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## TRANSMISSION ELECTRON MICROSCOPY OF DEFECTS IN ALKALI HALIDES

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**Résumé.** — Cet article examine les difficultés rencontrées en microscopie électronique sur lames minces d'halogénures alcalins et montre comment chacune peut être surmontée. Les mesures incluent une préparation soignée des feuilles minces et examen à la température de l'hélium liquide. En particulier, la microscopie à basse température retarde l'influence des défauts d'irradiation dus au faisceau du microscope. Un rapport de l'application de ces techniques à l'étude des agrégations de défauts d'irradiation et du comportement des dislocations dans des cristaux déformés et irradiés est présenté.

Abstract. — This paper considers the difficulties encountered in conventional thin-foil electron microscopy of alkali halides and demonstrates how each can — within certain limits — be successfully overcome. The measures required include careful thin-foil specimen preparation and examination at liquid helium temperature. In particular, low temperature microscopy is shown to significantly retard the onset of observable radiation damage effects induced by the investigating electron beam. A brief account of the application of these techniques to studies of irradiation defect aggregations and dislocation behaviour in irradiated and deformed alkali halide crystals is presented.

1. Introduction. — Although the history of alkali halide electron microscopy now spans twenty years [1], few results of real substance have emerged until recently, even though this period has seen the explosive growth of colour centre [2], irradiation [3] and deformation [4] research, and the development of direct electron microscopical methods into a powerful and sophisticated science [5]. This situation is in marked contrast to that in metals and semiconductor research where electron microscopy has contributed a wealth of detailed information about the structure of extended lattice defects in the size range 1 nm to 1 µm. It is especially lamentable because in the alkali halides complementary point defect techniques exist [2] for accurately characterising point defect populations which are, for the most part, unavailable to other materials.

The difficulties in alkali halide electron microscopy arise largely in two forms. First, suitable thin foil specimens are somewhat more difficult to prepare than for other commonly-studied materials, and a great deal more care must be exercised with them after preparation. In particular, it has proved difficult to obtain thin foils which are likely to be representative of the state of bulk material. Second, the immense scale of irradiation damage under the investigating electron beam has restricted study of defects in pure alkali halides by electron microscopy to the beaminduced damage itself, and then only for a few metastable defects surviving in thin foil regions [6], [7]. Until recently, it was not generally recognised that illumination levels commonly employed for microscopy were orders of magnitude too high to reflect irradiation behaviour in any way characteristic of that in more conventional irradiation defect studies. The investigating electron beam also induces an annoying static charge in insulating foils.

Difficulties of the first sort derive principally from mechanical and chemical properties of the alkali halides, those of the second sort from their electrical and radiolytic properties. This paper will demonstrate how these difficulties may be systematically overcome; the approach involves electron microscopy at the extreme lower limits of temperature and illumination. Nevertheless, highly successful application of the techniques to studies of point defect aggregation, dislocation behaviour and irradiation hardening is possible.

2. Specimen preparation. — Transmission electron microscopy requires production of specimen foils transparent to electrons in the energy range 100 keV to 1 MeV, usually by a two-stage process of sectioning from bulk material and thinning to  $< 1 \mu m$  thickness. Starting sections suitable for subsequent thin foil preparation are typically 2 mm diameter discs about 0.5 mm thick and must be produced with a minimum of incidental deformation. Alkali halides are remar-

kably soft yet extremely brittle, and the only acceptable sectioning technique for ensuring undeformed starting sections is precision chemical string-sawing. A wide range of alkali halides may be easily sectioned to 0.5 mm thickness using alcohol solvents (Table I).

### TABLE I

Typical solvents for cutting and thinning alkali halides

H <sub>2</sub> O		MeOH		EtOH	
		<u> </u>			
LiF	0.1	NaF	0.2	NaBr	1.5
NaF	1.5	KF	0.1	KBr	0.1
		NaCl	0.8	RbBr	0.4
		KCl	0.4	KI	0.9
		RbCl	0.7	RbI	0.4
		KBr	1.0	CsI	0.7
		CsBr	0.7		

Solubilities are indicated in volume %. Preferred range for thinning is between 0.2 and 1.5 vol. %.

Round discs are produced from the resulting slices by chemical dissolution at the corners. Cleavage is a useful technique for producing thin starting sections, but invariably introduces unacceptable bending deformation [8] in thin sections; it is also practically limited to { 100 } sections in rocksalt structure crystals and is not applicable to polycrystalline or CsCl structure crystals.

The simplest technique for preparing representative thin foils suitable for transmission electron microscopy is chemical dissolution. Electropolishing is not practical with insulator specimens, and ionbeam bombardment thinning introduces unacceptable radiation damage [9]. Electron-beam flashing [10] relies on large stresses from thermal gradients, as well as involving pre-irradiation, and cannot be relied on to preserve the integrity of the initial lattice.

Most alkali halides are readily soluble in water and susceptible to atmospheric moisture attack [11], so that if suitable polishing and washing chemicals are permitted to evaporate from the crystal in atmosphere, moisture may condense onto thin foil surfaces and lead to serious etching and dissolution effects (Fig. 1*a*). Particularly hygroscopic alkali halides are susceptible to atmospheric moisture attack even in the dry state (Fig. 1*b*). Therefore, most alkali halide foils must be produced by thinning in dry atmosphere using dried solvents if water attack is to be avoided; transfer in dry atmosphere to the electron microscope is necessary for the more hygroscopic crystals.

Foils are most reliably produced by a microjet thinning method ; apparatus developed for this purpose has been described in detail elsewhere [12]. Nearly all alkali halides are slightly soluble in common polar liquids, e. g. alcohols, and (with a few exceptions) insoluble in ketones [13]. These provide the basis for polish/wash solvent combinations (Table I). Controllable thinning is achieved for solubilities in the range 0.2 to 1.5 volume per cent.

