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EVIDENCE FOR POTASSIUM METAL COLLOIDS IN ION-IRRADIATED KI

G. CHASSAGNE, J. SERUGHETTI
Département de Physique des Matériaux, Université Lyon 1 (*)
43, bd du 11-Novembre-1918, 69621 Villeurbanne, France

L. W. HOBBS
Materials Development Division, AERE Harwell Didcot, Oxfordshire (**) OX 11 ORA, England

Résumé. — Des cristaux de KI irradiés avec des deuteurs ou des particules α de 14 MeV par nucléon, à des doses de 2-6 x 10^{18} m^{-2} sont recuits à 393 K. Des répliques de surface révèlent une distribution des inclusions colloïdales en fonction de la profondeur de pénétration, avec un fort maximum près de la zone d’arrêt. Ces inclusions de potassium sont mises directement en évidence par MET et leur structure apparaît c.f.c ; elles proviennent de la coagulation de centres F créés par ionisation et apparaissent préférentiellement dans la zone d’implantation. Certains contrastes observés suggèrent, avec les deuteurs, une possible formation d’hydrure, et, avec les particules α, des inclusions sphériques pouvant être des bulles d’hélium.

Abstract. — KI crystals were irradiated with deuterons or alpha particles of 14 MeV per nucleon to doses between 2-6 x 10^{18} m^{-2}, and subsequently are annealed at 393 K. Surface replicas reveal a colloid inclusion distribution as a function of ion penetration depth, with a strong maximum near the stopping zone. These K inclusions are directly revealed by T. E. M., with an f.c.c. structure; these arise from thermal aggregation of F centres created by ionisation and nucleate preferentially in the stopping zone. Certain contrast features suggest a possible hybide formation with deuterium-implanted crystals, and spherical inclusions which could be helium bubbles with α-irradiated ones.

1. Introduction. — In alkali halides, by any colouration process alkali metal colloids essentially form by F centre coagulation. If the crystals are irradiated, particularly with charged particles, the colloids can result from collisions by nuclear impacts and from particle implantation. The colloidal defect formation is directly related to different creation modes. The formation rates are function of initial defect relative concentrations; the initial relative concentration is larger for the irradiated crystals (∼ 10^{24} m^{-3}) than for the additively coloured ones (∼ 10^{23} m^{-3}).

The appearance of colloids after thermal treatment of irradiated crystals is revealed by an optical absorption band [1-9], by small angles X-ray scattering and X-ray diffraction [10], by EPR [11], by the Bassett technique [12], or finally by electron microscopy [13, 14, 15]. However direct evidence by transmission electron microscopy did not till now give the expected results. Thus one would hope to estimate the colloidal centre density with the depth of particle implantation in the irradiated crystal, the size distribution, their shapes and their crystalline nature. The observation of optical absorption bands reveals the colloid presence, but by the electron microscopical observations on replica and on thinned samples the behaviour of colloids can be studied.

2. Evolution of defects produced by irradiation and thermal treatment experimental results. — KI single crystals purchased from Quartz and Silice were irradiated by heavy ions either deuterons of 28 MeV or α particles of 56 MeV; this implantation was effected at room temperature in a vacuum of 10^{-5} torr (∼ 10^{-3} Pa). The irradiated area is about 1 cm² and the implantation depth is about 1 mm for α particles and 2 mm for deuterons. The obtained blue colouration permits so evaluation of the depth of implantation; the stopping zone of implanted particles appears dark blue and a diffuse blue colouration often follows it for several tenths of mm. The usual doses are about of 10^{18}-10^{19} particles per m².

2.1 Spectrophotometrical results. — 2.1.1 KI crystals irradiated by 28 MeV deuterons and annealed. — The doses for these crystals are 5.8 x 10^{18}-1.2 x 10^{19} deuterons per m², i.e. 0.42-0.85 Grad. The defects are principally created by ionization, their density is not homogeneous along
the implantation depth; nevertheless the integral spectra are made at room temperature, and the light beam is normal to the crystal face parallel to the implantation direction.

With the difference of additively coloured crystals the annealing temperatures are smaller (at 433 K the crystals are completely bleached). The thermal treatments are made at 373 K or 393 K during 1,2 or 4 hours; for a larger time the F centre concentration increased strongly and so the colloidal band.

