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### ON THE FORMATION OF DISLOCATION LOOPS IN GADOLINIUM

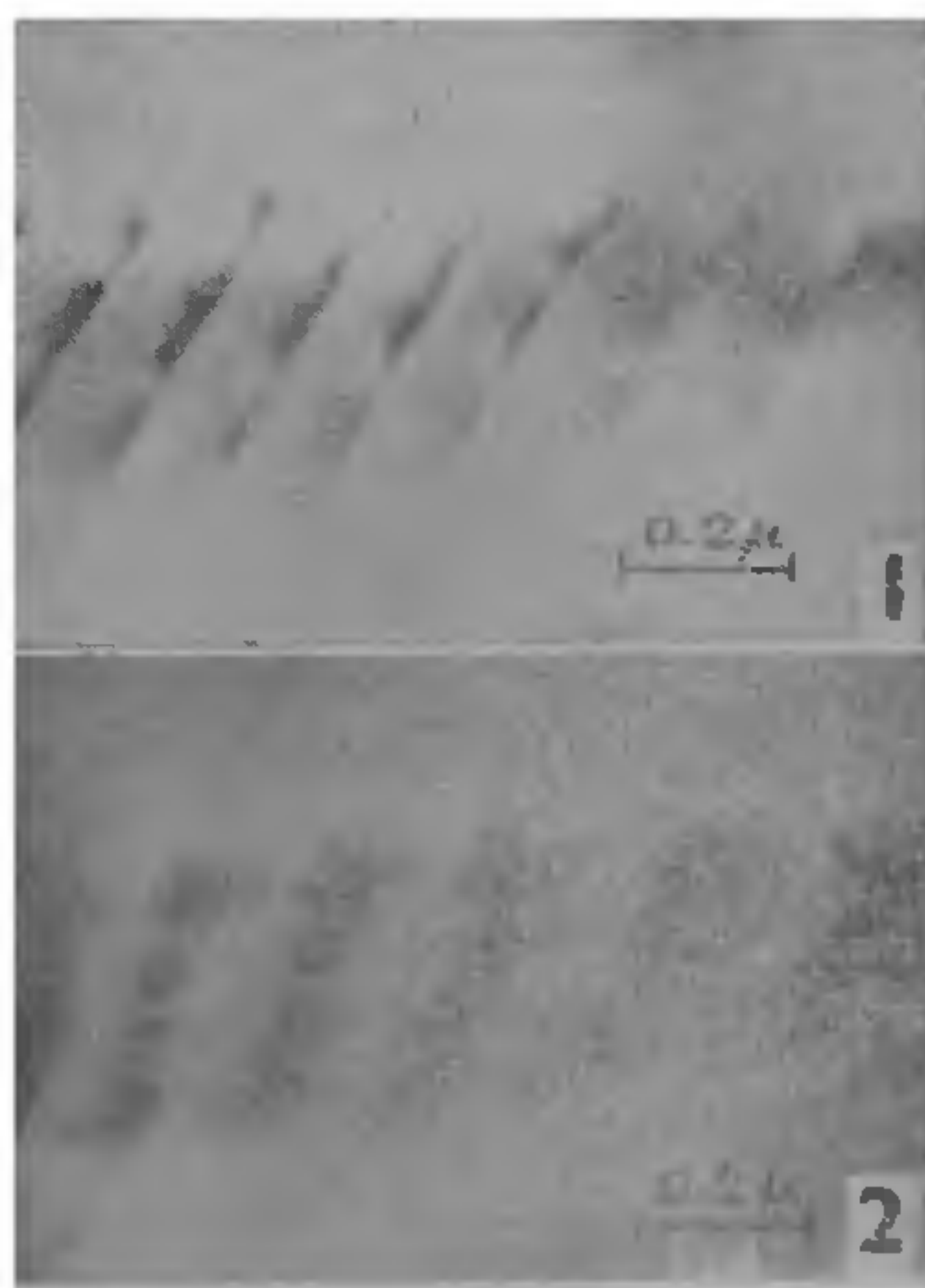
ELECTRON-MICROSCOPE observations of the formation of dislocation loops in basal oriented thin single crystal film of h.c.p. metal gadolinium have been made. Evidence and arguments are advanced to show that the loops are formed as a result of the interaction between vacancies and dislocations.

Basal oriented Gd films with thickness of about 200 Å were prepared by a method described previously.<sup>1</sup> Many basal grains contained a family of parallel dislocations which originated during deformation. These dislocations by their appearance seemed to be extending from the top surface to the bottom surface of the (0001) oriented thin film. Diffraction contrast experiments relevant to h.c.p. crystals<sup>2</sup> showed that the dislocations were of nearly screw-

character with Burgers Vector,  $\vec{b} = \vec{c} + \vec{a}$ , and were lying on (11 $\bar{2}$ 2) pyramidal planes. These dislocations, when subjected to several successive temperature gradient anneals employing electron-beam pulse annealing in the microscope, decomposed into rows of dislocation loops. A typical transmission electron micrograph exhibiting  $\vec{c} + \vec{a}$  dislocations and the corresponding rows of dislocation loops is shown in Figs. 1 and 2.

