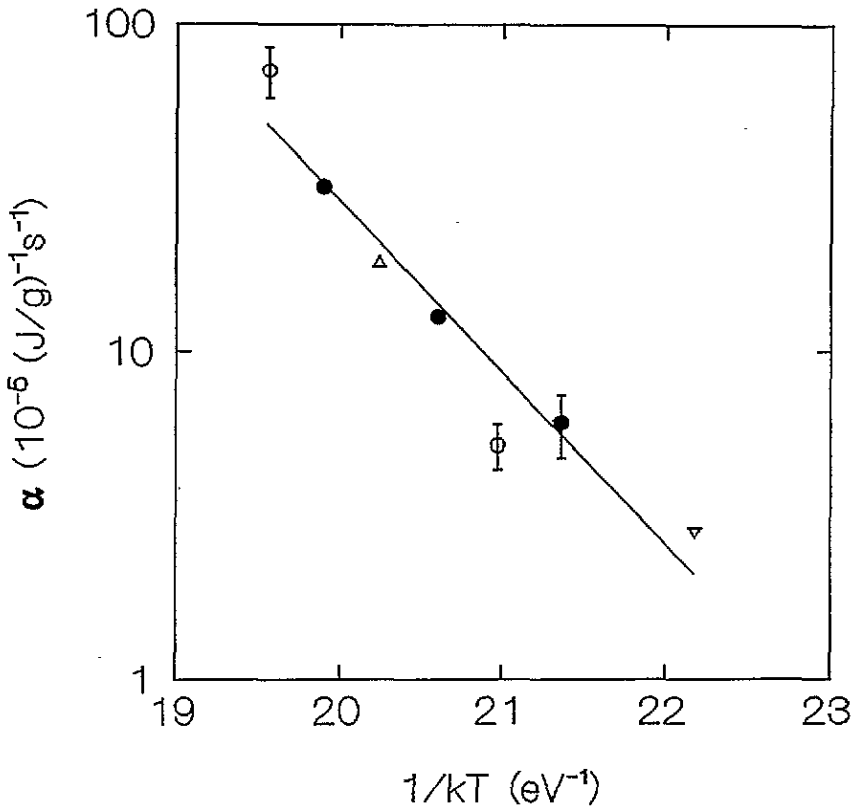
Figure 8. An Arrhenius plot of the rate parameter α, representing the rate of the back reaction for various heavily irradiated, KBF_4 doped crystals. The different symbols denote different crystals.

surrounding distorted matrix. Hereafter, the transition to the equilibrium structure takes place. Since the relaxation is relatively slow, we observe two peaks in the melting pattern.

The difference in the absolute rate of the back reaction for the type of crystal showing peak 3 in the melting pattern as compared to the crystals showing only peaks 1 and 2 in the melting pattern, together with the significantly different activation energies for the two types of crystal, implies that we are dealing with an entirely different mechanism for the back reaction in the two cases. This is an important conclusion because it has major consequences for modelling the production of radiation damage at large damage levels. The new mechanism leading to the formation of colloid, connected with melting peak 3, has to be implemented in the model, in order to describe the production of radiation damage in heavily irradiated crystals correctly. Probably the differences originate from the large distortion of the crystal matrix in the heavily irradiated crystals, which will strongly affect the diffusion and dissociation processes. The evaporation of F centres into the distorted matrix is possibly much more difficult. The colloids in the type of crystal that shows only peaks 1 and 2 in the melting pattern have grown in a relatively undistorted matrix and have a coherent interface, such that in these crystals the F centres evaporate easily and *subsequently recombine with the Cl in the crystal.*

The idea that the morphology of the colloids is highly irregular with a fine and dense structure is in line with the anomalous electron spin resonance (ESR) results obtained

for heavily irradiated crystals [16, 5]. ESR measurements carried out between 4 K and room temperature show an anomalous decrease of the line width with increasing measuring temperature. Both the integrated intensity and the line width, obtained with ESR experiments carried out at room temperature, remain constant during the annealing at moderate temperatures. Due to annealing at high temperatures the intensity decreases proportionally to the amount of latent heat. The line width decreases strongly at low measuring temperatures, while it remains constant at room temperature. These observations cannot be explained in terms of a regular, compact shape of the colloid.

Acknowledgments

References

[1] Seinen J, Weerkamp J R W, Groote J C and den Hartog H W 1994 *Phys. Rev.* B series of four papers, at press
[2] Groote J C, Weerkamp J R W and den Hartog H W 1991 *Meas. Sci. Technol.* **2** 1187
[3] Pawlow P 1909 *Z. Phys. Chem.* **65** 545
[4] Ross J and Andres R P 1981 *Surf. Sci.* **106** 11
[5] Seinen J 1994 *PhD Thesis* University of Groningen
[6] The correction factor of 0.16 for the parameter *A*, mentioned in this paper [1], can easily be explained from the reduction of the surface energy of Na metal, when the metal particle is embedded in the NaCl matrix. Interactions at the interface between the matrix and the metal atoms in the particle will lower the surface energy considerably
[7] Lambert M, Mazières C and Guinier A 1961 *J. Phys. Chem. Solids* **18** 129
[8] Hughes A E and Jain S C 1979 *Adv. Phys.* **28** 717
[9] Jain S C and Hughes A E 1978 *J. Mater. Sci.* **13** 1611
[10] Scott A B 1954 *Phil. Mag.* **45** 610
[11] Jain U and Lidiard A B 1977 *Phil. Mag.* **35** 245
[12] Hodgson E R, Delgado A and Alvarez Rivas J L 1979 *J. Phys. C: Solid State Phys.* **12** 1239
[13] Seinen J, van Maaren P J and den Hartog H W 1994 *J. Phys.: Condens. Matter* **6** 9053
[14] Jenks G H and Bopp C D 1977 *ORNL Report* 5058
[15] Groote J C and Weerkamp J R W 1990 *PhD Thesis* University of Groningen
[16] Vainshtein D I and den Hartog H W to be published