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SELF CLIMB OF DISLOCATION LOOPS IN MAGNESIUM OXIDE

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ABSTRACT

Quantitative measurements were made of self climb of dislocation loops, $b = \frac{1}{2}\langle 101 \rangle$, in magnesium oxide single crystals. The rate of motion of pairs of coplanar loops was studied by repeated observation of the same areas of a thin foil during a series of annealing treatments. A value of 60,300 $\pm$ 3,500 cal/mole for the activation energy for pipe diffusion and $(7.5 \pm 4.3) \times 10^{-18}$ cm^4/sec for the pre-exponential term $D_o a^p$ were obtained. The experiments show that up to about 1250°C self climb is a primary mechanism by which average loop size increases during annealing of plastically deformed magnesium oxide.

INTRODUCTION

Self climb of dislocation loops differs from the usual non-conservative growth or shrinkage in the sense that the total area of the loop projected perpendicular to its Burgers Vector remains unchanged and climb occurs by migration of atoms along the easiest path, i.e., the core of the dislocation. This type of climb was first proposed by Johnson (1960) in order to explain observations of vacancy loop coarsening on annealing bulk samples of quenched aluminum. Johnson considered the self climb of two square loops but unfortunately neglected the driving force term in his analysis. Later Kroupa et al. (1961) took this into account and analysed the movement of a square loop in the strain field of a circular loop. Price (1960), during electron microscopy of deformed zinc, observed that the prismatic dislocation loops moved due to interaction with a nearby edge dislocation, while remaining on the same basal plane layer. During this motion the area of the loop projected perpendicular to its Burgers Vector was unchanged. Theoretical treatment of these observations was given by Kroupa and Price (1961).

In self climb, the driving force for pipe diffusion arises from two sources. The first is due to interaction with neighboring loops (Westmacott et al., 1962; Barnes, 1963; Turnbull, 1970) or surfaces of the foil (Barnes and Mazey, 1962) or nearby dislocations (Price, 1960). This gives rise to differences in concentration of vacancies around the loop (i.e. energy of formation of a vacancy is affected). Coplanar pairs of dislocation loops have strong interaction only if the separation is small (about one diameter of the bigger loop). This interaction results in a net flow of vacancies around the loop. The second is due to direct loop-vacancy interaction. Vacancies once created at a given loop

interact with the surrounding elastic stress field and accordingly the energy for migration of a vacancy will be affected.

Reliable quantitative measurements of dislocation climb rates are largely still lacking because of the following experimental difficulties:

1) It is often hard to avoid concurrent prismatic slip; this is particularly true in metals;

2) It is necessary to carry out annealing treatments outside the microscope because of the inherent inaccuracy of temperature measurement in hot stage experiments.

These difficulties have been avoided in our experiments. Magnesium oxide was found to be an ideal material for observing self climb for the following reasons:

1) Prismatic slip in magnesium oxide is not easy even at temperatures high enough for self climb to occur readily;

2) Many of the prismatic dislocation loops, which are formed from the same dislocation dipole on annealing are coplanar;

3) Annealing of thin foils of magnesium oxide outside the electron microscope is relatively easy;

4) The high fracture strength and high yield strength of MgO made it less difficult than for metals to handle thin foils without making dislocations move during a series of electron microscope observations and annealing treatments.

The present report contains a quantitative analysis of self climb of coplanar pairs of loops. Only those loops were selected for measurements which were near the center of the foil to minimize the effects of

foil surfaces. The rate of self climb was measured at more than one temperature for the same set of loops to avoid the uncertainty due to poorly known pre-exponential factors. Self climb due to surfaces of the foil or nearby dislocations has also been observed, but it was not possible to make a quantitative analysis. A model, similar to that of Turnbull, has been used to calculate the activation energy for pipe diffusion and comparisons have been made with Turnbull's recent analysis of self climb in UO_2.

EXPERIMENTAL

Large grained polycrystalline MgO was purchased from Muscel Shoals Electro-chemical Corp., Tuscumbia, Alabama. Semi-quantitative spectrographic analysis revealed the following impurities: Al - 0.06%, Fe - 0.03%, Ca - 0.03%, Mn - 0.002%, Cr - 0.002%, Cu - <0.001%, Si - <0.001%.

