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A Scanning Electron Microscope Study of the Degradation of Electron Channelling Effects in Alkali Halide Crystals during Electron Irradiation

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The effects of *in-situ*, 25 kV electron irradiation on SEM electron channelling patterns from alkali halide crystals at room temperature are reported. Patterns were generated using wide beam and narrow beam methods. It is observed that after an initial period of irradiation, during which well defined high resolution patterns can be generated, degradation occurs. This is marked either by channelling line diffuseness or by waviness, depending on the method of generation. After prolonged irradiations, patterns can no longer be detected. Subsequent annealing experiments on irradiated NaCl show that patterns return to their original clarity if the annealing temperature is between 285 and 325° C. Initial distortions (i.e. diffuseness and waviness) are attributed principally to the effects on the incident beam of irradiation induced surface electric fields; pattern loss, and subsequent recovery on annealing, is attributed to lattice distortion effects arising from beam-induced defect clusters.

1. Introduction

Electron channelling contrast on scanning electron microscope (SEM) images from good single crystals [1, 2] is readily observed in conventional SEM's under suitable electron optical conditions [3]. Contrast arises from the enhanced channelling ($s > 0$) and/or the enhanced scattering ($s < 0$) of electrons incident near the Bragg reflecting positions for particular crystal planes (s being a measure of the deviation from the Bragg condition) and is observed usually in the form of a pattern of lines and bands, commonly called electron channelling patterns or Coates' patterns (after D. G. Coates who first observed them). Such patterns are useful for determining the orientation of thick crystals, and their angular resolution or sharpness is a direct measure of surface perfection.

In an early paper, Holt *et al* [4] reported that patterns can be generated from a variety of materials, including metals, semiconductors and ionic solids. They also noted that patterns from NaCl disappeared on prolonged observation in the SEM, and suggested that this was due to lattice distortions associated with beam induced F-centres. Pattern loss in NaCl was also taken as evidence to support the view that electron channelling contrast is sensitive to large point defect concentrations.

The purpose of this paper is to examine the effects of *in-situ* SEM electron irradiations on electron channelling patterns from alkali halide crystals. It will be shown that the effect observed by Holt *et al*, in NaCl is observed in other alkali halides, and is due not to F-centres *per se* but to a more stable type of defect. Crystal charging effects and the role of point defects on pattern sharpness are discussed.

2. Experimental

Crystals of NaF, KCl, NaCl and KBr, of optical quality, were obtained from the Harshaw Chemical Company. They were cleaved in air to give rectangular specimens approximately 1 cm × 1 cm × 3 mm having {100} faces. Specimens were kept in a desiccator prior to examination.

Electron channelling experiments using 25 kV incident electrons were carried out at room