It is essential that thinning proceeds dynamically particularly for foils of other than  $\{100\}$  orientation. Polar solvents standing statically on alkali halide surfaces etch preferentially along certain crystallographic directions (Fig. 1c). Consequently, to avoid wetting the top specimen surface when thinning from the underside, specimen disc edges must be sealed off. A convenient seal can be made with *Lacomit* [14] stopping-off lacquer which is softened by



FIG. 1. — Etching effects in thin foil preparation. a) Cubic etching in a (100) KCI foil polished in atmosphere. b) Etching and recrystallisation in a (110) NaBr foil polished in dry atmosphere but briefly exposed to normal atmosphere following polishing. c) Selective etching along < 100 > in a (110) NaCl foil where polishing was allowed to proceed statically.

ether absorption during washing and can be carefully peeled off immediately following foil preparation. Both sides of a specimen disc are normally dynamically polished in turn until perforation occurs; thin areas immediately adjacent (within  $\sim 20 \ \mu m$ ) to the resulting hole are then sufficiently electron transparent. Washing solvents are removed by vacuum evaporation following thinning.

3. Electron beam sensitivity. - 3.1 CHARGE ACQUISITION. -- Thin films of alkali halides are ionic conductors and thus good insulators, particularly upon cooling whereupon electrical conductivity diminishes exponentially with temperature [15]. The range of 100 keV electrons typically employed for electron microscopy is considerably greater than the foil thickness used (< 1  $\mu$ m) so that no static charge accumulates from the primary electron beam. However, secondary electrons are readily emitted from appreciable depths in the foil, and their loss results in accumulation of a positive charge which will set up a potential V at the illuminated foil area. This potential acts as a barrier to further emission of secondary electrons of energy less than Ve. An equilibrium is established between secondary emission current and ionic current in the foil, resulting in an equilibrium potential  $V_{eq}$ . The value of the resulting electric field in the foil is determined by the value of  $V_{eq}$ and by foil geometry, and can exceed the dielectric strength of the material ( $\sim 10^7 \text{ V}.\text{m}^{-1}$ ), particularly at low temperature where ionic conduction is negligible.

Nevertheless, the internal electric field in the foil, even at breakdown, does not act over sufficient distance to significantly deflect 100 keV electrons during their passage through the foil. Unfortunately, asymmetries in the external field set up above and below the foil to surrounding parts of the microscope do operate with sufficient strength over large enough distances to deflect primary electrons approaching or leaving the foil through angles  $> 10^{-2}$  rad [9], equivalent to one or more Bragg angles. It is this external field which is largely responsible for observed charging effects and which must be eliminated.

A sensible approach is to provide a conducting surface in intimate contact with the foil. Fine-mesh copper grids can provide a partial solution, at least at room temperature, provided the mesh size is kept small and close contact with the foil maintained. Grids are insufficient at low temperature for disc specimen geometry, and a more intimate conducting layer must be provided by evaporation. This layer has the effect of confining the electric field largely to within the foil and also reduces the radial component, as in a parallel-plate capacitor. It should be noted that only one surface need be coated. In practice, aluminium conducting films  $\sim 20$  nm thick are evaporated from a simple tungsten hairpin filament and are effective down to 4 K. 3.2 ELECTRON IRRADIATION DAMAGE. — Displacements on the anion sublattice are produced at comparatively low energy cost by an efficient ionisation mechanism in alkali halides [3], [16]. The mechanism now generally accepted [17] involves radiationless decay of a self-trapped exciton (V<sub>k</sub> centre with bound electron) which provides both energy and momentum along a close-packed row of anions to produce a halogen Frenkel defect pair (F centre + H centre) separated by several lattice sites [18]. The F centre is relatively stable in the unexcited state up to temperatures ~ 400 K, but the H centre becomes mobile above only ~ 30 K [3] and readily aggregates [19].

3.2.1 Energy deposition in thin foils. - It has been shown [20] that most electronic excitations (plasmons, core excitations, etc.) in alkali halides decay to single low-energy excitations having V<sub>k</sub>-like symmetry, so that rather crude estimates of total energy loss due to ionisation, such as Bethe-Bloch formulations [21], still provide an adequate quantitative measure of deposited energy available for anion displacement. Radiolysis requires at least the energy of the first exciton state  $\sim$  6 eV [22], but the displacement mechanism competes with exciton luminescence [23], and on average one displacement is produced for every 50 eV deposited energy [24]. Most of the Frenkel pairs produced suffer spontaneous correlated recombination, and the efficiency generally measured, ~  $10^3$  to  $10^4$  eV per Frenkel pair [25], is that for producing stuble F : H pairs.

In thin foils, where the range of energetic electrons is considerably greater than foil thickness, the energy loss from 100 keV electrons is uniform through the foil and amounts to ~  $10^9 \text{ eV} \cdot \text{m}^{-1}$ . Thus, each electron produces stable F : H pairs at a rate ~  $10^6 \text{ m}^{-1}$ (corresponding to a displacement cross section ~  $10^5$  barns). Since the Bethe loss scales approximately as  $\beta^{-2}$  for relativistic electrons, increasing electron energy will decrease the energy loss rate. The rate decreases precipitously between 40 keV and 200 keV, but further decrease for electron energies > 200 keV is marginal. The implications for high-voltage electron microscopy are discussed in section 4.

The minimum usable electron density incident on the foil in the electron microscope is governed by image statistics, both at the final photographic emulsion (or equivalent recording system) and at the phosphor screen (or equivalent viewing system) used to focus the image. Practically, both resolution limits are arrived at approximately simultaneously (section 4) at a total electron dose ~  $2 \times 10^{21}$  e.m<sup>-2</sup> at a rate ~  $10^{20}$  e.m<sup>-2</sup>.s<sup>-1</sup> (~ 30 A.m<sup>-2</sup>) for 5 nm object resolution. Thus, at this resolution level, the electron microscope beam deposits energy at the minimum rate of  $10^{29}$  eV.m<sup>-3</sup>.s<sup>-1</sup> (~ 1 Grad.s<sup>-1</sup> or 20 GJ.m<sup>-3</sup>.s<sup>-1</sup>), which is orders of magnitude above conventional radiation sources [26]. The consequence is point defect production at a rate  $\sim 10^{26} \text{ m}^{-3} \text{ s}^{-1}$ .