Single crystal specimens in the form of thin sheets (0.50 - 0.25 mm thick) were obtained by cleaving along 100 planes. The surface damage introduced during cleaving was removed by chemical polishing in hot orthophosphoric acid (150 - 160°C) to a thickness of about 0.2 mm. These sheets were then bent backwards and forwards ($\pm$5 cm radius) about 200 times until they were full of slip bands. Following the deformation, specimens were thinned further, after applying masking lacquer around the edges. Final thinning to obtain electron microscope foils was done by a jet polishing technique (Washburn et al., 1960). After cold working the thinning was done primarily from one side because plastic deformation is maximum near the surfaces.

In thin sheets bent along the [010] axis, dislocation dipoles are introduced on $(101)[\bar{1}01]$, $(\bar{1}01)[101]$ and on $(110)[\bar{1}10]$, $(\bar{1}10)[110]$ slip systems. Dipoles on $(101)[\bar{1}01]$ and $(\bar{1}01)[101]$ are of primary interest as dipoles on $(110)[\bar{1}10]$ are seen edge-on along [001] which is perpendicular to the surfaces of the foil.

All foils were examined in a Siemens 100 kV electron microscope. The same area was observed repeatedly after annealing at constant temperature outside the electron microscope in an atmosphere-controlled furnace and subsequently cooling in air. Care was taken not to turn the foil over during a series of observations. Changes in the positions of loops were measured directly from the electron micrograph plates using a Nikon enlarger at 20x. Magnification calibration of the microscope was carried out at every step of the picture making.

THEORY

In the following formulation it is assumed that motion is due only to pipe diffusion and that the only driving force is the interaction between the two loops. The direct vacancy-loop interactions are not included due to uncertainty in the relaxation around vacancies inside the core of a dialocation in ionic crystals. Also, in agreement with experimental observations, it is assumed that the loops remain circular while getting closer.

The flux of vacancies passing from the far half into the near half of a climbing loop is (see Fig. 6 and Eq. (4) of Turnbull (1970)):

$$J_1 = D^P a^P \frac{N_o^P}{r_1} \left\{ \left| \frac{dC^P}{d\theta} \right|_{\theta=90^\circ} + \left| \frac{dC^P}{d\theta} \right|_{\theta=-90^\circ} \right\} \tag{1}$$

$$= \frac{2D^P a^P N_o^P C_o^P b^2}{\pi r_1^2 \, kT} \frac{dE_{int}}{dX} , \tag{2}$$

where D^P = self diffusion coefficient at the core of the dislocation, a^P = area of cross-section of the dislocation pipe, C_o^P is the concentration of vacancies at $\theta = 90^\circ$, N_o^P = atomic density at the core of the dislocation $\frac{dE_{int}}{dX}$ is the change in interaction energy with the center distance of dislocation loops and r_1 is the radius of the loop.

The rate of displacement of the loop center is:

$$\left(\frac{dX_1}{dt}\right)_{\text{loop 1}} = J_1 \frac{b^2}{2r_1} ,$$

$$= \frac{D^P a^P b \, N_o^P C_o^P}{\pi kT r_1^3} \frac{dE_{int}}{dX} . \tag{3}$$

If both loops of an attracting pair are migrating, the total rate of change of X, $\frac{dX}{dt}$ is the sum $\left(\frac{dX_1}{dt}\right)_{\text{loop 1}} + \left(\frac{dX_2}{dt}\right)_{\text{loop 2}}$.

Therefore

$$\frac{dX}{dt} = \frac{D_o^P a^P b^4 N_o^P}{\pi kT} \frac{dE_{int}}{dX} \left[\frac{1}{r_1^3} + \frac{1}{r_2^3} \right] \exp - \frac{\mu_{mv}^P + \mu_{fv}^P}{kT} , \tag{4}$$

because $D^P = D_o^P \exp - (\mu^P{}_{mv/kT})$, $C_o^P = \exp - (\mu^P{}_{fv/kT})$; $\mu^P mv$ and $\mu^P{}_{fv}$ are the activation energies for migration and formation of a vacancy respectively at the care of the dislocation.

