

RADIATION DAMAGE AND DEFECT AGGREGATION IN ALKALI HALIDES

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is submitted to the
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
for the degree of
DOCTOR OF PHILOSOPHY

January 1977

ACKNOWLEDGEMENTS

Dr. A. B. Lidiard and Prof. A. K. Ghatak are the joint supervisors of the work reported in the thesis. I am deeply indebted to Dr. Lidiard for suggesting the problem and for his advice, guidance and encouragement on all aspects of this work and to Prof. Ghatak for his continuous interest and encouragement. Indeed I am grateful to both of them and to Prof. M. S. Sodha for their help and kind support without which my visit to Harwell would not have been possible. My special gratitude here is due to Dr. W. Marshall and U.K.A.E.A. for the provision of a fellowship at A.E.R.E., Harwell which made the work possible.

I would like to acknowledge the considerable benefit I have derived from several valuable discussions with the members of the Theory of Solid State Materials Group and the Radiation Damage Group in Theoretical Physics Division, A.E.R.E., Harwell. In particular I should like to mention Drs. A. M. Stoneham, R. Bullough, A. H. Harker, M. R. Hayns, R. Perrin and A. Mainwood. I would especially like to thank Dr. Harker for his generous assistance with the CNDO and ATMOL programs and for providing me his results on F-centre calculations and Dr. Hayns for his kind advice on the use of the computer program utilised in the calculations described in chapter 3.

I am grateful to Prof. L. W. Hobbs for several useful discussions and for providing me with his experimental results on colloid growth.

I have profited particularly from many valuable comments of Prof. N. Itoh on the present work.

May I thank all the members of the Theoretical Physics Division, Harwell for making my stay there so pleasant.

Finally I would like to thank Mrs M. Slade and Mrs P. Bishop for their efforts to produce a faultless typescript.

ABSTRACT

It is now well established that ionizing radiation causes damage in the halogen sub-lattice of alkali halide crystals - the primary defects produced being F-centres and interstitial halogen atoms (H-centres). Experimental observations have shown that aggregation of H-centres at even very low temperatures leads to the formation of perfect interstitial loops. At moderate temperatures the F-centres become mobile and cluster together to form F-aggregate centres and ultimately alkali metal colloids.

Our aim in this thesis is to study theoretically this process of aggregation of F- and H-centres. Recent experimental studies on the growth of colloidal Na centres by F-centre aggregation in NaCl irradiated to high doses have shown several features in common with the growth of voids in heavily irradiated metals. Chapter 2 presents a theoretical model suggested by this analogy and by other knowledge of defects and radiation damage in the alkali halides*. Though some of the parameters needed for quantitative predictions are not known accurately enough, the properties of the model in general are in good agreement with the available, rather limited experimental data on colloid growth in NaCl. For example, the predicted dependence of colloid growth upon temperature and dose are correct. The model also describes the growth in F-centre concentration and its approach to saturation and shows how several earlier discussions of the rates of growth of the F-centre concentration during irradiation can be obtained as special cases of our theory. We have further pointed out how and where additional experimental data could help test the model more rigorously and determine the values of the various parameters more accurately.

*This part of the work has been separately reported in AERE Report TP.650 (1976) and in Phil.Mag. (in press).

Chapter 2 considers only the post-nucleation stage in the growth of colloids. In chapter 3 we investigate the nucleation stage in the growth of both colloids and interstitial dislocation loops in irradiated alkali halides. We have examined various approaches to the problem including both rate-theoretical approach and approach based on classical precipitation theory and have deduced the density of colloids and loops formed during nucleation. In the absence of clear indications to the contrary, we have throughout assumed the nucleation to be homogeneous. At this stage, however, we have not been able to predict the nucleation densities accurately largely because the available experimental data is not sufficient. For example, the theory shows that if the binding energy of the F_2 aggregate centre is small compared to the activation energy of motion of the F-centre, the rate of dissociation of F_2 -centres will play a significant role in the process of nucleation of colloids. Also, in order to know if the F-aggregate centres represent the first stage in the formation of colloids, we need to know the binding energies of these centres.

Therefore, we have devoted the rest of the thesis to a study of the binding energies of the various F-aggregate centres, namely M-, R-, N_1 - and N_2 -centres. In chapter 4 we examine the predictions of the continuum model. We have calculated the M-centre binding energies in this model. The model, however, predicts the R-centre to be unbound with respect to an M- and F-centre. The continuum model cannot be really applied to the F-centre because of the compact nature of the F-centre wave-function. Nevertheless the transition energies of the M-centre obtained in the continuum approximation are known to agree quite well with the experimental values and therefore we might expect the same to be true for the binding energies.

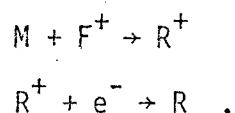
We next appeal to molecular theory and in chapter 5 use the valence-bond method to calculate the binding energies of M- and R-centres in a number of alkali halides. We treat the crystal in the point-ion approximation and use 2s-type F-centre wave-functions. The binding energy of the M-centre is higher than that obtained in the continuum model, although the valence-bond theory too predicts the R-centre to be unbound with respect to an M- and an F-centre.

Chapter 6 uses the molecular orbital approach, treating the region of the solid containing the defect and its neighbouring ions as a large molecule. The interactions of the F-centre electrons with the electrons of the nearest-neighbour and the next-nearest-neighbour ions of the defect are treated explicitly. The presence of the rest of the crystal surrounding the cluster is allowed for by adding at each site in the cluster the Madelung potential due to the crystal outside the cluster. Since ab-initio calculations of all the integrals involved will not be computationally feasible, we employ a semi-empirical approach, based on complete neglect of differential overlap (CNDO). It is an all-valence self-consistent-field (SCF) method which consistently neglects terms of the order of the overlap between orbitals on different atoms. The original CNDO program has been extended and modified at AERE, Harwell. We have used this modified version and have parameterised it for application to LiF, NaCl and KCl . We have then calculated the binding energies of M-, R-, N_1 - and N_2 -centres in these crystals.

The binding energies predicted by the CNDO calculations are different from those obtained in the valence-bond and continuum theory although all of the calculations make some common predictions on the stabilities of these centres. For example, the binding energies of the aggregate centres are found to decrease with increasing lattice constant whichever theory we use, a feature also observed in other theoretical calculations. The

calculations also predict that the R-centre is the least stable amongst all the centres considered, in agreement with the experimental observations. In fact, it is only slightly bound or unbound with respect to an M- and an F- centre.

We therefore propose the following alternative mechanism of formation of the R-centre



We expect the R^+ -centre to be strongly bound to the M- and F^+ -centre because of the electrostatic attraction between the positively charged F^+ -centre (i.e. the anion vacancy) and the polarisable M-centre electrons. The results of the CNDO calculations show this to be the case.

Both N_1^- and N_2^- centres are, according to the predictions of CNDO theory, stable with respect to an R- and an F-centre. The N_1^- -centre is found to be more stable than the N_2^- -centre.

We also note from these results that even though there is a lack of agreement between the values of the M-centre binding energy obtained in different theories, they appear generally to be high enough compared to the migration energy of the F-centre (for NaCl, in particular) to play any significant role in determining the nucleation densities of the colloids.

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