For a 1 h anneal at 373 K, a very large colloidal band appears although the peak position is not observable, and the F band decreases notably. For 2 or 4 h anneals, the F band decreases further and the colloidal band peak position is still not visible (about 860 nm), but this band is very broad and overlaps certainly several bands corresponding to different sizes. The V₃ band (310 nm) disappears, but a band located near 322 nm appears with a small optical density which decreases with the annealing time.

At 393 K (Fig. 1, curves 2, 3, 4) a similar evolution exists, but the F band decreases more quickly and for an annealing of 4 h it has about disappeared. The colloidal band is very intense after an annealing of 1 h and shows a shoulder at 905 nm (the peak position is not visible); it decreases substantially following 2 1/2 hours of thermal treatment and a peak position is clearly visible at 875 nm; the F band decreases further. A band at 318 nm appears instead of the V₃ band.

The quasi-equilibrium existing in additively coloured KI crystals between F centres and colloids does not exist in this case, indeed both bands decrease during the annealing. Shoulders are observed near 350 and 400 nm when the F band decreases strongly, i.e., for an annealing at 393 K during 2.5 and 4 h.

2.1.2 KI crystals irradiated with 56 MeV α particles and annealed. — The doses are

\[ 9 \times 10^{-17} - 2.75 \times 10^{18} \alpha \text{ particles per m}^2, \]

i.e. 0.26-0.79 Grad. Because the high energy of implanted particles, the defects are principally created by ionization; F and V centres appear at room temperature. Their density is inhomogeneous, so the optical spectra are made on the whole irradiated crystal like previously.

Before annealing, the absorption spectrum (Fig. 2, curve 1) shows the F₁, F₂, F₃ bands and the V₃ band; the U band is always partially overlapped by the absorption edge in U. V. Between the F band and the F₂, F₃ bands appears a presumed colloidal band located about 740-750 nm. The estimated F centre concentration is \( 8.4 \times 10^{23} \text{ m}^{-3} \) corresponding to a dose of \( 9 \times 10^{17} \alpha \) particles m\(^{-2}\).
For both thermal treatments, the F and colloidal bands decrease more and more, with the time and temperature; F centres evaporate out of the crystal, recombine with V centres, or give the electron to a cation interstitial; the irradiated crystal recovers. The quasi-equilibrium between F centres and colloidal centres no longer exists.

2.2. REPLICA ELECTRON MICROSCOPY RESULTS. —

The shape of the observed particles is different from that of colloids observed in additively coloured crystals [18]. For any size of these defects, the facies is not spherical but nearly octahedral. From the shadowing the defects stay in relief. This feature exists so for irradiated LiF crystals.

2.2.1 KI crystals irradiated with 28 MeV deuterons and annealed (393 K-4 h). — The implantation direction is ever the <100> one of the crystal and the shadowing direction is the same. To estimate along the implantation depth the density and the volume fraction of defects we used marked grids to support the replicas.

The density of defects is very heterogeneous. The estimated volume fractions occupied by these defects along the implantation depth are plotted and a profile is drawn (Fig. 3). To obtain significant values an average calculation is made on many grid squares corresponding to the same implantation depth, indeed the ion beam is lightly divergent and defects are present in the crystals prior to the irradiation. Nevertheless the measurements of density and volume fractions are made in a replica narrow band parallel to the implantation direction.

![Fig. 2. — KI crystals irradiated with 56 MeV alpha particles (1.9 x 10^{18} m^{-2}): Annealing at 393 K (sample thickness = 1.42 mm). Spectrum 1: before annealing; spectra 2, 3 and 4: annealing during 1, 2 and 4 h. The colloid band locates about 860-865 nm, a secondary maximum is distinct about 925-930 nm. The F centres are about bleached after 4 h. The V3 band (310 nm) is replaced by a band at 325 nm.](image1)

