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Dislocation Dynamics at Low Temperatures

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A model for low-temperature dislocation motion is developed using the concept of nucleation and growth of kinks in dislocations lying in Peierls potential troughs. The model is compared with existing experimental data.

INTRODUCTION

LYTTON *et al.*[1] have found an activation energy for the low-temperature creep of single crystals of pure aluminum which they suggest may be associated with the Peierls[2] energy. In the following treatment a creep mechanism requiring the presence of the Peierls energy barrier is proposed which yields results which are in agreement with experimental evidence.

DISLOCATION KINETICS

1. Definitions and Presentation of the Problem

An otherwise straight dislocation line lying along a close packed direction in the Peierls potential valley will contain an equilibrium number of steps where the dislocation line is displaced by a simple lattice vector.[3] We shall follow the notation of Read[4] in terming such a step a kink if it lies in the glide plane; a jog if it does not lie in the glide plane. A dislocation acted on by a stress less than the Peierls stress will advance by a two-stage process involving the nucleation of kinks and the lateral propagation of kinks along the dislocation line.

New kinks must be formed by the nucleation of double kinks. These double kinks, shown in Fig. 1, then can separate under the action of both the applied stress and fluctuating thermal stresses. For a separation d_c the external shear stress will balance the kink-kink attraction. As the kink-kink attraction is of short range, we can consider, in all cases to be discussed later, that the critical separation, d_c, beyond which the interaction between kinks is negligible, will be given by

$$d_c \cong 2w, \tag{1}$$

where w is the kink width (Fig. 1). The activation energy for thermal production of a kink pair of separation larger than d_c will thus be about

$$W = 2W_k - \sigma b a d_c, \tag{2}$$

where W_k = energy of formation of one kink; σ = component of external shear stress in glide plane along the Burgers vector, σ_a, minus the Taylor stress due to elastic interaction of the dislocation with other dislocations in the lattice, σ_e; b = the magnitude of the Burgers vector $\frac{1}{2}\langle 110\rangle$; and $a = \frac{1}{2}\sqrt{3}b$ = distance between neighboring close-packed rows in the glide plane.[5]

A kink on a dislocation line will diffuse under thermal stresses. Thus a kink pair will not necessarily separate once it has reached a separation greater than d_c because the probability for back diffusion against the shear stress and subsequent kink-kink annihilation will be great. In fact it will later be argued that only a small fraction of the nucleated kink pairs will reach a separation beyond which the recombination probability is negligible. A kink pair nucleated in the direction opposed by the shear stress will be forced to annihilate.

Hence, in order to form a theory of dislocation creep over the Peierls barrier, the rates of double-kink nucleation and of kink diffusion must be evaluated. Double-kink nucleation has previously been considered in a theory for the Bordoni[6] peak by Seeger and Donth[7,8] who employ the theory of stochastic processes in determining the interaction of a dislocation line with sound waves. Seeger[9] has also suggested a formula for the

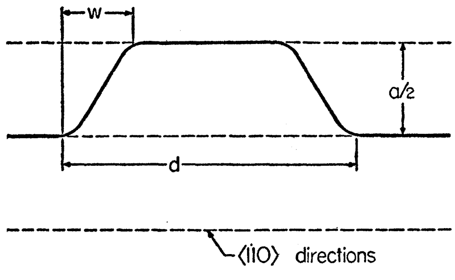

FIG. 1. A double kink in a dislocation line segment lying in a {111} plane.

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[1] Lytton, Shepard, and Dorn, Trans. Am. Inst. Mining, Met., Petrol. Engrs. **212**, 220 (1958).

[2] R. Peierls, Proc. Phys. Soc. (London) **52**, 34 (1940).

[3] W. Shockley, Trans. Am. Inst. Mining, Met., Petrol. Engrs. **194**, 829 (1952).

[4] W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill Book Company, Inc., New York, 1953), p. 46, 80.

[5] Evidently we consider only a face-centered cubic lattice throughout this treatment since we shall compare the model with experimental results obtained for aluminum. Nonetheless, the model is general and could be applied to other crystal structures by a suitable change of parameters.