Defining $\bar{X} = X/_{r_1}$ where r_1 is the radius of the larger of the two loops and rearranging Eq. (4), we have

$$d\bar{X} \cdot \frac{d\bar{X}}{dE_{int}} = Kdt \ , \tag{5}$$

where

$$K = \frac{D_o^P a^P N_o^P b^4}{\pi kTr_1^2} \left[\frac{1}{r_1^3} + \frac{1}{r_2^3} \right] \exp - \frac{\mu_{mv}^P + \mu_{fv}^P}{kT} \ .$$

On integration of Eq. (5), we have:

$$\int_{\bar{X}_1}^{\bar{X}_2} d\bar{X} \cdot \frac{d\bar{X}}{dE_{int}} = \int_{t_1}^{t_2} Kdt. \tag{6}$$

The integral on left side in Eq. (6) was evaluated numerically for the sets of loops suitable for self climb measurements. This required first the double integration for E_{int} at small intervals of $\bar{X}$ and then evaluation of $\frac{d\bar{X}}{dE_{int}}$ vs $\bar{X}$.

Graphical integrations were performed from $\bar{X}_1$ to $\bar{X}_2$ corresponding to intervals of time Δt to get A_1, A_2 etc. Therefore, for an interval of time Δt_1 at temperature T_1

$$A_1 = K_1 \Delta t_1 \ . \tag{7}$$

Similarly for another time interval Δt_2 at temperature T_2

$$A_2 = K_2 \Delta t_2 \quad . \tag{8}$$

From Eqs. (7) and (8) we have:

$$\frac{A_1}{A_2} \frac{\Delta t_2}{\Delta t_1} = \frac{T_2}{T_1} \exp \frac{E_{act}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad , \tag{9}$$

where $E_{act} = \mu^P_{mv} + \mu^P_{fv}$.

Therefore

$$E_{act} = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{A_1 \Delta t_2 T_1}{A_2 \Delta t_1 T_2} \quad . \tag{10}$$

RESULTS AND DISCUSSION

The set of pictures in Fig. 1 is an example where the same area was photographed after annealing treatments at three different temperatures (1100°C, 1200°C and 1237°C). The coplanar groups of loops at 1, 2, and 3 move closer together by self climb and form single loops of approximately conserved total area. Figure 2 is a set of pictures at two temperatures (1086°C and 1250°C). The coplanar groups of loops at 1 and 2 moved closer together and formed single loops with unchanged total area. Other examples of self climb are at 1, 2, 3, 4, and 5 in Fig. 3 at 1195°C. Changes in the sizes of dislocation loops

due to bulk diffusion were negligible for loops near the center of the foil. A few loops which were near the surfaces of the foil slipped out by prismatic slip along their glide cylinders (see loops 4 and 5 in Fig. 1)

The values of activation energy for pipe diffusion, obtained by measuring the rate of climb of various sets of loops of different sizes are given in Tables I through III. The average value of activation energy is 60,300 ± 3,500 cal/mole. An estimate of the uncertainty due to limits of precision in the measurements of separation, radius and temperature are given for each value. To maximize the precision of measured separations and radii of loops, pictures were taken with both $\bar{2}00$ and 200 diffraction conditions. The results reported in Tables I through III represent the average of measurements for the two diffraction conditions. Stereomicroscopy was also done at each step to locate the loops in the foil. Surface dirt particles were used as reference points. Only those loops which were located near the center of the foil and were relatively isolated from other loops were selected for the measurements. Surface effects were not important in the calculations because these are of short range and are negligible for loops situated at a depth more than about two diameters of the loop (Groves and Bacon, 1970; Narayan and Washburn, 1972).

In the theory of self climb one of the assumptions was that loops remain circular due to line tension while moving closer together. The dislocation loops at 3 in Fig. 1D and at 2 in Fig. 2D show that loops do remain circular even up to the time of contact. This should be

expected because the loop self energy remains large compared to the interaction energy right up to the point where the loops come into contact. Turnbull (1970) has mentioned that his formulation for the rate of self climb explains why both loops remain circular while coming closer together. However, his analysis considered only the shape of near halfs of the loops. When the forces on the entire loop are accounted for, the net force acting on far halfs is repulsion which, in the absence of loop self energy, would make the loops elongate rather than remain circular.