![Fig. 3. — Distribution profile of the defects observed on replicas: occupied volume fraction C_v against the penetration depth of 28 MeV deuterons in KI crystals (5.8 x 10^{18} m^{-2}). Before annealing the dashed curve shows a broad defect zone on the stopping zone. After annealing (393 K-4 h) the defects concentrate on the stopping zone. At the beginning of the ion implantation appears a small defect concentration. The defect region goes beyond a 2.5 mm depth (implantation depth 2 mm).](image2)
The replicas correspond to irradiated KI crystals for which the dose was $5.8 \times 10^{18}$ deuterons m$^{-2}$ (0.42 Grad) and the F centre concentration, $10^{24}$ m$^{-3}$. Before annealing the profile of defect volume fractions shows a maximum in the stopping zone of implanted deuterons (the depth is $\sim 2$ mm). In the replica regions of high defect concentration are observed many cracks and cleavage steps. The diameters of observed defects range from 180 to 720 Å, but larger sizes (1 500 Å) are present in the zone of maximum volume fraction and represent the half of defect volume fraction.

The profile shows two secondary maxima just at the beginning of the ion penetration and after the stopping zone. This effect was recently observed on KCl crystals irradiated with 11 MeV protons (dose $= 7.5 \times 10^{16}$ m$^{-2}$) by Thompson and Murray [19]. Delbecq et al. [20] observed so this interface effect on LiF crystals irradiated with deuterons.

After 4 h anneal at 393 K, the plotted profile is similar enough but the observed maximum is narrower and corresponds exactly to the stopping zone estimated for 28 MeV deuterons by Perez [21] using measurements of energy loss. The slopes of this maximum are characteristic for a peak of defect due to collisions and implantation [22]. The volume fraction is smaller than before annealing. Many cracks and cleavage steps are still observed in the maximum zone. The region of implantation beginning is less perturbed, the cleavage surface presents lines and steps in V and zig-zag forms (Fig. 4). The defect diameters range from 200 to 780 Å and arise to 1 160 Å in the maximum zone.

2.2.2 KI crystals irradiated with 56 MeV $\alpha$ particles. — For a dose of $1.88 \times 10^{18}$ $\alpha$ particles per m$^2$ (0.57 Grad), the F centre initial concentration was about $1.75 \times 10^{24}$ m$^{-3}$.

The same irradiated crystal was annealed at 373 K during 5 h and at 393 K during 4.5 h. The plotted profile of observed defects exhibits so a peak corresponding to the stopping zone of $\alpha$ particles, the maximum volume fraction is important (370 ppm) at the depth of 1 mm.

The different observed regions are more perturbed for implanted $\alpha$ particles than for deuterons in KI crystals, of course the observations are more difficult. The sizes range from 200 to 1 500 Å and some defects arise to 2 300 Å (the occupied volume fraction is high).

2.3 Direct electron microscopy results. — After experimental results by spectrophotometry and on replicas we studied thin samples of irradiated and annealed KI crystals; the samples are generally cleaved parallel to the implantation direction. We specially observed the middle of the ionization region and the stopping zone (collisions and implantation of ions). It is very easy to recognize these regions by the blue colouration, the stopping zone is dark blue. Some samples are cleaved perpendicularly to the beam direction in the same regions. Samples are chemically polished to obtain a small hole exactly in the interesting zone [15, 23].

The irradiation damages by the microscope electron beam are minimized by appropriate observation conditions, at 15 K and with a very weak current density (15 A m$^{-2}$) [24, 25].

2.3.1 KI crystals irradiated (28 MeV deuterons) and annealed (393 K-4 h). Interstitial loop observation. Before annealing and for any implanted region interstitial loops are observed as already observed by Hobbs et al. [26], but with diameter between 240 and 800 Å; these interstitials are ions, $X^-$ anions and $M^+$ cations moved off by substitutionnal $X_2^0$ molecules, which result from combination of two H centres, $X_2^0$ occupies both anionic and cationic sites and so can be quoted $[X_2^0]^+$ molecule. The interstitial aggregation forms perfect loops with a Burgers vector $\frac{1}{2}a < 110 >$; $V_3$ centres correspond to $X_2^0$ molecules. During the irradiation or the following annealing these loops grow and evolve. They are surrounded by $[X_2^0]^+$ defects. At each interstitial ion pair in the loops corresponds a substitutional
molecule, i.e. two H centres (and two F centres). The nucleation of the loops was explained by Hobbs et al. [27, 28]. The F centre concentration deduced from optical spectra agree with the H centre one estimated from the loop number.