[6] P. G. Bordoni, J. Acoust. Soc. Am. **26**, 495 (1954).

[7] H. Donth, Z. Physik. **149**, 111 (1957).

[8] Seeger, Donth, and Pfaff, Discussions Faraday Soc. **23**, 19 (1957).

[9] G. Leibfried and Discussions to G. Leibfried, *Dislocations and Mechanical Properties of Crystals*, edited by J. C. Fisher (John Wiley & Sons, Inc., New York, 1956), p. 495.

nucleation rate of double kinks. However, it is not easy to see how these methods could be correlated with the diffusion of kinks in an unequivocal way. Yet it is noteworthy that all models employed for activation of the dislocation line are such that one may rightly assume that the dislocation line can be treated as a mechanical system whose average state is determined by the partition function

$$Z=\int e^{-H/kT}dpdq, \tag{3}$$

neglecting quantum effects. This assumption will be employed in a direct evaluation of the thermal concentration of kinks. The nucleation rate will be determined by balancing it against the annihilation rate due to the collisions between diffusing kinks.

2. Thermal Density of Kinks

In the Appendix the partition integrals Z' for a dislocation line containing a single kink, and Z for a nonkinked dislocation line are evaluated. From these expressions [Eqs. (36), (60)] the equilibrium density, n, of double kinks per unit length is given by

$$n=\left(\frac{Z'}{Z}\right)^2=1.1\frac{\sigma_p ab}{kT}\left(\frac{\pi b\sigma_p}{2aS}\right)^{\frac{1}{2}}\exp\left(\frac{-2W_k}{kT}\right), \tag{4}$$

where σ_p= Peierls stress, k= Boltzmann's constant, T= absolute temperature and S= line tension of the dislocation.

3. The Diffusion of Kinks

A dislocation kink will be of small extension, say $w=10a$. The mean square amplitude of thermal stress over this distance, $\sigma_T=(2\mu kT/w^3)^{\frac{1}{2}}$ (μ= shear modulus), will, except at very low temperatures, exceed the applied stress, and it will certainly far exceed any crystalline resistance to motion of the kink. The kink can therefore effectively be regarded as a *free* effective mass oscillating under thermal stresses, in agreement with the continuum model of the kink presented in the Appendix. Also the motion of a kink under an external shear stress of ordinary magnitude can be looked upon as a drift superimposed on diffusion, as the external shear stress only perturbs the thermal stresses.

But the forced oscillations of the kink under thermal waves do not describe the diffusion process when the waves are considered to be coherent. The diffusion is rather to be considered as due to thermal fluctuations in the radiation force (analogous to acoustic radiation pressure) on the kink. This force is determined by the scattering of sound waves by the kink. When the kink moves, it runs into more waves on one side than on the other establishing a net radiation force which determines the mobility of the kink. Diffusion and drift are thus controlled by the same factors, indeed by the Einstein[10] relation,

$$v=D\sigma ba/kT, \tag{5}$$

where v is the velocity of the kink along the dislocation line and D is the diffusion coefficient.

Dislocation mobility has been discussed by Leibfried,[11] whose work was later extended by Nabarro.[12] Nabarro concludes that the Leibfired formula is correct in form and order of magnitude, although it probably yields a somewhat low mobility. The cases considered were radiation from oscillating dislocations, each segment radiating as if it were part of an infinite rigid dislocation; and scattering by the deformed lattice around the dislocation. Only the latter process was found to be important. Because of the small extension of a kink, the radiation emanating from kink oscillations of not too high frequency will correspond to the radiation from a point rather than from a line segment. This will certainly contribute to the resistance to motion. Radiation of waves along the dislocation may also be significant. We hope to discuss these problems at a later opportunity; at present we shall assume that the Leibfried-Nabarro process is dominant. We should also mention that the Leibfried formula has had some success in the interpretation of megacycle internal friction.[13] It is possible that in crystals with no external shear stress, the dislocations largely lie along non-close-packed rows and contain so many kinks that they can be considered as being essentially free in megacycle experiments. Then the Peierls barrier would only be evinced during plastic flow and large bow-outs of dislocations.[14]