Depending upon the vacancy saturation around the loops, bulk diffusion can cause slight increases or decreases in the sizes of the loops during annealing. If loop size changes, the pipe diffusion path length changes during the experiment. These changes have been neglected in the formulation for rate of self climb. However, in the temperature range of our experiments these changes were very small for the dislocation loops which were near the center of the foil and relatively isolated from other loops. The dislocation loop (near the dirt particle on the right side of photographs in Fig. 1), which is close to center of the foil, did not shrink appreciably inspite of being one of the smallest loops therefore having had a large driving force for shrinkage. Therefore, the variations in the calculated values of activation energy due to this simplification were within experimental errors.

By making measurements of climb rate for a given loop pair at more than one temperature, errors due to inadequate knowledge of the appropriate pre-exponential terms, particularly D_o^P and a^P, have been avoided.

Measurements at one temperature (Turnbull, 1970) require a theoretical estimate of D_o^P and a^P to permit calculation of the activation energy. The activation energy calculated from rate measurements at two temperatures was used to calculate the pre-exponential term $D_o^P a^P$ $(7.5 \pm 4.3) \times 10^{-18}$ cm^4/sec. This value of $D_o^P a^P$ was then used to calculate the activation energy for measurements done at constant temperature. The small variations in measured activation energy over the temperature range 1100 to 1250°C and for various sizes of loops justifies confidence in the model and analysis. If we take a^P as 10^{-15} cm^2, D_o^P is about 5×10^{-3} cm^2/sec. This is in good agreement with previous results on pipe diffusion along screw dislocations* (Narayan, 1970).

This rather low value of D_o^P may be due to precipitation of impurities along the dislocations, which act as traps for vacancies and/or a reduced value of the frequency of atomic vibration inside the core of a dislocation.

In Turnbull's paper, arguments are also presented for not taking into account direct loop-point defect interaction. He argues that relaxation around vacancies in ionic crystals is generally small. However, Hickman and Walker (1965) found that in MgO, the relaxation around a vacancy is tension and is about 0.2 to 0.4 times the molecular volume, but it is not clear how the relaxation around a vacancy in the core of a dislocation might be estimated from this value for an isolated vacancy.

* A configuration was used in which a dislocation loop, $b = \frac{1}{2}[101]$, was connected to both surfaces of a thin foil by a screw dislocation of the same b-vector.

By measuring the shrinkage rate of dislocation loops due to bulk diffusion in the temperature range 1080-1427°C (Narayan, 1971), the activation energy for intrinsic bulk diffusion was determined to be 110,000 ± 4,200 cal/mole. This is in agreement with that for intrinsic diffusion of oxygen ions obtained from electrical conductivity measurements (Davies, 1963). The value of activation energy for self climb is about 0.55 times that for oxygen ion bulk diffusion. This ratio is in agreement with that in fcc metals (James and Leak, 1965). This leads to the conclusion that pipe diffusion is controlled by oxygen ion mobility which is expected in view of ionic radii of O^{--}(1.32Å) and Mg^{++} (0.66Å).

CONCLUSIONS

1. The activation energy for pipe diffusion and pre-exponential factor $D_o^p a^p$ from measurements of rate of self climb of coplanar pairs of loops, $b = \frac{1}{2}\langle 101 \rangle$, are 60,300 ± 3,500 cal/mole and $(7.5 \pm 4.3) \times 10^{-18}$ cm^4/sec respectively.
2. Self climb is the primary mechanism of dislocation loop coarsening during annealing of plastically deformed magnesium oxide up to 1250°C.
3. The rate of self climb is controlled by oxygen ion mobility.

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Table I.

Group of Loops	$\bar{X}$	Time in Sec	Temp. °K	Activation Energy
1 in Fig. 1 A	2.78			
		5402	1373	
B	2.68			60,300 ± 3600 cal/mole
		3257	1473	
C	2.44			
		2925	1510	
D	1.588			
E	Collapse			
2 in Fig. 1 A	3.42			
		5402	1373	
B	3.35			60,700 ± 3300 cal/mole
		3257	1473	
C	3.14			
		2925	1510	
D	Collapse			

Table II.

