Nature of Interstitial Clusters in Alkali Halides

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(Received 6 December 1971)

Planar clusters of interstitials in alkali halides, giving rise to dislocation-loop contrast, have been studied using transmission electron microscopy. These loops are produced together with *F* centers by ionizing radiation. It seems very likely that they consist of planar aggregates of ⟨110⟩-aligned halogen molecules.

When alkali halides are irradiated with ionizing radiation, both *F* centers and complementary interstitial halogen atoms are created.[1] It is now widely accepted that this occurs in a process involving nonradiative electron-hole recombination.[2,3] The *F* centers are stable to about 400–500 K and can easily be observed through their strong optical absorption band, but the fate of the complementary interstitials is less clear. At low temperatures they exist as well-characterized point defects,[4,5] but at room temperature no appropriate point defects are present, and it has been inferred that they exist in cluster form.

Transmission electron microscopy is very powerful in defining the nature of large defects such as interstitial clusters, but it has not previously been applied successfully to the problem of interstitials in alkali halides for two main reasons. Firstly, the thin foils that are necessary for electron microscopy are very sensitive to moisture and must be prepared and used under suitably dry conditions if results which relate to bulk conditions are to be obtained. Techniques have now been developed[6] for producing and handling thin alkali-halide foils which are adequate for even the more moisture-sensitive materials such as NaBr. Secondly, in alkali halides the radiation damage caused by the viewing electron beam can be very rapid, making extended observation of particular defects impossible. This problem has been overcome in the present work by using a low-temperature specimen stage[7] and by careful choice of alkali halide. Thus in KI at ~10 K the basic radiation damage rate is much lower than in KCl or in KI at 300 K.[8] A further increase in viewing time in KI can be obtained by using samples containing a few hundred parts per million of Na^+. By trapping interstitial atoms,[9] the Na^+ ions greatly inhibit the rate of cluster formation. The increase in viewing time which can be obtained is from less than 1 sec in pure KCl at 300 K to many tens of minutes in KI(Na) at 10 K, making possible elaborate tilt-contrast experiments. A further advantage to be gained from suppressing the *in situ* damage rate is that defects created by external irradiation can be examined.

Figure 1 shows defects created in four alkali halides by *in situ* irradiation at room temperature. With the exception of NaBr, which has a very low radiation damage rate even at room temperature and shows very small clusters, the crystals contain defects with contrast typical of dislocation loops. The loop size reaches an equilibrium value after about 1 sec in the microscope beam, consistent with the radiation dose giving *F*-center saturation. Other types of clus-

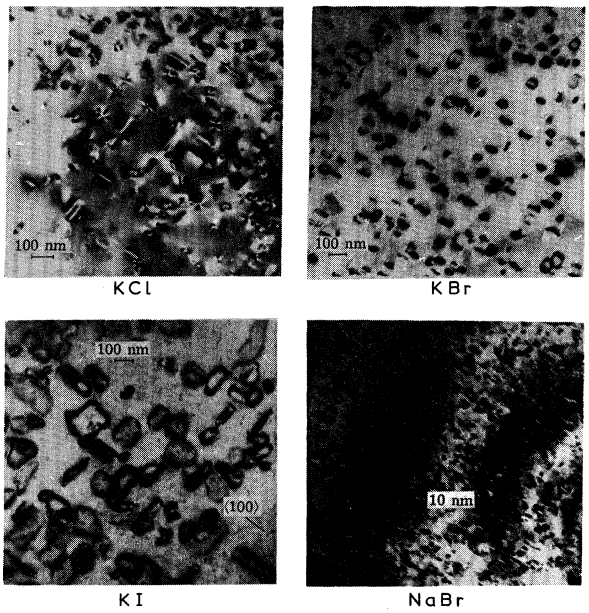

FIG. 1. Loop clusters observed at room temperature in KCl, KBr, KI, and NaBr.