The Leibfried formula reads

$$V=10\sigma c/\bar{E}, \tag{6}$$

where V= normal velocity of the dislocation, c= velocity of sound, and $\bar{E}$ is the energy of thermal vibrations per unit volume. For a kink, then,

$$v\cong 10c\sigma/\bar{E}. \tag{7}$$

By the Einstein relation, Eq. (5),

$$D\cong 10ckT/\bar{E}ba. \tag{8}$$

Inserting the classical value $\bar{E}\sim 3kT/b^3$, one obtains finally the diffusion coefficient

$$D\cong \nu_D b^2, \tag{9}$$

where $\nu_D=c/b\cong$ Debye frequency.

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[10] A. Einstein, *Investigations on the Theory of Brownian Movement* (Methuen and Company, Ltd., London, 1926), p. 9.

[11] G. Leibfried, Z. Physik. **127**, 344 (1950).

[12] F. R. N. Nabarro, Proc. Roy. Soc. (London) **A209**, 278 (1951).

[13] A. Granato and K. Lücke, J. Appl. Phys. **27**, 789 (1956).

[14] A. H. Cottrell, Discussion to K. Lücke and A. Granato, *Dislocations and Mechanical Properties of Crystals*, edited by J. C. Fisher (John Wiley & Sons, Inc., New York, 1956), p. 457.

4. Dislocation Velocities and Creep

On a straight dislocation line, double kinks will be nucleated by a thermal activation process. The probable separation, d_c, of a critical-size double kink nucleus will be about $2w$ for the following reasons. The longer the separation d, the larger is the activation energy required to overcome the Peierls barrier, and the lower is the frequency factor for direct nucleation of double kinks, both factors reducing the probability of nucleation of a double kink of wide separation. When the separation between the double kinks is small they will interact strongly leading to collapse of such a double kink. Thus a nucleation of kinks of separation d_c will be balanced by kink annihilation by kink-kink collision, establishing the equilibrium concentration of kinks.

Let $n(l)dl$ be defined as the number of double kinks per cm of dislocation with length between l and $l+dl$. At the moment consideration is restricted to non-interacting double kinks. Kink-kink collisions are summarily taken into account by the boundary condition (12) to follow. Under equilibrium conditions, $n(l)$ is constant for $l>2w$, because in the region $l>2w$, there are neither sources nor kinks and the diffusion coefficient is constant (see Fig. 2).

When an applied stress is present, the diffusion current is, by Eq. (5),

$$J=-2D\frac{dn(l)}{dl}+2D\left(\frac{\sigma ba}{kT}\right)n(l). \qquad (10)$$

Under steady-state conditions, this current must be constant in the region $l>2w$. The solution of (10) is then

$$n(l)=\frac{kTJ}{2\sigma baD}\left\{1-\exp\left[\frac{\sigma ba}{kT}(l-2w)\right]\right\}+n(2w)\exp\left[\frac{\sigma ba}{kT}(l-2w)\right]. \qquad (11)$$

Now suppose that an unfolding double kink is annihilated when it reaches a length X. In an infinite dislocation line X would be related to double kink-double kink collisions. The corresponding boundary condition in the diffusion problem is

$$n(X)=0. \qquad (12)$$

Equations (11) and (12) yield

$$J=2n(2w)D\frac{\sigma ba}{kT}\exp\left[\frac{\sigma ba}{kT}(X-2w)\right]\Big/\left\{\exp\left[\frac{\sigma ba}{kT}(X-2w)\right]-1\right\}, \qquad (13)$$

which reduces to

$$J=2n(2w)D\sigma ba/kT, \qquad (14)$$

independent of X, when

$$X-2w>l_c=kT/\sigma ba. \qquad (15)$$

The physical meaning of l_c can be explained in the following way: Double kinks which have reached a length greater than l_c+2w will only have a small probability of recombining under thermal fluctuations and will expand under applied stress until they annihilate upon reaching a length X; while double kinks much shorter than this critical length will have a high probability of recombining.