Group of Loops		$\bar{X}$	Time in Sec	Temp. °K	Activation Energy
1 in Fig. 2	A	3.19			
			2438	1359	
	B	3.17			
			2392	1523	59,300 ± 3200 cal/mole
	C	3.04			
			1570	1523	
	D	2.98			
			1202	1523	
	E	2.845			
	F	Collapse			
2 in Fig. 2	A	3.99			
			2438	1339	59,700 ± 3700 cal/mole
	B	3.96			
			2392	1523	
	C	3.57			
			1570	1523	
	D	2.80			
			1202	1523	
	E	Collapse			

Table III.

Group of Loop	$\bar{X}$	Time in Sec	Temp. °K	Activation Energy
1 in Fig. 3 A	4.91			
		4565	1468	
B	4.81			60,100 ± 3000 cal/mole
		2305	1468	
C	4.74			
		1810	1512	
D	Collapse			
4 in Fig. 3 A	4.49			
		4565	1468	
B	4.30			
		2305	1468	59,500 ± 3600 cal/mole
C	4.16			
D	Collapse			
5 in Fig. 3 A	4.37			
		4565	1468	
B	4.15			60,600 ± 4000 cal/mole
		2305	1468	
C	3.97			
D	Collapse			

FIGURE CAPTIONS

Fig. 1. Self climb at 1, 2 and 3; prismatic slip at 4 and 5 due to surfaces of the foil at three different temperatures. In all figures intermediate pictures have not been included.

Annealing treatments:

A → B, 4502 secs. at 1100°C; B → C, 3257 secs. at 1200°C;

C → D, 2925 secs. at 1237°C; D → E, 3880 secs. at 1200°C;

E → F, 2720 secs. at 1200°C.

Fig. 2. Self climb at 1 and 2 at two different temperatures. Some of the smaller loops have slipped out of the foil. Annealing treatments:

A → B, 2438 secs. at 1186°C; B → C, 2392 secs. at 1250°C;