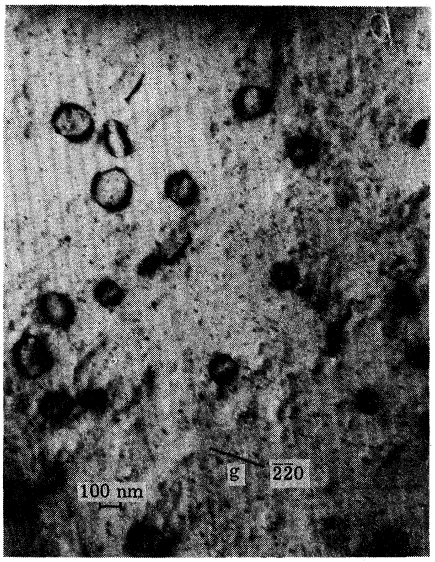

FIG. 2. Micrograph of KI irradiated externally with γ rays at room temperature and observed at 10 K. The irradiation dose was 10^9 Rad ($\sim 10^{23}$ eV cm^{-3}).

ters can also be observed after room-temperature irradiation in the microscope, but they are not formed under the wide variety of conditions which produce loops and they will not be discussed here. The loops are also created by external irradiation (Fig. 2). Detailed electron-microscopical investigations of the loops formed in KI have shown that (i) they have a displacement vector $\vec{R}$ which is in a $\langle 110 \rangle$ direction and has a magnitude of the order of $a/\sqrt{2}$, where a is the $\langle 100 \rangle$-lattice parameter; (ii) they are interstitial in character; and (iii) they are essentially two-dimensional, occupying $\{100\}$ planes when produced *in situ* in thin foils. In this case $\vec{R}$ lies in one of the $\langle 110 \rangle$ directions not in the loop plane. In externally irradiated crystals the loops occupy planes well separated from $\{100\}$, being about midway between the $\{100\}$ and the $\{110\}$ normal to $\vec{R}$.

We believe that these loops represent the primary clusters of the interstitial halogen atoms formed together with F centers for the following reasons:

(i) They have interstitial character.

(ii) Within experimental error the number of atoms involved in the loops is always the same as the number of vacancies present as F centers, which can readily be determined optically in externally irradiated crystals. Very little vacancy clustering occurs, even at high doses.

(iii) The rate of growth of the loops under *in situ* irradiation varies with temperature in the same way as does the mobility of interstitial atoms. For example, in KI cluster growth becomes appreciable in the range 35–65 K, which is just where H centers become mobile.[10]

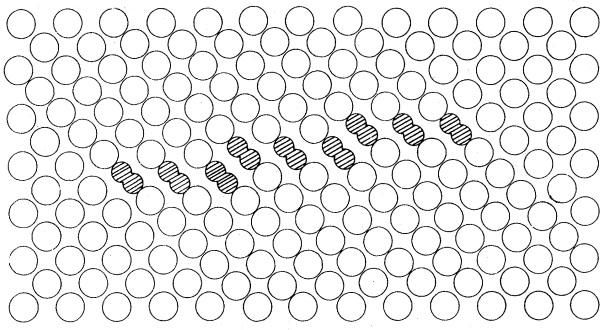

FIG. 3. Planar precipitate of X_2 molecules in a (100) halide sublattice.

(iv) No large-scale defect other than the loops is seen in the microscope in externally irradiated crystals, and the only point defect observed in large numbers is the F center. It is therefore difficult to ascribe the loops to straightforward dislocations, since, in order to obtain equal numbers of cation and anion interstitials, one would expect to produce isolated or clustered cation vacancies. If large clusters were produced they should be visible in electron microscopy but none are seen. If the cation vacancies were present as point defects they should have associated holes, corresponding to the electron in the F center, and therefore exhibit optical or EPR absorption.