Now for all cases we will consider, the stress-dependent term in Eq. (2) is less than the uncertainty in the activation energy W and can be neglected. Also in all cases $l_c>h$, h being the diffusion path leading to double-kink collapse (see Fig. 2). Now as long as $l_c>2w$, most of the double kinks nucleated must collapse, so, since the stress dependence of the nucleation is small as noted above, the double-kink density $n(2w)$ will be about the same as the equilibrium value n. Hence, employing Eq. (4), Eq. (14) becomes

$$J=2.2D\frac{\sigma}{\sigma_p}\left(\frac{ab\sigma_p}{kT}\right)^2\left(\frac{\pi b\sigma_p}{2aS}\right)^{\frac{1}{2}}\exp\left(\frac{-2W_k}{kT}\right). \qquad (16)$$

The velocity of advance of an infinite dislocation in its glide plane in a direction perpendicular to the dislocation line will be

$$V_\infty=aXJ, \qquad (17)$$

provided $X>l_c$, where X is the distance along the dislocation swept out per kink pair,

$$X=2\tau v, \qquad (18)$$

and τ is the average time required for a nucleation event in the newly exposed ledge within a growing kink pair,

$$\tau=2/XJ, \qquad (19)$$

so that by Eqs. (5) and (14)

$$X=(v/J)^{\frac{1}{2}}=(2/n)^{\frac{1}{2}}. \qquad (20)$$

Inserting Eq. (20) into Eq. (17), we obtain

$$V_\infty=2a(Jv)^{\frac{1}{2}}. \qquad (21)$$

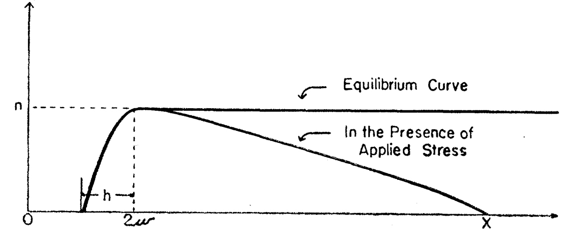

FIG. 2. Distribution of double kinks as a function of kink length l.

In general, for a dislocation segment of finite length L, Eq. (21) will be modified to

$$V=2a(Jv)^{\frac{1}{2}}(L/L+X), \tag{22}$$

which reduces to two limiting expressions:

$$V=2a(Jv)^{\frac{1}{2}} \quad \text{for} \quad L>X, \tag{23}$$

and

$$V=2aJvL/X=aLJ \quad \text{for} \quad X>L. \tag{24}$$

Finally the dislocation velocity will be related to the creep rate $\dot{\epsilon}$ by the expression

$$\dot{\epsilon}=\lambda bV, \tag{25}$$

where λ is the total length of active dislocation line per cm^3.

COMPARISON OF THEORY WITH EXPERIMENT

The above model will be compared with the results of Lytton *et al.*[1] on the creep of aluminum.

The following constants will be used: $\mu=2.7\times10^{11}$ dynes/cm^2, $b=2.86\times10^{-8}$ cm, and $\nu_D\cong10^{13}$ sec^{-1}. The dislocation line tension is given by $S\cong\mu b^2$.

The main experimental facts obtained by Lytton *et al.*[1] which are relevant to the present discussion are as follows:

In creep experiments on 99.995% pure aluminum single crystals oriented to favor slip on a single slip system, a stress-independent activation energy,

$$\Delta H=3400 \text{ cal/mole } (0.15 \text{ ev}),$$

was found for strains less than 10% in the temperature range 80°K–400°K. For strains higher than 10% and temperatures higher than 400°K, other creep mechanisms which presumably are associated with cross-slip and climb became predominant. These other mechanisms were manifested by larger activation energies.

Typical stresses used were $\sigma=10^{-4}\mu$ at 80°K and $\sigma=2\times10^{-5}\mu$ at 295°K. At a temperature of 395°K, with a stress $\sim2\times10^{-5}\mu$, a creep rate $\dot{\epsilon}\sim0.3\times10^{-4}$ sec^{-1} was found.