Since Frenkel pair saturation (~  $10^{25}$  m<sup>-3</sup>) normally occurs in most alkali halides at room temperature in the dose range  $10^{29}$ - $10^{30}$  eV.m<sup>-3</sup> (1-10 Grad), electron microscopy clearly results in defect saturation in times of the order of 1 s, and the point defect distributions resulting are those occurring in the saturation or post-saturation regimes. The distribution is significant because, at these high defect densities, extensive defect aggregation occurs (Fig. 2) which



FIG. 2. — NaCl irradiated as a bulk crystal to 40 Grad with 450 keV electrons at 0.1 A.m<sup>-2</sup>, then thinned and examined in the 100 kV microscope at 10 K. Thin foil irradiation in the microscope at room temperature produces a similar result.

introduces lattice strains of sufficient extent to obscure pre-existing lattice defects such as dislocations or the products of prior irradiation. In fact, the scale of aggregation at doses considerably less than saturation (Fig. 3) presents serious difficulties.

3.2.2 Use of low temperature. — The sole variable available to the microscopist in these circumstances is temperature. Since the gross mobility of the aggregating defect(s) is thermally activated [3], reducing foil temperature below defect mobility thresholds must be expected to retard observable aggregation. It has been shown [26] that the aggregating species at and below room temperature is the halogen interstitial; thus this approach must entail microscopy at liquid helium temperature (< 30 K).

Lowering the foil temperature does not, however, simply produce the expected retardation of defect



FIG. 3. — NaCl irradiated in bulk with 0.8 MeV  $\gamma$  to 500 Mrad.

aggregation by reducing the rate of thermally-activated defect diffusion. At the near-saturation defect densities involved in microscopy, considerable athermal (spontaneous) aggregation occurs [27], even at 10 K (see Fig. 5b). Near-saturation defect densities in fact result in observable aggregation at any temperature ; only the distribution is altered : at high temperatures, a small density of large clusters with longrange strain fields results; at low temperatures, a high density of small clusters with shorter-range strain fields [26]. The important point is that at a critical defect density  $F^*$  [since F centres remain largely unaggregated at and below room temperature, they are a good measure of stable Frenkel pair production] conventional microscopical observation becomes obscured. This tends to occur at a lower  $F^*$ at room temperature ( $F^* \sim 5 \times 10^{23} \text{ F.m}^{-3}$ ) than at low temperature ( $F^* > 5 \times 10^{24} \text{ F}.\text{m}^{-3}$ ) because of the longer-range strain field of larger aggregates [electron microscopy of defects in crystalline materials generally utilises strain-field contrast].

3.2.3 Saturation kinetics. — Nevertheless, with basic point defect production rate ~  $10^{26}$  m<sup>-3</sup>.s<sup>-1</sup>, any effect of temperature, to be useful, must alter the effective rate of defect production enormously as well; it can do this through alteration of the recombination kinetics which govern the rise in defect population at high defect densities. When F : H pairs are created in sufficient density, the effective rate of stable defect production is increasingly diminished by recombination of F centres and H centres, until

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the stable defect population eventually saturates (usually at concentrations  $\sim 10^{-3}$  or  $1-2 \times 10^{25}$  m<sup>-3</sup>) and the overall stable defect production rate drops to zero.

In the simplest case, F: H recombination can be considered to take place athermally, for example an H centre may be created very near an existing F centre or vice versa. It has been shown [28] that in such cases, the approach to saturation is logarithmic in dose and depends on the state of defect aggregation. If one of the defects in exceptionally mobile and can stabilise at large sinks before another defect creation event occurs in its vicinity, this defect is effectively removed from the recombination process. For example, the interstitial halogen atom readily stabilises at room temperature in large interstitial aggregates [26]. In this case, recombination kinetics are primarily determined by the [immobile] F centre distribution, viz. by the probability of creating an H centre within some athermal recombination volume v surrounding an F centre. F centre growth is then governed by kinetics of the form

$$F \approx (1/v) \ln v R t$$
 (1)

where R is the initial rate of defect production at zero defect density. At very low temperature, where interstitial defects are also relatively immobile (at least beyond their initial replacement sequences) and remain initially isolated, the volume fraction of lattice effective in athermal recombination is considerably higher (it now includes contributions from the interstitials as well) and leads to saturation kinetics of the form

$$\mathbf{F} \approx (1/4v) \ln 4 \, vRt \,. \tag{2}$$

(2) represents considerably slower defect accumulation than (1).

This difference in saturation kinetics is indicated in figure 4 for measured F centre production curves at 300 K and 4 K. The times  $t^*$  for reaching critical densities  $F^*$  are

$$t_{300}^* \approx (\exp v F_{300}^*) / v R$$
 (3a)

$$t_A^* \approx (\exp 4 v F_A^*)/4 v R . \tag{3b}$$

Since  $F_{300}^* \ll 4 F_4^*$  as discussed above, the time advantage factor at low temperature is given by

$$t_4^*/t_{300}^* \approx 1/4 \quad \exp 4 \, vF_4^*$$
 (4)

which with  $v \sim 2.5 \times 10^{-25} \text{ m}^{-3}$  [28] can be enormous (> 2 000). At room temperature with

$$R \sim 10^{26} \,\mathrm{F.m^{-3}.s^{-1}}$$
,

 $t_{300}^* \sim 1/40$  s and the time to absolute saturation is  $\sim 0.5$  s. At low temperature, the full advantage (4) is not realised much beyond F > 5 × 10<sup>24</sup> m<sup>-3</sup> because at this critical defect density (see Fig. 4), corresponding to a mean H centre spacing of the order of the athermal aggregation radius [27] when interstitial defects begin to aggregate athermally, saturation kinetics revert to more nearly room temperature form. Nevertheless, from (3b),  $t_4^*$  can be as large as 60 s, depending critically on v.