After annealing the previous described interstitial loops evolve, many of them disappear and larger loops develop; in the same time the F and V₂ absorption band decrease. Diller et al. [28] suggested an evolution mechanism; in a first time the X₂ molecular centres recombine with the F centres forming divacancies, later they recombine with the interstitial loops: the crystal recovers. The size evolution process analysed by Diller is probably a glide and self climb mechanism followed by coalescence: when two loops have the same Burgers vector, they can move towards each other by diffusion of the surrounding vacancies and form a larger one.

Between the stopping zone and the ionization region the loop evolution is somewhat different after annealing. In the ionization region the loops are more numerous and smaller, very few interstitials disappear (20 % instead of 50 %). The larger stability could come from a smaller amount of available divacancies, i.e. from a larger stability of F centres.

2.3.2 KI crystals irradiated (28 MeV deuterons) and annealed (393 K-4 h). Colloidal defects study. — a) Observation of the stopping zone. — In this dark blue region the loops are larger with a diameter between 400 and 2,000 Å and even some times 2,500 Å. The number of interstitials, thus the H centres number, is still between 2 and $2.5 \times 10^{24} \text{ m}^{-3}$.

We distinctly observe colloids similar to the ones observed in KI additively coloured and annealed [29, 30]. The picture 6a, b shows two very large colloids (several thousands angstroms). We observe for one of them a structure factor contrast and an absorption contrast; its edge presents a black-white contrast along the g direction; this contrast is either characteristic of a strained precipitate close to the surface or characteristic of a colloid intersecting the surface. The other colloid shows a contrast with an internal structure which is difficult to comment; its clear
facies is the association of one cube and one octahedron, association forming small facets.

From the large volume fraction occupied by the colloids we were able to get a diffraction pattern on a selected area (Fig. 6c). Beside the (001) KI reflections extra spots from diffraction along the [110] * direction are observed. The pattern geometry and the measured distances indicate the existence of potassium with an f.c.c. structure and a lattice parameter of 6.28 Å.

On the micrograph 7 the respective densities of interstitials and of colloids can be evaluated.

The polygonal colloid shape has the same aspect and orientation with respect to the matrix as the ones observed in KI crystals additively coloured and annealed [29]. A chemical contrast corresponding to a print of a colloid etched by the chemical polishing can be also observed.

A particular contrast of the observed colloids is shown on the micrograph 6a; this black-white contrast suggests that small defects or precipitates on the colloid interface could result from a reaction between the potassium and the implanted deuterium and could form an hydride. Hughes and Pooley [31] have suggested such a possibility for KI crystals irradiated with protons.

b) Observation of the middle region. — The loops are larger after annealing, but no colloids are visible except near the stopping zone.

2.3.3 KI crystals irradiated with 58 MeV alpha particles and annealed (393 K-4 h). — The observations are achieved near and on the stopping zone. The interstitial loops are relatively small (between 230 and 1 100 Å) and numerous. They have the usual characteristics previously described. Their size
increases after annealing and the number of interstitials decreases.

Smaller inclusions with a diameter between 700 and 1,000 Å are observed by their absorption and strain field contrasts (Fig. 8). Their facies are very regular; they are probably metallic colloids. For the spherical inclusions the observed absorption contrast suggests the presence of helium gas bubbles (Fig. 9). In the stopping zone its presence would not be surprising. Micrograph 10 ($w = s, \xi_2$ increased) shows these inclusions with a better contrast. They correspond possibly to bubbles.

![Image](image-url)

**Fig. 10.** KI crystals irradiated with 56 MeV alpha particles ($10^{18} \text{ m}^{-2}$): Annealing at 393 K-4 h. For the condition $w = s, \xi_2$ large, the absorption is important, inclusions appear by the absorption contrast (white aspect), they are probably helium gas bubbles.

3. Colloidal defect observation in the stopping zone.

So far we have not observed colloids in the ionization region where the F centre concentration is large. Perhaps the F centres aggregate homogeneously without preferential nucleation sites into very small colloids invisible by electron microscopy [7].