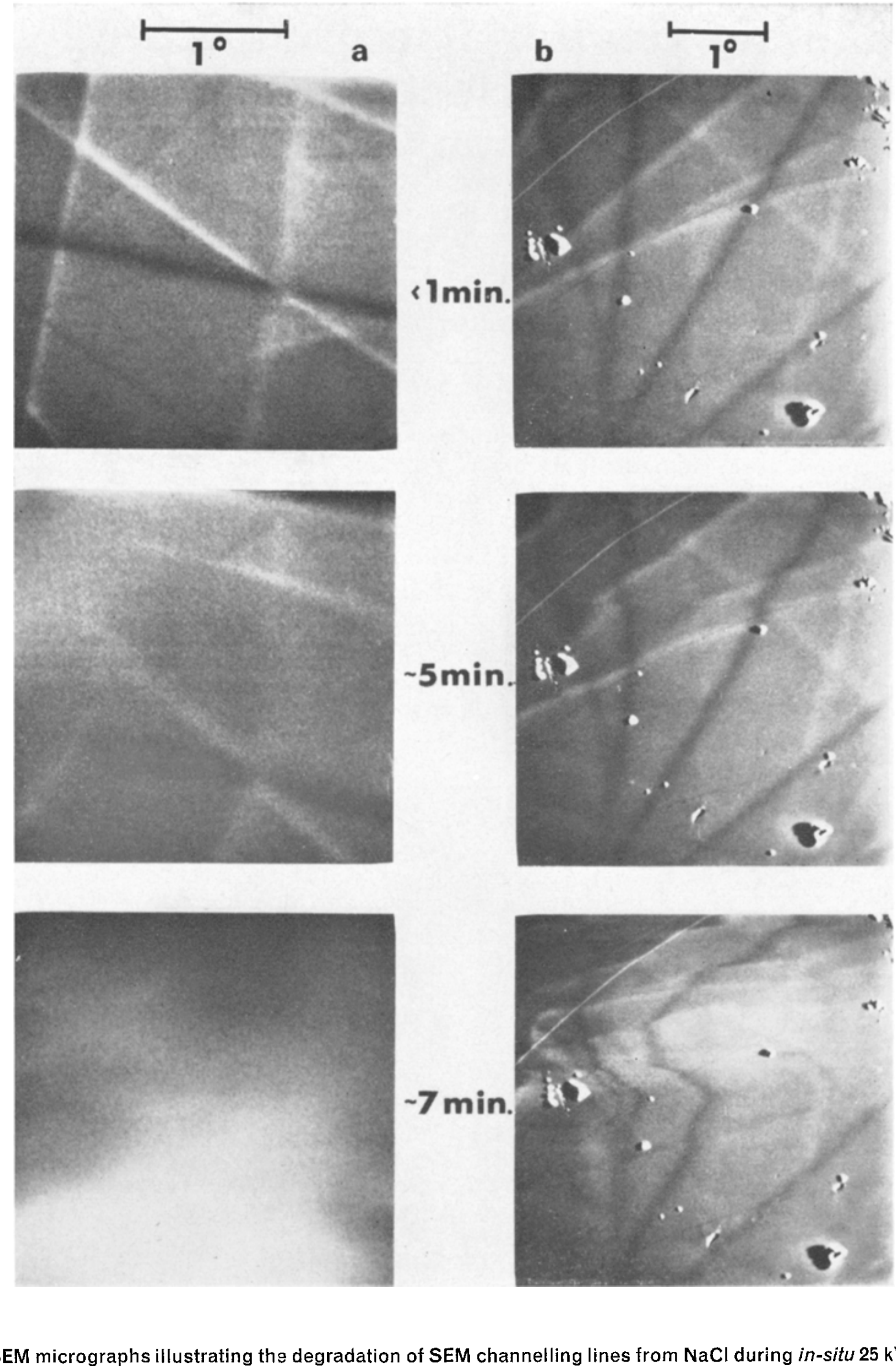


Figure 1 SEM micrographs illustrating the degradation of SEM channelling lines from NaCl during *in-situ* 25 kV electron irradiations: (a) diffuse lines, using wide beam method. (b) wavy lines, using narrow beam method. (Irradiations times are included.) Full scale ~1 mm.

temperature in a standard JSM-11 scanning electron microscope. Patterns were generated by two scanning beam methods: the first used a wide beam approximately 500 μm in diameter of 2×10^{-4} radians divergence; the second used a narrow beam about 10 μm in diameter of 3×10^{-3} radians divergence. In both cases, the beam current at the specimen was approximately 10^{-7} amps. Taking into account SEM picture point geometry, this corresponds to an electron flux of approximately 10^{14} electrons/cm^2/sec. Images were formed by collecting the reflected primary electrons. The instrumental settings for establishing wide and narrow beams in the JSM-II have been discussed in detail elsewhere [5].

3. Results

The observations can be summarised as follows, and can be taken as representative of each of the alkali halides examined unless otherwise stated.

3.1. Pattern Degradation

Patterns generated from cleaved surfaces not previously irradiated are well defined and show a series of electron channelling lines corresponding to particular Bragg reflections; because the total scan angle, 2γ, in the JSM-II is rather small (for the wide beam, $2\gamma \simeq 2.6°$) channelling bands were not seen. The wide beam patterns contain crystallographic information only (having integrated out of the image surface features of repeat distance smaller than the beam size), and have an angular resolution of $\simeq 4 \times 10^{-4}$ radians; the narrow beam patterns contain both channelling lines and surface features, and have angular and topographical resolutions of $\simeq 5 \times 10^{-3}$ radians and ~ 5 μm respectively. Patterns generated from areas subject to continued electron irradiation, however, are no longer sharp, but tend to deteriorate at an accelerating rate once deterioration starts. The lines on the wide beam pattern become diffuse and slightly displaced, and then disappear into a background of uneven illumination, while the lines on the narrow beam pattern become "wavy" though remaining fairly sharp. For the narrow beam case, channelling lines, though greatly distorted, can still be seen when the wide beam contrast is lost; however, contrast is eventually lost in a background of uneven illumination. The line displacement associated with the narrow beam line waviness is in a direction opposite to the direction of the SEM line scan (x). The amplitude of the wave can be reduced (i.e. the lines partially straightened), at least during the initial period in which distortion is detected, by decreasing the time of the frame scan (Y). On translating to unirradiated areas, good patterns can once again be generated.