This fortunate effect is illustrated in consecutive 15 s micrographs (Fig. 5) of a KCl foil observed at 10 K in a liquid helium temperature microscope stage (see section 4.3) at a beam current density  $\sim 15 \text{ A} \cdot \text{m}^{-2}$ . Contrast from existing defects, in this case dislocations arising from cleavage, is preserved and observable

CENTRE SATURATION IN KCI 2×10<sup>25</sup> CENTRE DENSITY, Fm<sup>-3</sup> 10<sup>25</sup> ROOM TEMPERATURE U. --- 4 K 10<sup>31</sup> n 10<sup>29</sup> 10<sup>30</sup> 10<sup>28</sup> eV m<sup>-3</sup> 100 10 G RAD 1 0,1

DOSE FIG. 4. — F centre saturation kinetics in KCl at 300 K and 4 K, from the work of [28].







(b)

FIG. 5. — Foil of previously deformed KCl observed at 10 K with 100 keV electrons at 15 A.  $m^{-2}$ , showing eventual masking of dislocation images by low temperature clustering. *a*) After 15 s. *b*) After 30 s.

defect aggregation does not occur for at least the first 20 s of irradiation.

3.2.4 Damage quenching. — It should be noted that KCl exhibits approximately equal damage rates at both room temperature and lower temperatures (Fig. 6). Additional advantage can accrue from the reduction in the efficiency of radiationless decay



FIG. 6. — Temperature dependence of the primary defect production efficiency in several representative alkali halides.

of the  $V_k$  exciton in certain other alkali halides [23], most notably in KI, NaCl and NaBr, each of which exhibits a corresponding depression in defect production efficiency of one or more orders of magnitude, at low temperature. The advantage obtained is not found to be exactly proportional to the reduction in R because of differences in recombination (and aggregation) volumes which reflect exponentially in (3b). NaCl (Fig. 7) is found to survive three times as long as KCl at 10 K, KI [26] nearly ten times as long. The particularly low defect production rate in NaBr permits limited microscopy even at room temperature ; interstitial motion is difficult in the NaBr lattice, and this can account for the small interstitial aggregate size observed [26], as well as more favourable saturation kinetics.

3.2.5 Effect of impurities. — Substitutional monovalent cation impurities of a size smaller than the lattice ions they replace are capable of stabilising interstitials and can be particularly effective at low temperature, further delaying onset of observable aggregation. The effect is well known spectroscopically in the formation of  $H_A$  centres [29]. For example, KI : 200 ppm Na exhibits remarkable resistance to defect aggregation below 30 K [Fig. 8], although its radiolytic properties at room temperature remain largely unaltered. Large concentrations of divalent cation impurity are capable of suppressing observable aggregation even at room temperature [*e. g.* 10], perhaps because the accompanying charge-compen-



(a)



(a)



(b)

FIG. 7. — Foil of NaCl previously irradiated at room temperature and annealed, observed at 10 K with 100 keV electrons at 45 A.m<sup>-2</sup>, three times that of figure 5. *a*) After 15 s. *b*) After 30 s.

sating cation vacancies are effective interstitial traps [30]. However, divalent doping in no way retains the mechanical or radiolytic properties of pure crystals.



(b)

FIG. 8. Foil of K1: 200 ppm Na irradiated at room temperature, observed at 20 K with 100 keV electrons at 200 A.m<sup>-2</sup>.
a) After 15 s. b) After 15 min. No new cluster nucleation is observed, and only negligible growth of existing clusters.

4. Electron microscopy at the extremes of intensity and temperature. The parameters outlined in section 3.2 clearly point to electron microscopy at the lower extremes of intensity and temperature. These conditions impose limitations on the information which can be extracted by electron microscopical techniques.

4.1 RESOLUTION STATISTICS AND MINIMUM BEAM INTENSITY. — Formation of electron microscope images is a statistical process to which Poisson statistics apply. The minimum electron density  $\varphi_0$  at the *object* plane needed for statistically meaningful resolution is of the order of

$$\varphi_0 = K^2 / d_0^2 C^2 \tag{5}$$

where  $d_0$  is the dimension of object detail to be resolved, C is its image contrast and  $K \sim 5{-}10$  is the physiologically-determined signal-to-noise ratio required for recognition of detail. For  $d_0 \sim 5$  nm and  $C \sim 0.2$  (reasonable for diffraction contrast),  $\varphi_0 \sim 10^{20}$  e.m<sup>-2</sup> (~ 15 C.m<sup>-2</sup>).

 $\varphi_0$  is the electron density at the object plane used to form the image of the object and in general will be considerably smaller than the electron dose  $\varphi_i$ incident on the specimen. This is because the angular scatter of electrons emerging from the foil ( $\sim 10^{-1}$  rad) arising from elastic (diffraction) and inelastic (energy loss) scattering is considerably larger than the angle embraced by the objective lens aperture ( $\sim 10^{-3}$  rad) through which must pass those electrons selected for image formation. Diffraction contrast from crystalline specimens is normally imaged with a stronglyexcited line of systematic diffracted beams ng  $(n = 0, \pm 1, \pm 2, ...)$  and either transmitted (g = 0)or a single diffracted beam selected for imaging. Diffracted beam amplitudes are functions of the elastic scattering lengths  $\xi_g$  (extinction distance), inelastic scattering lengths  $\xi_g^i$  and crystal orientation.