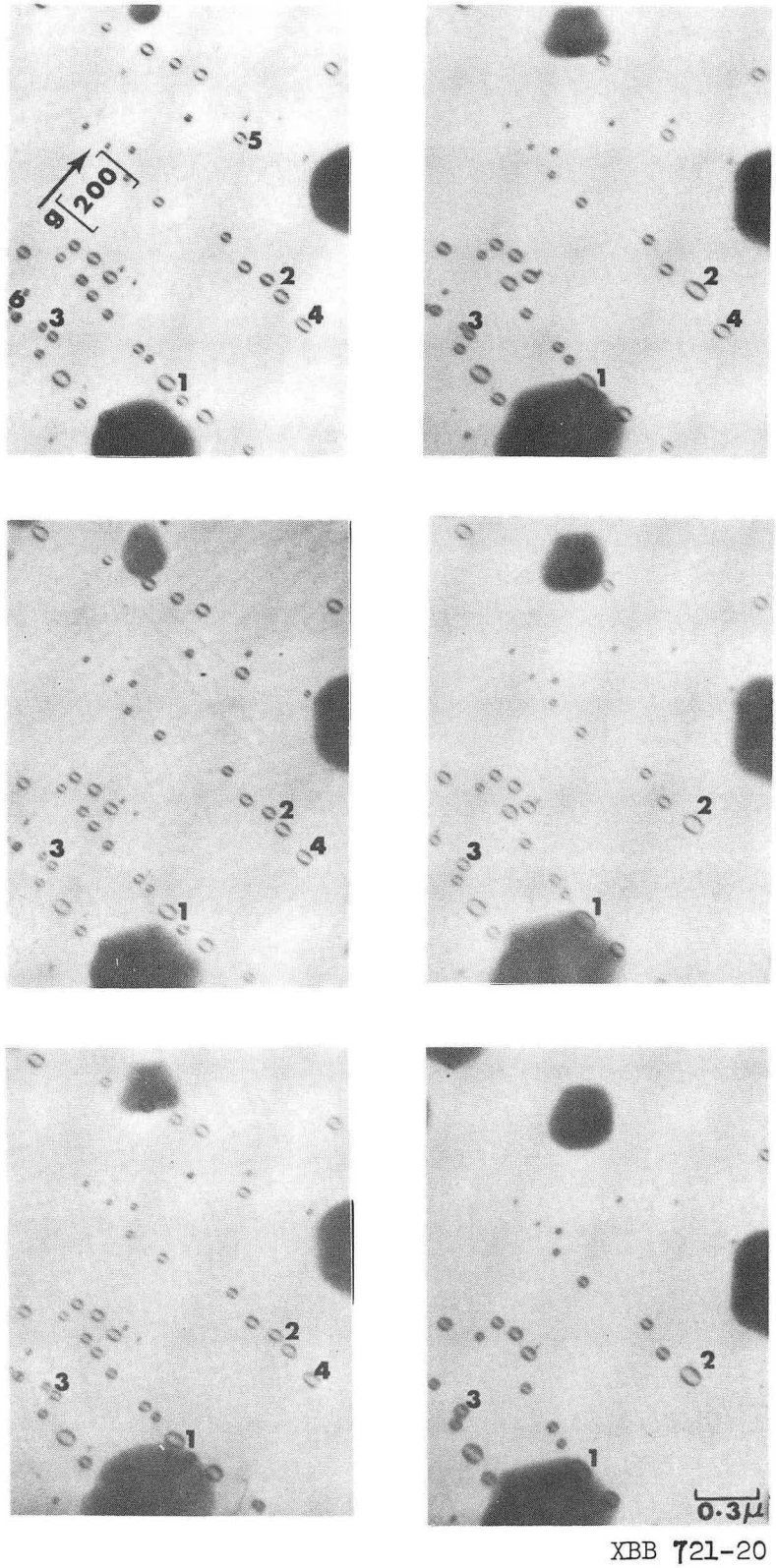
C → D, 1570 secs. at 1250°C; D → E, 1202 secs. at 1250°C;

E → F, 2369 secs. at 1250°C.

Fig. 3. Self climb at 1 through 5 at 1195 and 1239°C. Annealing treatments:

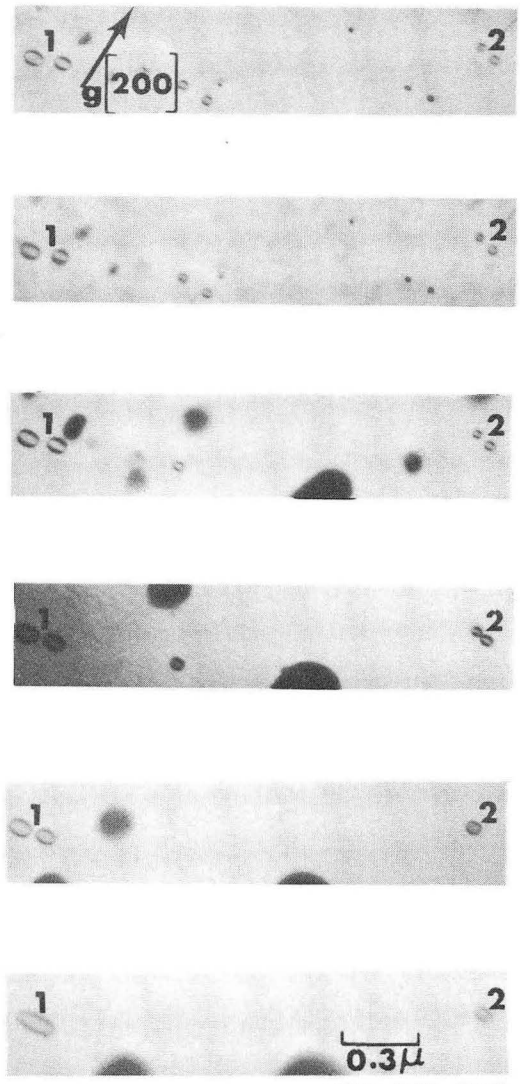
A → B, 4565 secs. at 1195°C; B → C, 2305 secs. at 1195°C;

C → D, 1810 secs. at 1239°C.