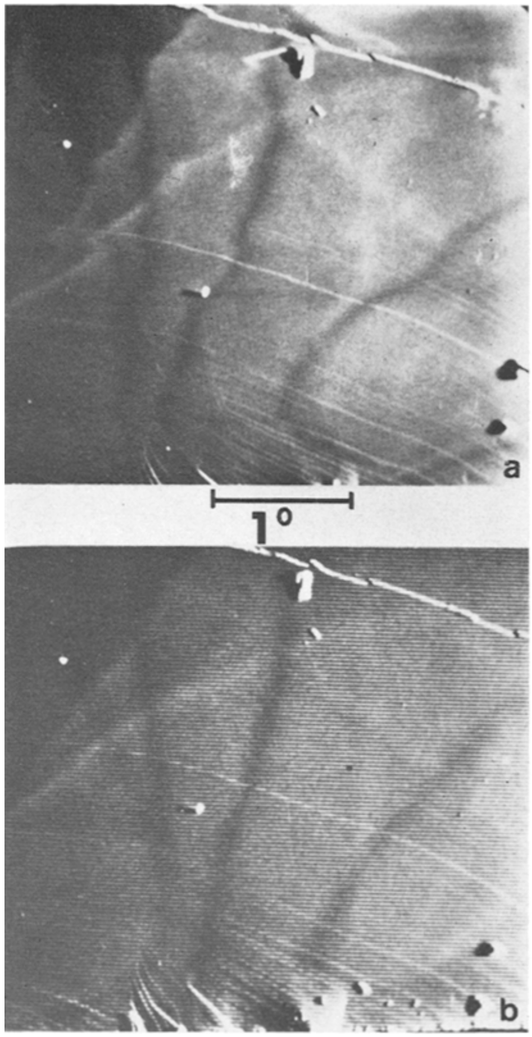


Figure 2 SEM micrographs illustrating the effect of scan frame time on the extent of line waviness from irradiated (3 min) KCl: (a) frame time = 25 sec. (b) frame time = 2.5 sec. Full scale ~ 1 mm.

The onset of pattern degradation varied for each material, occurring almost immediately for NaF, within ≈ 2 to 3 min for KCl, and within 6 to 7 min for NaCl; for KBr, degradation was not detected after 25 min, the maximum exposure given. Irradiation induced colour centres (F-centres) were seen in KCl (purple) NaCl (yellow) and KBr (blue); centres were not seen in NaF since the F-band is in the ultra-violet.

Figs. 1a and b illustrate the degradation of the electron channelling effects in NaCl for the wide beam and narrow beam methods respectively; the irradiation times are given in the figure. Fig. 2 shows the effect of scan frame time on narrow beam pattern waviness in KCl. The scanning sequence on the photographs is from left to right and from top to bottom. (The horizontal lines in figs. 1b and 2b are CRT line traces.)

3.2. Pattern Recovery

Specimens of NaCl irradiated for 10 min were given successive anneals in air and then re-examined in the SEM. For these experiments, the narrow beam method was used so that the previously irradiated areas could be located. Fig. 3 shows the recovery effects on annealing. The observations are summarised as follows: Room temperature anneals for one week and anneals at $230 \pm 5°C$ for 5 mins give no improvement, but are sufficient to cause considerable F-centre bleaching in the first case and complete bleaching in the second; the SEM image is dominated by uneven background contrast due to charging effects (Figs. 3b and c). At $285 \pm 5°C$, a 5 min anneal tends to eliminate some of the charging effects so that irregular channelling lines can be seen (fig. 3d); (channelling lines are labelled A and B for clarity). Complete recovery occurs at $325 \pm 5°C$ during a 3 min anneal (fig. 3e). In the case of irradiated (5 min) KCl, only room temperature anneals were given. The results after one week are similar to NaCl. It appears, therefore, that pattern recovery in NaCl occurs in the temperature interval between 285 and 325°C. *In-situ* SEM annealing experiments are planned to investigate further the recovery effects in irradiated alkali halide crystals.