 $\xi_g$  and  $\xi_g^i$  are inversely related to the real and imaginary Fourier components of the crystal lattice potential [31] and have been computed (Table II)

Table II

Two-beam electron diffraction parameters

NaCl				K(			
g	$V_g$ [V]	$\xi_g$ [Å]	$V_g$ [V]	$\overline{\xi_g}$ [.1]	$V_g^i[V]$	$\xi_y^i$ [A]	
			_				
000	8.42	404	9.36	363	0.573	5 940	
111	- 1.46	2 330	- 1.95	1 744	- 0.207	16 410	
200	5.27	645	6.35	535	0.276	12 300	
220	3.89	874	4.85	701	0.260	13 040	
222	3.09	1 099	5.93	865	0.240	14 180	
311	0.98	3 481	1.38	2 467	0.183	18 550	

for the present study from ionised-atom electronscattering factors [32] and lattice complex-potential calculations [33]. Computed values of  $\xi_0^i$  had to be substantially adjusted (owing to neglect of exchange terms in [33]) to obtain agreement with experimental extinction profiles. Rocking curves (Fig. 9) were computed to obtain information about the orientation-



FIG. 9. — Computed 9-beam bright field rocking curve for the 220 systematic row in a 400 nm thick KI foil at 20 K. Maximum bright field intensity is only 4 % of incident intensity.

dependence of electron transmission for several loworder systematic excitations and realistic foil thicknesses (~ 400 nm). Transmitted intensities seldom exceed 5 % of incident intensity, i. e.  $\varphi_0 < 0.05 \varphi_i$ . Consequently the minimum incident electron dose for 5 nm resolution is

$$\varphi_i = 20 \ \varphi_0 = 2 \times 10^{21} \text{ e.m}^{-2} (300 \text{ C.m}^{-2}).$$
 (6)

This dose corresponds to an energy deposition  $\sim 20 \text{ Grad} (2 \times 10^{30} \text{ eV}.\text{m}^{-3}, 400 \text{ GJ}.\text{m}^{-3}).$ 

There is some improvement in thinner foil regions, since  $\varphi_0/\varphi_i$  increases with decreasing foil thickness, but surface effects render observations in foils less than a few  $\xi_g$  thick unreliable. For electron energies above 100 keV, the decrease in Bethe loss is largely offset by corresponding reduction in phosphor screen (section 4.2) and photographic emulsion (section 4.3) response; however, the increased penetration can raise  $\varphi_0/\varphi_i$  by a factor of 2 or 3 and more than offset the more cumbersome operation of higher voltage electron microscopes.

When delivered over reasonable times (~ 10 s; see sections 4.2, 4.3 and 4.4), (6) corresponds to an incident beam current density ~ 30 A.m<sup>-2</sup>, which is one or more orders of magnitude smaller than that normally utilised by electron microscopists. Since it is desirable to focus the illumination in order to irradiate *only* the area under examination, the only way to reduce incident intensity to such low levels is to reduce the size of the second condensor aperture to 50 µm or less. This has the added advantage of reducing beam divergence to reasonable values (~ 5 × 10<sup>-4</sup> rad).

4.2 PHOSPHOR SCREEN RESPONSE. — A magnified electron image of the object must first be focussed before recording, and this is usually accomplished using a phosphor viewing screen situated at camera level. Phosphor efficiency is ~ 25 % for an ultimate resolution ~ 100  $\mu$ m with 100 keV electrons, and decreases markedly with increasing electron energy. Visual acuity (i. e. image detail resolved) improves roughly hyperbolically with logarithm of screen brightness [34]; it can then be shown [9] that there

will be an optimum magnification  $M_{opt}$  for best image resolution for a given contrast level and electron current density  $j_0$  available at the object. Electron dose rate  $j_i$  incident on the specimen must be adjusted so that focussing time occupies a small fraction of total irradiation time, but not so much that a weak image becomes impossibly difficult to focus or unstable; an acceptable compromise is total irradiation over ~ 10-20 s, i. e.  $j_0 = 0.1 \varphi_0 s^{-1}$ . For example, if  $\varphi_i = 300 \text{ C.m}^{-2}$  and  $\varphi_0 = 15 \text{ C.m}^{-2}$ , then  $j_0 \sim 1.5 \text{ A.m}^{-2}$ ; at this level  $M_{op1} \sim 10^4$ ,  $d_0$  (minimum) ~ 70 nm and resolution decreases rapidly for  $M > M_{opt}$ . There is therefore no point in increasing magnification above  $10^4$  unless  $j_0$  can be increased ; if  $j_0$  can be increased to  $5 \text{ A.m}^{-2}$ ,  $M_{opt}$  rises to  $2 \times 10^4$  and  $d_0$  (minimum) falls to ~ 35 nm.

The aperture of the human eye collects only a small fraction of light emitted from a flat screen. It is possible to collect emission from a larger solid angle using a wide-angle magnifying lens of magnification m; this permits detail m times larger to be discerned for the same image brightness. There is no point in increasing m beyond the point where either the resolution of the phosphor screen or limiting electron statistics begin to confuse image definition (image picture points separated by > 1 mm); for the marginal illumination levels considered here, m > 2 leads to diminishing returns. However, m = 2 permits e. g. dislocation images (maximum width ~  $\xi_q/2 \approx 35$  nm) to be discerned at intensities consistent with 5 nm resolution in the final recorded image. This is adequate acuity to limit defocussing error to < 5 nm at the object. Thus both recording statistics and focussing limitations are reached approximately simultaneously.

Use of image intensifiers cannot improve upon electron statistics (in fact, they introduce additional noise) and are of only marginal aid to focussing [35] compared with the fully dark-adapted eye. Complete dark adaptation requires > 15 min, and total darkness must be maintained throughout observation.