The defect profiles indicate an increasing of the defect density after annealing in the stopping zone, indeed the energy loss profiles suggested the same conclusion for this region where are produced the collisions and implantation of particles. The stopping zone is strongly perturbed [7, 32] and intrinsic colloid would be able to form.

The defects on the replicas have not the aspect observed on the ones in the experiments concerning crystals additively coloured and annealed, but their particular aspect is also observed with LiF crystals irradiated with 28 MeV deuterons, annealed at 573 K and exhibiting an optical colloidal band. Thus the aspect is due to an irradiation effect.

In any region of the irradiated crystals interstitial loops are observed but their evolution is lightly different, according to the observed region. After annealing the loop size increases but the loop number decreases more quickly in the stopping zone. This evolution of interstitial loops is well explained by the previous model.

Potassium intrinsic colloids are observed in the stopping zone. Their nature is suggested either by determined contrasts (structure factor, absorption) or by diffraction patterns. The shape, if it is clear, corresponds to a facies of cube and octahedron. The lattice parameter of potassium colloids is deduced from diffraction patterns (6.28 Å) and probably corresponds to an f.c.c. structure for the potassium.

The colloid sizes are large for the annealing (393 K-4 h) of KI crystals irradiated with deuterons; in the same conditions of annealing but for crystals irradiated with α particles the sizes are smaller. The internal structure of some colloids is particular and must be again examined to know clearly the formation of microcrystallites in bulk or on the interface.

The colloid precipitation corresponds to the F band decreasing; the F band is bleached at 393 K after 4 h. The F band evolution was already ascertained by Hobbs [15] during thermal treatment on NaCl crystals irradiated by 70 keV electrons (dose ~ 4 Grads).

The colloid formation can result from several causes and it is actually difficult to determine the pre-eminent cause. In the stopping zone both damages have an influence on this formation, the damages resulting from ion knock-on along the implantation depth and the ones produced by ionization. Thus the colloids can proceed from the reorganization of the K cationic interstitials moved by the particle collisions, indeed the moved cations operate like nuclei. The spikes induced by the implanted ions are disturbed regions of the crystal and can be the first stage of the colloid formation. The following growth would result from the conjoined coagulation of available F centres by bulk diffusion. But the colloids can likewise result from the high concentration of F centres; the mechanism is thus similar to the one for the additively coloured crystals: the F centres aggregate thermally or by the dislocation strain field (the stopping zone is very disturbed [29]). Finally the implanted ions stop certainly neutral, they can give arise to a lattice deformation and also to a reorganization induced by this deformation or by the particle reactions with the moved metal atoms. Wardle et al. [32] observe an F centre diffusion in the strongly disturbed region for proton irradiated...
KCl crystals, indeed after annealing at 473 K a colloidal band appears. In our experiments after 393 K-4 h annealing, for both deuterons and alpha particles, a broad but symmetrical colloidal band was present, the peak position locates respectively at 875 and 865 nm and corresponds thus to big colloids.

Helium gas bubbles are put in evidence in the zone implanted with alpha particles, but no with deuterons. Perhaps the deuterons can interact upon other defects like the colloids or can evaporate out the crystal, the hydride formation is possible.

4. Conclusion. — For crystals coloured by irradiation with deuterons and alpha particles (14 MeV by nucleon) and annealed, the optical spectra indicate no quasi-equilibrium between F centres and metal colloids. The increasing of colloidal band proceeds however from the decreasing of the F band, but the appearance temperature and the stability of the colloidal band are less high.

On replicas made in the regions of ionization and particle stopping, the defect distribution has a strong maximum in the stopping zone.

On thinned samples interstitial loops are observed, and after annealing they grow and their number decreases in the stopping zone. In this latter region we observe damages produced by ionization and by ion knock-on; after annealing K colloids are directly observed for the first time. The K colloids have a cubic facies in the crystals irradiated by deuterons. They are visible principally by absorption contrast in the crystals irradiated by alpha particles. The K structure appears f.c.c.. Helium gas bubbles are also visible in the alpha implanted crystals.

The nucleation process is probably different of the one described for the additively coloured crystals [33]. The moved metal ions and the cationic interstitial spikes form certainly nuclei. The relative excess of F centres in the stopping zone can also participate to the colloid nucleation.

References