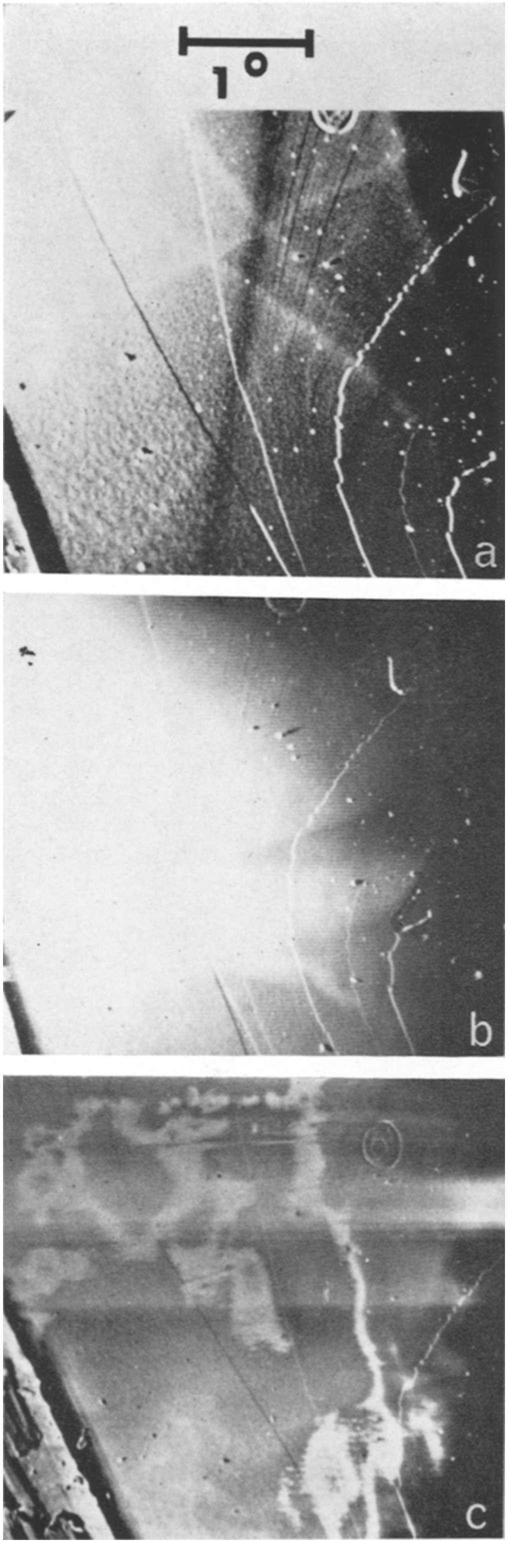
4. Discussion

The results of these experiments show that electron channelling patterns from the alkali halide crystals NaF, KCl and NaCl (and presumably KBr for doses greater than those given) suffer extensive degradation during room temperature bombardment with 25 kV electrons Metal crystals and the common semiconductors Si, Ge and GaAs do not show this effect. The origin of pattern degradation, and subsequent recovery on annealing, will now be considered.

4.1. Beam-Induced Surface Electric Fields

Alkali halide crystals are essentially electrical insulators. Consequently an electron beam incident on the crystal surface will probably give rise to variable local charge distributions, and hence to steep potential gradients. Thus, surface electric fields develop which can deflect and decelerate the incident beam. In the present experiments, the wide beam is considered to be sufficiently large to illuminate several "charge centres" for each direction of incidence, while the narrow beam is considered to be of the same size as the spacing between the "charge centres." During one complete scan therefore, the wide beam detects on average little change in beam induced fields acting above the crystal surface, while the narrow beam illuminates essentially a different field for different directions of incidence. Thus, different parts of the wide beam are deflected in different directions by the horizontal components of the induced fields, so that the beam divergence is increased and the patterns so generated become diffuse; wide beam pattern displacement is ascribed mainly to changing Bragg reflection conditions due to the deceleration of the incident electrons through interactions with the vertical components of the field. Similarly the narrow, beam interacts with the induced fields: the beam as a whole is deflected closer to or further from the Bragg conditions for particular $\{hkl\}$ planes by the horizontal components of the field so that, while the divergence is essentially unchanged, the lines on the pattern are displaced in a direction opposite the field direction, and by an amount dependent on the field strength; some displacement is also due to the vertical component of the field. The effect of scan frame time on narrow-beam image distortions (fig. 2) indicates that the beam-induced fields are transient in nature, at least during the early stages of pattern degradation.