4.3 PHOTOGRAPHIC EMULSION RESPONSE. — Photographic emulsions are nearly noiseless detectors of high energy electrons and are therefore usually used to record electron microscope images. Their response to electrons (unlike light) is approximately linear with dose [36] up to useful developed densities (D < 3). Maximum contrast for any emulsion occurs at about 0.6 saturation density  $(D_{sat} \approx 6)$  which is for all purposes opaque. Therefore, the procedure for selecting a suitable photographic emulsion is the simple one of ensuring that at a total tolerable electron dose the emulsion is a fully exposed as practicable.

The measured response to 100 keV electron for commercially available emulsions useful in low intensity work is tabulated in Table III : an emulsion intended for conventional electron microscopy is

### TABLE III

Response of photographic emulsions to 100 keV electrons

Emulsion	Dose for $D = 1$ (e.µm <sup>-2</sup> )	Equivalent dose to typical foil at $M = 2 \times 10^4$ (Grad)
llford EM 4	1.0	80
(standard)		
LN	0.15	12
XK	0.09	7
XM	0.07	5

included for comparison. Ilford LN emulsion on  $65 \times 90$  mm glass plates is used most frequently and exposed to D = 2-3 with typical exposure times 10-20 s; XK emulsion is reserved for lowest intensity work. Prints from such dense plates must be made on soft grade paper. The sensitivity of these emulsions also requires scrupulous attention to stray light sources.

4.4 ELECTRON MICROSCOPY AT LIQUID HELIUM TEMPERATURE. — The requirements for satisfactory electron microscopy using a low temperature stage are adequate thermal and mechanical stability, economy, stage and specimen integrity, contamination protection and some certainty in estimation of foil temperatures. These points will be dealt with in turn.

Vibration and drift are the worst enemies of image stability and must be kept less than object resolution desired (say, < 5 nm) during the recording period (> 10 s). Liquid helium reservoir systems can be vibrationally unstable due to extensive nucleate boiling arising from the small latent heat of liquid helium. Liquid helium continuous-flow systems are inherently unstable for stage temperatures in the range 7-15 K [37]. The most stable form of specimen cooling for electron microscopy is cold helium gas in forced convection; gas at 4 K is readily available just above liquid level in a liquid helium dewar (it can be guaranteed at 4 K if drawn through heat exchanger immersed in the liquid) and is easily delivered to the microscope via a standard transfer tube. Forced convection can be obtained by pressurising the dewar by resistance heating or pumping on the exit line, and stage temperature may be raised by mixing in warm gas.

For economy and lowest stage temperature, heat inputs must be minimised. This requirement is somewhat at variance with adequate mechanical stability, for which the minimum requirement is rigid threepoint suspension. Fused quartz is the insulating material best combining mechanical strength, thermal insulation and dimensional stability [38], and use of spring-loaded fused quartz balls in the present stage implies a minimum conduction input  $\sim 0.5$  W. Radiative losses are small in comparison, and there is little point in shielding any part of the stage, except the specimen itself, from higher temperature surroundings. Heat inputs to other parts of the flow system are comparable, so a gas flow system capable of dissipating  $\sim 1$  W is required; with a simple stage heat exchanger, temperatures < 10 K can be achieved easily with liquid helium consumption < 1  $1.h^{-1}$ .

The considerable contraction in cooling by  $\sim 300$  K must be allowed for, both in differential contraction strains in stage materials and foil mounting, and self contraction stresses in the foil itself. As much of the stage as possible should be made of the same material (e.g. copper or phosphor-bronze); with this precaution observed, standard tilting cartridges [39] are perfectly stable and usable at 4 K. Stage supports must be spring-loaded to allow for stage contraction. The specimen foil must not be mounted in such a way as to result in differential contraction stresses which are invariably catastrophic in brittle foils ; thermal expansion coefficients of alkali halides are considerably larger than in most other materials [40]. Mounting from a single point on the periphery precludes differential stresses. The rate of cooling is also important and must be slow enough to preclude self-contraction stresses in the foil. Calculations [9] for typical foil geometry indicate that cooling rates  $< 1 \text{ K}.\text{s}^{-1}$  must be employed to avoid exceeding alkali halide yield stresses; even at this rate, dislocation rearrangement may take place in previously deformed specimens [41].

An unprotected foil maintained at < 30 K in normal microscope vacuum (~  $10^{-5}$  torr) condenses residual gases on its surfaces at a rate ~ 3 nm.s<sup>-1</sup> (10 µm.h<sup>-1</sup> !). Therefore, collimation above and below the foil must be employed to reduce the solid angle for contamination to < 0.2 sterad (contamination <  $10^{-2}$  nm.s<sup>-1</sup>). Collimation need not be with cold apertures provided vacuum is in the regime of straight-line molecular paths (<  $10^{-5}$  torr); for example, the objective aperture collimates effectively, and it is worth keeping at least a 400 µm aperture in place at all times. Water vapour adsorbed on photographic emulsions is the worst source of contamination, and emulsions must be thoroughly prepumped to <  $10^{-5}$  torr.

It is important that good thermal conduction is maintained between the specimen cartridge and the stage and between the specimen and the specimen cartridge. In the former case, adequate thermal contact can be made with a thin film of silicone grease which transforms to a conducting glass at low temperature. In the latter case, normal clamping is inadequate [42]; a conductive cement such as colloidal silver or low temperature varnish must be used.

Stage temperature is easily measured with an appropriate thermocouple, e.g. gold-0.03  $\frac{9}{6}$  iron vs chromel [43], the thermometric response of which is nearly linear with temperature over the whole range 0-300 K. Actual foil temperature is more difficult to estimate. It is advisable to shield the

specimen itself from warmer surroundings with an integral shield at helium temperature ; such a shield can double as contamination protection. Electron beam heating can be calculated for a given foil geometry, *e.g.* for a flat disc of uniform thickness [44] ; the temperature rise for a jet-polished disc is certainly less than this. Thermal conductivities of alkali halides at low temperature are high, ~ 100 W.m<sup>-1</sup>.K<sup>-1</sup> [45], and for the low beam intensities used,  $j_i \sim 100 \text{ A.m}^{-2}$ , the temperature rise is < 0.2 K at 4 K. An upper limit to foil temperature can be set by condensing nitrogen (sublimation point 30 K), neon (10 K) or hydrogen (5 K) [46]. Neon can be successfully condensed on alkali halide foils even during examination (Fig. 10).