Let us tentatively assume that the creep law Eq. (24) applies. Then the observed activation energy should equal $2W_k$, i.e.,

$$W_k=0.075 \text{ ev}.$$

By Eq. (30) of the Appendix, then

$$\sigma_p\cong2\times10^{-3}\mu.$$

With this value of σ_p, the width of the kink, defined in the Appendix by Eq. (47), becomes

$$w=2d\cong7b.$$

These values are not unreasonable, but of course they should only be taken as rough order of magnitude estimates showing that σ_p is about $10^{-3}\mu$ and w is about $10b$. Incidentally this estimate shows that it is consistent within our model to assume the Peierls barrier to be larger than the applied stress in the creep experiment.

With $\sigma_p\cong10^{-3}\mu$ and $2W_k=0.15$ ev, the calculated values for X, from Eqs. (4) and (20), are

$$100°\text{K}: X=0.65\times10^5 b \ (1.85\times10^{-3} \text{ cm}),$$
$$300°\text{K}: X=3.5\times10^2 b \ (1\times10^{-5} \text{ cm}),$$
$$400°\text{K}: X=2\times10^2 b \ (0.57\times10^{-5} \text{ cm}).$$

For creep law (24) to apply, the requirement $L<X$ must be fulfilled. The value of L will be determined by such factors as:

(a) The average length of operative sources.
(b) The average spacing between locking impurities.
(c) The average distance between intersecting dislocations.
(d) Average length of straight dislocation segments in the Peierls valley (see Fig. 3).

An intersection of a dislocation with dislocations having one of six $\frac{1}{2}\langle110\rangle$ Burgers vectors mutually sharing a $\{111\}$ glide plane will result only in the formation of one kink in each dislocation. In aluminum this cutting process is expected to have a low activation energy, of the same order as double kink formation, say 0.2 ev. The energy of interaction between a dislocation and an impurity in a f.c.c. metal will typically be of the same order of magnitude.[15] So, in these cases we expect for reasonable stresses that small pile-ups of kinks will provide the necessary stress concentration for break-away. These pinning points should therefore influence the creep only by playing a role in the determination of L. Dislocation—dislocation intersections leading to jog formation would require a much higher activation energy and would provide strong pinning points at the lower temperatures where diffusion is slow. It may be necessary for our model to apply that the spacing between these pinning points be sufficiently large to allow the dislocations to bow out between them, although it is possible to think in terms of a modification of the Seeger[16] theory for the yield point, in that for high stresses the buildup of stress concentrations at the intersecting points is rate controlling, while for lower stresses these buildups are so rapid compared with the break-through frequency that Seegers theory applies. This mechanism is possible because the break-

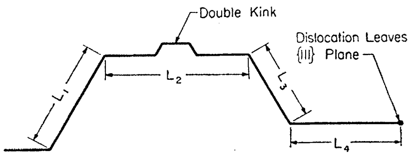

FIG. 3. Straight segments of a dislocation line lying in a $\{111\}$ plane.

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[15] J. Weertman and E. J. Salkovitz, Acta Met. 3, 1 (1955).

[16] A. Seeger, *Dislocations and Mechanical Properties of Crystals*, edited by J. C. Fisher (John Wiley & Sons, Inc., New York, 1956), p. 243.

through frequency increases much more rapidly with stress than kink nucleation.

All possibilities considered, it is likely that $L > 10^{-4}$ cm, and considering case (d) above, caused by internal stresses, it might be of the order 10^{-5} cm. Referring to the above-listed values of X, it can be seen that the condition $L < X$ should be fulfilled.

The condition (15), with L substituted for X, is well fulfilled for the lower temperatures and the higher stresses. But for $T = 300°\text{K}$ and $\sigma \sim 2 \times 10^{-5}\,\mu$, we obtain $l_c = 1.2 \times 10^{-5}$ cm, which is close to the smaller possible values of L. But the effective kink nucleation rate is only slightly changed if condition (15) is not quite fulfilled, so this point is not considered critical.

With $\sigma_p \sim 10^{-3}\,\mu$, $\dot{\epsilon} \sim 10^{-4}\ \text{sec}^{-1}$, $\sigma \sim 10^{-5}\,\mu$, $2W_k \sim 0.15$ ev, $T \sim 300°\text{K}$, and $L \sim 10^{-5}$ cm, Eq. (25) yields $\lambda \sim 10^5\ \text{cm}^{-2}$, a reasonable value for active dislocation length in a good single crystal. Thus formula (24) describes the experimental data in a self-consistent manner.