One possible structure for the primary interstitial clusters, the loops, is that of a planar precipitate of halogen molecules. The molecules would need to lie parallel in a $\langle 110 \rangle$ direction, squeezed between neighboring halide ions (Fig. 3). This model is then able to account for the direction and magnitude of $\vec{R}$ as well as for a number of morphological features such as the tilt out of $\{100\}$ planes. This model is also consistent with optical-absorption studies of the V bands produced by room-temperature irradiation. It is now well established that these occur in the region of V_2 and V_3 bands, and are generally similar to those produced by additive coloration with halogen gas.[11] By comparison with bands arising from ions in solution, Konitzer and Hersh[10] have suggested that in KI these V bands are due to aggregated halogen-molecule species, probably similar to I_3^- molecular ions. Similar conclusions have also been reached for KBr.[12] In many

alkali halides[13,14] it has been shown that the V_3 band grows in proportion to the F band for F-center concentrations up to 10^{19} cm^{-3}, suggesting that it is due to a defect complementary to the F center. It is natural to associate this defect with the clusters we have observed. If this is the case, the proportionality to the F band seems to rule out perfect dislocation-loop clusters since optically active interstitial species could only occupy the core of such loops. Since the loop size increases with dose, the proportionality between the interstitial absorption band and the F band would not occur. Furthermore, the oscillator strength of $f = 0.2$ derived for the V_3 band,[14] assuming one absorbing species per F center, shows that most of the interstitials contribute significantly to the absorption (f cannot exceed ~1). This could not be the case if most of the interstitials were part of perfect dislocation loops. The association of the interstitial halogen clusters with the V bands could also explain their variation in shape with dose and temperature of irradiation,[15] since the environment of the majority of interstitials will change as the loop size increases.

We are thus led to conclude that the most likely model for the loop clusters is an approximately {100} planar precipitate of molecular halogen molecules oriented in ⟨110⟩ directions. Such a loop might be expected to show fault-contrast effects if the displacement vector differs from a perfect shear $\frac{1}{2}a\langle 110\rangle$, but detailed considerations show that conditions for their observation are marginal. The ionic nature of the alkali-halide lattice, involving as it does long-range Coulomb forces, may also give rise to complex lattice relaxations around the loop. In such a case it is not obvious that fault-contrast effects would be apparent.

A detailed account of this work is in course of preparation.[16] We should like to thank Professor P. B. Hirsch, Dr. R. Bullough, Dr. M. J. Goringe, Dr. A. M. Stoneham, and Dr. M. J. Whelan for many useful discussions.

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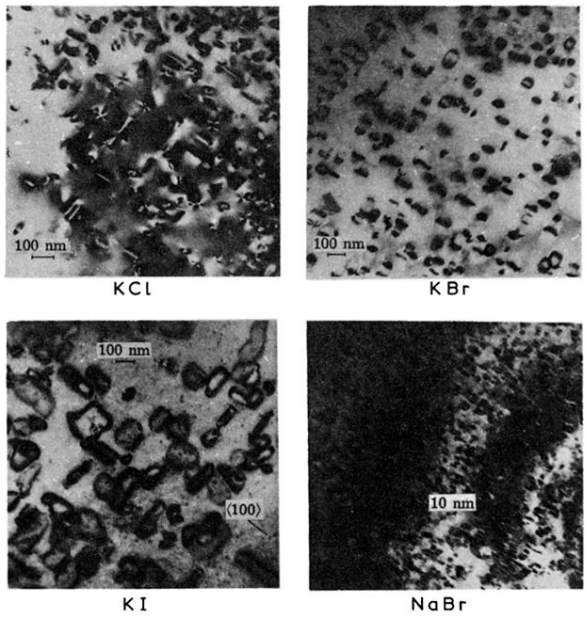

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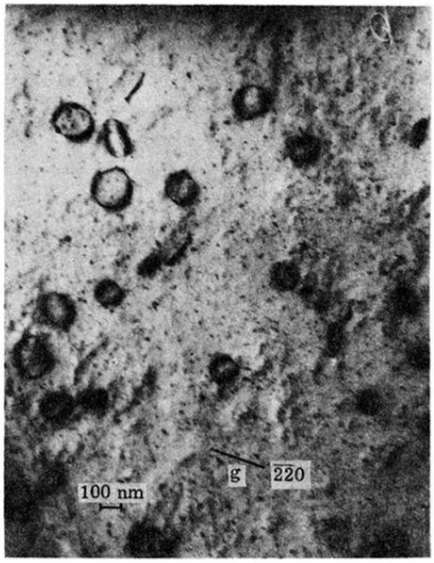

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