Screw dislocations are known to decompose to helical dislocations and then to loops by interaction<sup>3,4</sup> with vacancies through climb-process. It is thought that the generation of dislocation loops in the present case occurs as a result of the formation and interaction of helices. The inclined  $\vec{c} + \vec{a}$  dislocations are intersecting the (0001) foil at opposite ends and will thus be subjected to strong image-forces.<sup>5</sup> The image-forces will pin up the dislocation at opposite ends where these intersect the film surfaces, since the dislocations are lying on (11 $\bar{2}$ 2) planes and thus cannot become oriented perpendicular to (0001) foil plane. The film is subjected to temperature gradient anneal

employing pulse annealing technique, there will thus be a vacancy current,<sup>1</sup> the dislocations will interact with these vacancies and produce helical dislocations in the usual way. Evidence for the presence of helical dislocations was obtained during intermediate stages of pulse anneal and this shows that helix formation precedes the loop formation. It has been conjectured that the temperature gradient-induced vacancy current will be very suitable for climb in opposite senses of the nearby nearly screw dislocations.<sup>3</sup> No experimental observations have been however reported regarding this. In the present case, since the vacancy current is temperature gradient-induced, the vacancies will migrate away from one place and towards a nearby place in the crystal foil. This flow will induce climb in opposite senses in the two nearby  $\vec{c} + \vec{a}$  dislocations, leading to formation of two helices of opposite senses. These helices will then interact and produce row of dislocation loops.<sup>3,4</sup> It is evident that the equilibrium distances between rows of loops will not be the same as that between initial dislocations, this feature can be easily noticed in Figs. 1 and 2.



FIGS. 1-2

For temperature gradient-induced vacancy flow the non-equilibrium concentration  $c$  of vacancies in terms of the local equilibrium concentration  $c_0$  can be expressed by the expression<sup>1,6</sup>

$$\ln \frac{c}{c_0} = \frac{Q^* - H}{R T} \left( \frac{T}{T_0} - 1 \right)$$

where  $Q^*$  is the coupling coefficient,  $H$  is the vacancy formation energy,  $R$  is the gas constant,  $T$  and  $T_0$  are respectively the highest attained temperature and the temperature near the boundary of the circular region over which the temperature gradient is superimposed.

Substituting the values of the above parameters applicable to the present case,<sup>1,6</sup>  $Q^* - H = 0.1$  eV,  $T = 1100^\circ\text{C}$ ,  $T_0 = 300^\circ\text{C}$ , we find that  $c/c_0 \approx 39$ . This is much greater than the value of about  $10^{-3}$  which is thought to be necessary for helix and loop formation in bulk specimens.<sup>3,4</sup> In the present case, since the specimen is in the thin film form, as is well known, a large portion of the vacancy population will go to surfaces. However, even if a small part of the vacancy population goes to interact with the dislocations, the formation of helixes and the consequent loops will take place.

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### OXIDIMETRIC DETERMINATION OF PHLOROGLUCINOL

THOUGH cerium(IV) salts in sulphuric and perchloric acid media have been extensively employed in the oxidimetric determination of organic compounds, the oxidation of phloroglucinol has not yet been investigated. Since hydroquinone containing two hydroxy groups is oxidized instantaneously to quinone with ceric sulphate it was considered interesting to study the oxidation of phloroglucinol containing three hydroxy groups with the same reagent. Phloroglucinol occurs as a constituent of many resins and is a useful starting material in the synthesis of naturally occurring flavone and flavanol pigments.

**Reagents:** *Ceric sulphate*.—The requisite amount of ceric ammonium sulphate (B.D.H.) is made into a paste with concentrated sulphuric acid, warmed, dissolved in distilled water and made up to one litre. Final normality of sulphuric acid is one and that of

cerium(IV)  $\approx 0.100$ . This solution is standardised employing the usual methods. *Phloroglucinol* (Rideal de Haen) was dissolved in distilled water to give a 0.010 molar solution of the compound. *N-phenyl anthranilic acid* solution is prepared by dissolving 0.1 gm. of the acid along with 0.1 gm. of sodium carbonate in 100 ml. distilled water.

*Ferrous ammonium sulphate*.—B.D.H. AnalaR ferrous ammonium sulphate was employed in preparing 0.05 M Fe(II) solution in one molar sulphuric acid. The solution was standardised everyday with standard potassium dichromate solution. All other reagents used were of standard and tested purity.

To a measured aliquot of phloroglucinol solution taken in a 250 ml. Erlenmeyer flask a known excess of ceric sulphate solution is added. Sufficient amount of sulphuric acid is added to bring the acid normality to the desired level and the volume made up to 75 ml. The solution was heated on a water-bath, and after cooling the excess cerium(IV) remaining in the solution is titrated with Mohr's salt solution using *N-phenyl anthranilic acid* as indicator. The effect of the following variables was investigated:

(1) Effect of acidity; (2) Effect of time of heating; (3) Effect of excess cerium(IV). In all cases blanks were run and suitable blank corrections applied to the final titre value.

From a study of the different variables it was found that heating for 30 minutes on water-bath in presence of one molar sulphuric acid employing a minimum of 30-fold excess cerium(IV) gave the best possible results. The results given in Table I employing dif-

TABLE I

*Oxidation of phloroglucinol with ceric sulphate*

Phloroglucinol milli-moles taken	0.010	0.020	0.030	0.040
Cerium (IV) milli-moles consumed	0.241	0.480	0.723	0.960
No. of moles of cerium (IV) consumed per mole of phloroglucinol	24.1	24.0	24.1	24.0

ferent amounts of phloroglucinol under these conditions indicate that 24 equivalents of cerium(IV) are utilised in the oxidation of each mole of the compound. For the complete oxidation of phloroglucinol to carbon dioxide and water according to the equation

$\text{C}_6\text{H}_6\text{O}_3 + 9\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 24\text{H}^+ + 24\text{e}^-$ ,  
each mole of phloroglucinol requires 24 moles of