In some additional experiments on ThO_2 crystals using the narrow beam method, chanelling line waviness was observed immediately on examination. In this case, lines could be seen only during the fastest frame scans (0.5 sec) and even these appeared to move across the image in a direction opposite to the line scan. Wide beam images showed only charging contrast. These observations are also attributed to crystal charging effects. Charging effects might be alleviated by using a low energy (500 to 1000 V) auxiliary electron gun near the specimen to supply an electron spray, similar to the procedure



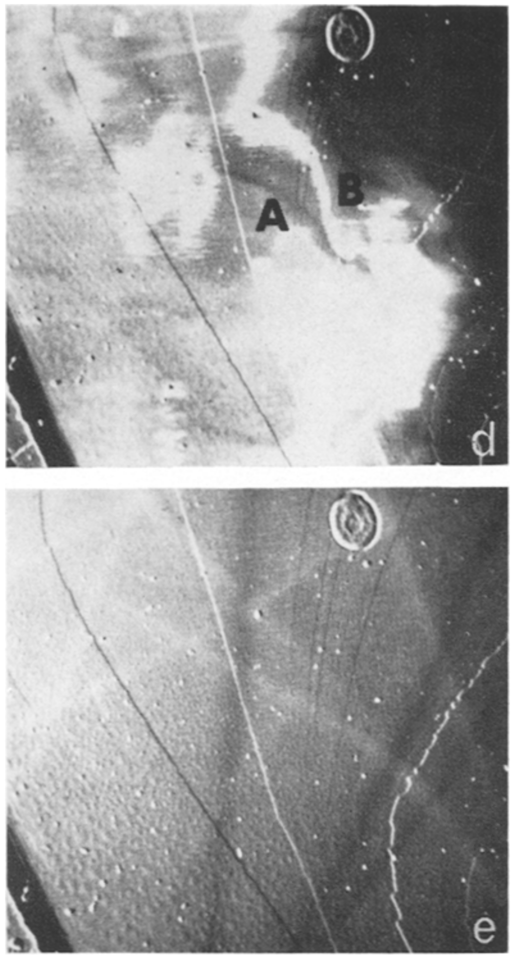


Figure 3 SEM micrographs illustrating the recovery of electron channelling lines from irradiated NaCl. (a) initial pattern ($t_{irr} < 1$ min). (b) degraded SEM image after 10 min irradiation. (c) 5 min anneal at 230° C. (d) 5 min anneal at 285° C. (e) 3 min anneal at 325° C. Full scale ~ 1 mm.

followed in reflection electron diffraction of insulating crystals.

For the narrow beam case, the displacement of a particular line on the pattern due to crystal charging effects can be given approximately by the expression:

$$\Delta\theta = \frac{-|e|}{mv^2}\left\{\frac{h}{2mv}|\mathbf{g}|\int_{-\infty}^{0}(\mathbf{E}\cdot\mathbf{k})\,\mathrm{d}z + \frac{1}{|\mathbf{g}|}\int_{-\infty}^{0}(\mathbf{E}\cdot\mathbf{g})\,\mathrm{d}z\right\} \quad (1)$$

where **g** is the reciprocal lattice vector of the associated Bragg plane, **E** (z) is the beam induced surface electric field, **k** is a unit vector in the $-z$ direction (z being parallel to the undeflected incident beam), h is Planck's constant, and m, v and $|e|$ are the mass, initial velocity and charge of the incident electron respectively. The displacement varies in time because of the transient nature of the charging, and varies with the specimen area illuminated because of the localised nature of the charge build-up. If more information were available about the "charge centres", then, by measuring $\Delta\theta$ at various points on the crystal surface, it should in principle be possible to estimate the induced fields. Surface fields are known to develop on alkali halides during sputtering experiments [6]; by performing such experiments in the SEM, (see reference [7]) the electron channelling pattern technique might be useful for estimating field strengths.

4.2. Ionisation Damage

While electrical charging effects alone can account for the degraded patterns from NaF, the eventual loss of patterns from KCl and NaCl cannot be attributed to charging only. Otherwise, one week anneals at room temperature should have been long enough to dissipate surface charges and consequently to give good patterns. It is well known that ionising radiation creates point defects in alkali halides [8]; under continuing irradiation, single defects can migrate to form clusters (particularly if local heating under the beam is appreciable) which can then grow and interact with each other. For instance, Izumi [9] has observed the formation of {100} plate shaped defects in KCl and NaCl during room temperature, 100 kV electron irradiation in the transmission electron microscope. Thus, the role of beam induced damage must be considered.