FIG. 10. — Neon (sublimation point  $\sim$  10 K) condensed onto a NaCl foil during examination in the microscope.

5. Applications. — The new possibility of applying direct electron microscopical methods to alkali halides provides a much-needed definitive source of information about extended lattice defects heretofore unavailable for these crystals. It is clear from sections 3 and 4 that at least 20 s observation time is available, by alteration of saturation kinetics at low temperature, with resolution at the 5 nm level even in the least amenable materials (e. g. KCl). Considerably more time is available for certain other alkali halides (e. g. KI, NaCl, NaBr) in which defect production is depressed at very low temperatures. Under these conditions, moderately sophisticated contrast experiments on extended defects such as dislocations or radiation damage aggregates may be performed.

5.1 INTERSTITIAL STABILISATION IN IRRADIATED ALKALI HALIDES. — The ability to separate the irradiation effects of the investigating electron beam from the products of previous irradiation, particularly irradiation external to the microscope, is crucial for establishing a direct relation between microscopical observations and point defect information obtained by other means, *e. g.* spectroscopy. A particular case in point is the stabilisation of interstitial halogen atoms into aggregates large enough to be observed even in the range of conventional colour centre studies ( $10^{23}$  to  $10^{24}$  F.m<sup>-3</sup>).

Below 30 K, aggregation occurs only when interstitials become numerous enough (>  $5 \times 10^{24}$  m<sup>-3</sup>) to interact athermally and results in a high density (~  $10^{22}$  m<sup>-3</sup>) of small (< 5 nm) clusters. At higher temperatures, interstitials become stabilised in a decreasing density of larger clusters which take the form of planar, unfaulted, nearly prismatic interstitial dislocation loops [26] exhibiting conventional diffraction contrast [47]. These loops have a/2 < 110 >Burgers vectors in rocksalt-structure alkali halides ; analagous loops are also observed in CsCl-structure crystals. Existing dislocations climb by a process analagous to loop growth ; helices generated from climb of dislocations near screw orientation can even break up into strings of interstitial loops.

Models for aggregation of available interstitial halogen atoms into dislocation loops must take account of the microscopical evidence, particularly their unfaulted nature, and the evidence from spectroscopy, e. g. the V bands which have been associated with interstitial aggregates [48]. Perfect interstitial loops must consist of equal numbers of both anion and cation interstitials, and as a consequence cation interstitials must be created either during primary radiolysis or during subsequent stabilisation of primary irradiation defects, despite the overwhelming evidence that primary radiolysis occurs only on the anion sublattice [16]. It is also clear that since the optical V bands grow in direct proportion to the F band [49], they cannot be associated with the dislocation loop itself because optically active sites exist solely along the dislocation core at the loop perimeter and would increase as  $\sqrt{F}$ .

A possible model to reconcile the two observations [26] proposes that secondary displacements on the cation sublattice can be produced to accommodate interstitial halogen *molecules* formed during stabilisation of two mobile H centres. Near an existing dislocation core, such displacements are made less difficult than in perfect lattice by nucleation of an interstitial double-jog. The halogen molecule can then occupy the resulting Schottky vacancy pair in a nearly strain-free state as a non-magnetic  $X_2$  molecule or bound to a nearest neighbour  $X^-$  ion to form an  $X_3^-$  molecular ion, the number of which is always half the number of F centres. While the dynamics of such a stabilisation process must remain obscure, the overall energy gain,  $\sim 4 \text{ eV}$  per molecule, is an attractive feature of the model.

At room temperature, loops are observed at F centre densities as low as 10<sup>23</sup> F.m<sup>-3</sup>. They grow initially by elongation along < 100 > normal to b; this directed growth may arise from different jog geometry for [001] and [110] growth directions in, for example, the (110) loop plane. Two stable loop morphologies develop after subsequent growth : in NaCl, KCl, LiF for example the loops remain as elongated dipoles with maximum length > 200 nm and width 5 nm; in KI on the other hand they broaden into round loops with maximum diameter  $\sim 200$  nm. Loop density decreases somewhat with increasing irradiation dose since neighbouring loops of the same Burgers vector can coalesce during growth (redistribution by glide and self-climb may also operate). At saturation, loop density for dipole loops is ~  $10^{20}$  m<sup>-3</sup> while for round loops ~  $10^{19}$  m<sup>-3</sup>. There are strong indications that loop nucleation is heterogeneous on interstitial-stabilising impurities, since little dose-rate dependence of loop density is observed over orders of magnitude in dose rate, and doping with interstitial-trapping impurities (e.g. Tl) increases loops density and decreases loop size.

Upon annealing to above room temperature, there is little redistribution in loop population in the region where F centres bleach thermally. However, further annealing causes dipole loops to bulge out at dipole extremities (Fig. 11a) and eventually break up into two or more round loops (Fig. 11b); this occurs after several hours' anneal between 423 K and 523 K in NaCl. The mechanism is pipe diffusion along the loop core [50] and suggests that the difference in stability of round and dipole loop morphologies resides in the relative ease of pipe diffusion. Continued annealing effects an increase in mean loop size (Fig. 11c). Isothermal annealing kinetics suggest a glide and self-climb mechanism [51] for loop growth. Prolonged annealing above 600 K is accompanied by logarithmic decrease in total number of interstitials stabilised in the loops, indicating either extensive recombination [52] or a bulk-diffusion-limited growth mechanism also operating; after 12 h anneal at 623 K, nearly all loops have shrunk and disappeared.