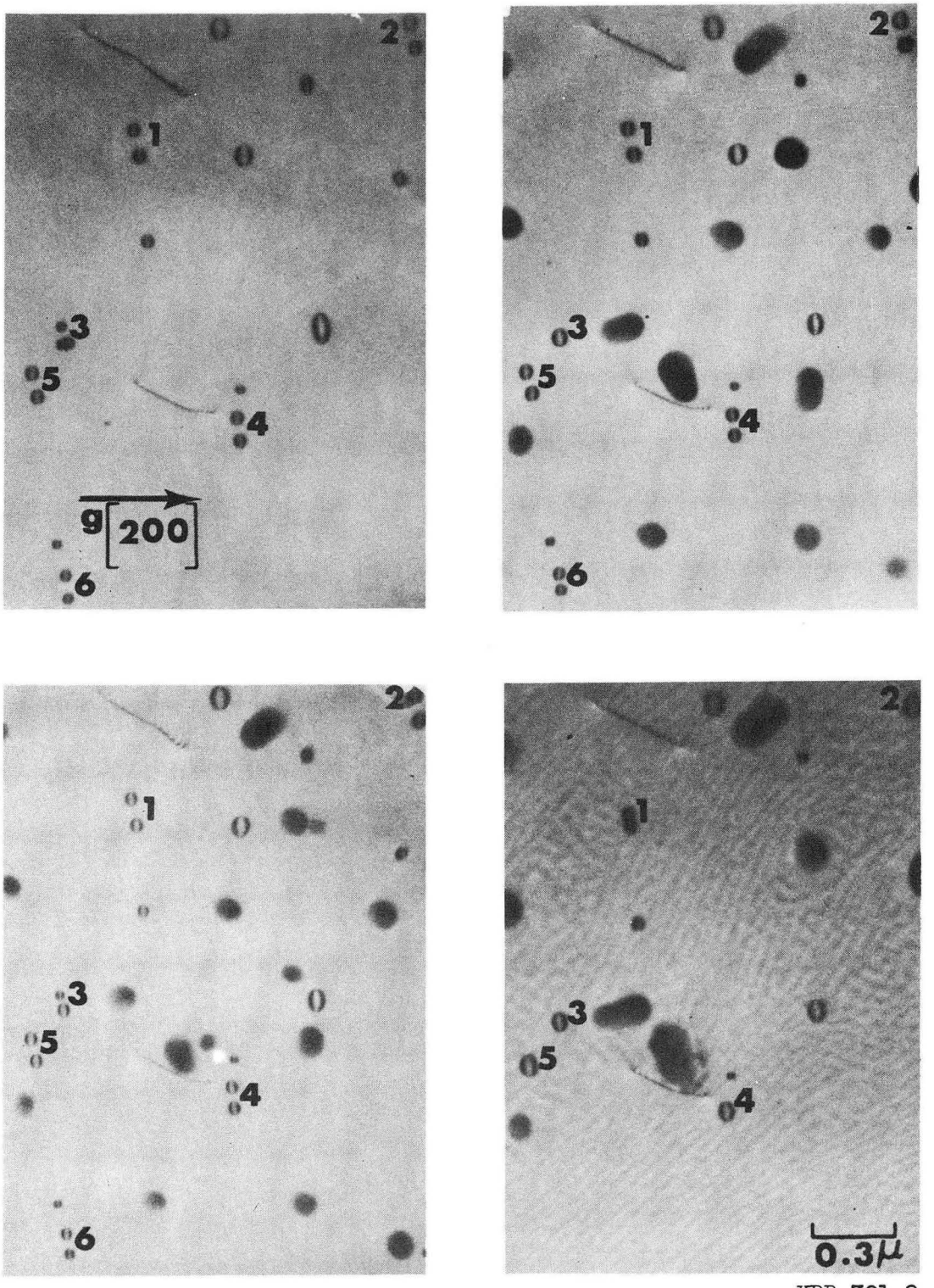
XBB 721-20

Fig. 1



XBB 721-117

Fig. 2.



XBB 721-3

Fig. 3

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