Holt *et al* [4] suggested that pattern loss observed in NaCl is due to lattice distortions associated with F-centres. (We note that their observations were made under essentially wide beam conditions.) The role played by F-centres *per se*, or indeed by any point defect, can be approximately described as follows. Given a random, uniform distribution of point centres of dilatation, Eshelby [10] has shown that a strain is produced which is uniform and isotropic throughout the crystal. This gives rise to changes in the lattice parameter, and hence, to changes in the Bragg reflection conditions. For a prototype defect consisting of a sphere of radius r_0 where the relaxed misfit strain is ϵ, it can be shown that for N defects per unit volume the displacement $\Delta\theta_d$ of a line ($\mathbf{g}$) on the SEM pattern is given approximately by:

$$\Delta\theta_d = \frac{-2\pi}{3} r_0^3 N\epsilon\lambda\mathbf{g} \qquad (2)$$

where λ is the deBroglie wavelength of the incident electrons. The smallest defect content, N_m, which gives a measurable displacement is obtained by setting $\Delta\theta_d$ equal to the angular resolution of the patterns, ω. Thus, for $\omega \sim 10^{-4}$ radians, and taking $\epsilon \sim 0.3$, $r_0 \sim 2$Å, $\lambda = 0.074$ Å and $\mathbf{g} = 2(\text{Å})^{-1}$, $N_m \simeq 10^{20}$/cc (i.e. $\sim 0.2\%$). The actual F-centre content in NaCl was determined by using optical absorption techniques and applying Smakula's equation [11]:

$$N = \frac{k\phi}{x}$$

where k is a constant (incorporating oscillator strength, refractive index and absorption band width), ϕ is the optical density, and x is the thickness of the coloured region. For NaCl, $k = 6 \times 10^{15}/\text{cm}^2$ [12] and $x = 10$ μm for 25 kV electrons [13]; after 10 min irradiation (i.e. patterns disappeared) $\phi = 0.22$. Thus, substituting these values into the above expression gives $N = 10^{18}$/cc. (i.e. $\sim 0.002\%$). The view is taken, therefore, that F-centres *per se* do not distort the lattice sufficiently to account for the degradation effects. This is also supported by the annealing experiments on NaCl. In this general regard, we note that silicon crystals irradiated with thermal neutrons to a dose of $\approx 5 \times 10^{20}$ neutrons/cm^2 (equivalent to a residual room temperature defect content of $\simeq 0.1\%$) show no apparent change in channelling patterns [14], a further indication that SEM channelling effects are not very sensitive to large point defect concentrations.

In all likelihood, the eventual loss of patterns from KCl and NaCl is related to lattice distortion arising from the overlap of defect clusters produced during irradiation. That clusters are thought to be responsible is concluded mainly from the NaCl annealing observations: pattern recovery is complete on annealing at $\simeq 300°$C which is about the temperature at which Izumi [9] noted the annealing of electron beam induced defect clusters in thin foils. This view is further supported by the observation that a certain "incubation" time is required before pattern loss occurs, a period in which clusters can grow and then interact. Although the nature of the defect clusters cannot be determined from the present SEM experiments, it is believed that they are similar to those observed by Izumi, namely plate shaped defects of alkali metal colloids parallel to one of the {100} planes and elongated in ⟨100⟩ directions; that 25 kV electrons were used here, and not 100 kV electrons, does not invalidate this belief since mainly ionisation rather than knock-on processes create defects in alkali halides bombarded with medium energy electrons.

We note that an alternative explanation for pattern recovery on annealing was thought initially to be evaporation of damaged surface layers. However, calculation suggests that the amount evaporated from NaCl at 325°C in 3 min is negligible. This explanation is therefore discarded.

Finally, we point out that beam-induced charging and defect clusters might also perturb ion channelling in the alkali halides. This is supported by some recent experiments at Chalk River [15] which show that 1 MeV helium ion channelling in NaCl improves either by neutralising the crystal with an electron spray during bombardment or by heating above $\sim$250°C.

5. Conclusion

From these results, it is to be concluded that prolonged *in-situ* SEM electron irradiation gives rise to degraded electron channelling patterns from alkali halide crystals. In certain cases, for instance NaF, degradation is attributed principally to crystal charging effects, while in others, for instance KCl and NaCl, it is attributed both to surface charging and to lattice distortion due to electron irradiation damage. In cases to which radiation damage contributes, defect clusters rather than point defects are considered to be important.

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