Immense radiation doses (many displacements per ion) can also alter the form of interstitial stabilisation. After 10 Grad dose at 523 K (2-3 times saturation dose delivered in ~ 1 h), interstitial distribution is similar to that expected for anneal of a saturation dose for 1 h at 523 K. By 40 Grad an extremely dense strain-field network has developed (Fig. 2) which must arise from extensive reactivated growth of interstitial clusters. This is because any increase beyond initial saturation density in the number of interstitials stabilised requires an alteration in F centre distribution, *viz.* that F centres begin to aggregate, for example as alkali metal colloids ; a large colloid band ( $\sim 650$  nm) is certainly present after 40 Grad irradiation.

Microscope irradiation of thin alkali halide foils results very quickly in a similar dose and consequent formation of a similar complex strain-field network. Further irradiation at room temperature (KCl) or elevated temperature (NaCl) results in nucleation and





FIG. 11. — Annealing of dipole oops in NaCl  $\gamma$  irradiated to 4 Grad. a) 12 h at 423 K. b) 12 h at 523 K. c) 12 h at 573 K.

growth of large three-dimensional defects [6] (Fig. 12) exhibiting appreciable misfit strains [53]. These defects can eventually occupy a substantial fraction of the lattice volume (several %) and could be the elusive alkali metal colloids. However, an alternative explanation which better fits experimental evidence is redistribution of halogen molecule/divacancy defects on the model [26] into halogen gas bubbles.



FIG. 12. — Radial strain-field contrast from three-dimensional clusters in a KCl foil heavily irradiated with 100 keV electrons in the microscope at room temperature.





5.2 ELECTRON MICROSCOPY OF DISLOCATIONS AND IRRADIATION HARDENING. — It is clear that observation of dislocation arrangements in alkali halide crystals resulting from prior deformation is equally possible by low temperature microscopy, though particular caution must be exercised during foil preparation and cooling to ensure that extensive dislocation rearrangement does not occur.

Consistent observations in deformed crystals (e. g. Fig. 13) are strong interaction of primary and oblique



FIG. 13. — Dislocation structure on the primary slip plane of a NaCl crystal deformed in < 110 > compression to a shear stress of 2.5 MN.m<sup>-2</sup>.

slip systems, extensive network formation, production of debris (edge dislocation dipoles and small dislocation loops) and frequent cross-slip on other than the normal { 110 } slip planes of the rocksalt structure. Dislocation density counts indicate that the  $\tau \propto \sqrt{\rho_s}$ ( $\rho_s =$  screw dislocation density) relationship is followed well into stage II deformation beyond the region where etch pit information becomes unreliable [54].

Irradiated alkali halides exhibit marked increases in yield stress  $\tau_y$ , indicating that at least one species of irradiation defect is an effective obstacle to slip. In several alkali halides (LiF, KCl, NaCl) the increase is proportional to  $\sqrt{F}$  and has been previously ascribed to Fleischer hardening [55] by interstitial tetragonal strain centres leading to hardening of the form

$$\Delta \tau_{\rm y} = (G/n) \ (F/\rho_{\rm i})^{1/2} \tag{7}$$

where G is the shear modulus,  $\rho_i$  the ion density and  $n \sim 5-13$  experimentally.

Electron microscopical observations of efficient interstitial clustering (section 5.1) and direct observation of the dislocation-interstitial loop interaction (Fig. 14) indicate that interstitial loops rather than



FIG. 14. — Dislocation-interstitial loop interaction in K1  $\gamma$  irradiated to 1 Grad and deformed in < 100 > compression, observed along < 010 >.

isolated interstitials are the effective obstacles to slip. This is in accord with the temperature independence of the hardening [56] which indicates large obstacles to slip. It is possible to treat such hardening on an Orowan model for obstacles in the slip plane [57] for which

$$\Delta \tau_{\rm v} = Gb/kL \tag{8}$$

where L is the average distance between loops intersecting a slip plane and  $k \sim 1.2$  [57] for the strong dislocation/loop interactions.

The morphology of interstitial clustering differs amongst alkali halides, and the form of hardening will be different for dipole loops and round loops. For dipole loops elongating along < 100 > found in *e.g.* LiF, KCl and NaCl, the expected hardening on an Orowan model is

$$\Delta \tau_{\rm v} = (Gb/3 \ k) \ a(F/d)^{1/2} \tag{9}$$

where *a* is the lattice parameter, *d* the dipole width which remains constant throughout irradiation; thus (9) predicts the observed  $\sqrt{F}$  dependence and is independent of cluster density.

For round loops on  $\{110\}$  found in *e. g.* KI, the expected hardening is

$$\Delta \tau_{\rm v} = (Gb/k) (a^2 N_{\rm I}/\pi)^{1/4} {\rm F}^{1/4}$$
(10)

where  $N_1$  is the loop density which remains roughly constant throughout the later stages of irradiation; thus (10) predicts  $\Delta \tau_y \propto F^{1/4}$  which is observed for KI irradiation hardening (Fig. 15) [58].



FIG. 15. —  $F^{1/4}$  dependence of the yield stress in y irradiated K1.

Annealing of dipole loops above room temperature should lead to an abrupt drop in hardening as the dipoles convert to round loops (423-523 K in NaCl), and gradual recovery as the loops begin to disappear (above 573 K in NaCl). Exactly this behaviour has been reported recently for NaCl hardening [59].

The actual dislocation-interstitial loop interaction is evidently complex, as might be expected from the loop model advanced [26]. Extensive deformation tends to renucleate loops along a single { 110 } plane

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and evolve loop structures elongated along < 100 > which are curiously decorated (Fig. 16).



FIG. 16. — Curious decorated loop structure observed on a slip plane of KI  $\gamma$  irradiated to 1 Grad and deformed in < 100 > compression. The loops appear to be imaged in residual contrast.

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