The creep formula (23) can definitely be ruled out as inapplicable. If it were accepted, it would be necessary to put $2W_k \sim 0.30$ ev, which at 100°K would lead to values of X of the order of hundreds of meters, which is impossible.

SUMMARY

The creep Eq. (25) applies to a creep mechanism that gives a stress-independent activation energy at low temperatures. This mechanism is substantiated by the observation of a stress independent activation energy for the low-temperature creep of aluminum. Although the agreement between theory and experiment is good, the following reservations are noted.

Condition (15) must be fulfilled for the model to apply. Thus high temperatures and low stresses limit the application of Eq. (25). Also at very large stresses, the kink concentration $n(2w)$, the boundary condition on the diffusion problem, could be reduced below the equilibrium value. In this case the gross nucleation rate would have to be considered, involving Eq. (2) and a transmission coefficient analogous to the Zeldovich[17] term in classical nucleation theory: both of these terms would introduce a stress dependence into the activation energy, although clearly the Peierls barrier would still control the creep rate. Finally, quantum effects have been completely neglected in the theory. However, the temperature $h\nu/k$ corresponding to the lowest frequency of dislocation vibration in the Peierls valley is ~10°K, and the frequency changes of the higher frequencies during kink activation are shown (in the appendix) to be moderate. Thus it seems reasonable to apply the classical treatment above ~10°K.

The present treatment is felt to be important in demonstrating that a translating dislocation line can be treated as a *continuous* line. If, in the frequency-change calculation in the Appendix, the contributions of short wavelengths had been important, it would have been necessary to introduce a cutoff wavelength ($\sim a$) which would have introduced the discrete nature of the dislocation line. The calculations show that it is not necessary to introduce this discreteness. It is hoped that the continuous line model can later be applied to the Bordoni[5] effect.

Lastly, it is noted that other investigators[18–20] have found temperature-independent activation energies for low-temperature creep to which Eq. (25) may apply. Conrad[18] also shows the stress dependence of the creep rate and notes that no theoretical explanation exists for the stress dependence. No such explanation is attempted here, but it is noted that the unknown stress dependence in Eq. (25) is in the factors λ and L, both of which are probably dependent on stress and strain.

ACKNOWLEDGMENTS

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APPENDIX. PARTITION FUNCTION FOR KINKED DISLOCATION LINE

A dislocation line is taken to satisfy the equation of motion

$$\rho\partial^2\xi/\partial t^2 - S\partial^2\xi/\partial x^2 + b\sigma_p \sin(2\pi\xi/a) = 0, \tag{26}$$

where ρ = effective mass per unit length and ξ and x are explained in Fig. 4. In the static case (26) reduces to

$$\frac{\partial^2\xi}{\partial x^2} - \frac{b\sigma_p}{S}\sin\left(\frac{2\pi\xi}{a}\right) = 0. \tag{27}$$

Considering the case of one kink with its center at $x = 0$, the solution of (27) is

$$\xi_0 = \frac{a}{\pi}\arcsin\left[\frac{\exp(2xG) - 1}{\exp(2xG) + 1}\right], \tag{28}$$

where $G = (2\pi b\sigma_p/aS)^{\frac{1}{2}}$. The energy of the kink is

$$W_K = \int_{-\infty}^{\infty}\left\{\tfrac{1}{2}S\left(\frac{\partial\xi}{\partial x}\right)^2 + \frac{\sigma_p ab}{2\pi}\left[1 + \cos\left(\frac{2\pi\xi}{a}\right)\right]\right\}dx. \tag{29}$$

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[17] J. B. Zeldovich, Acta Physicochim., U.R.S.S. **18**, 1 (1943).

[18] H. Conrad, Acta Met. **6**, 339 (1958).

[19] J. W. Glen, Phil. Mag. **1**, 400 (1956).

[20] H. Conrad and W. D. Robertson, Trans. Am. Inst. Mining, Met., Petrol. Engrs. **209**, 503 (1957).

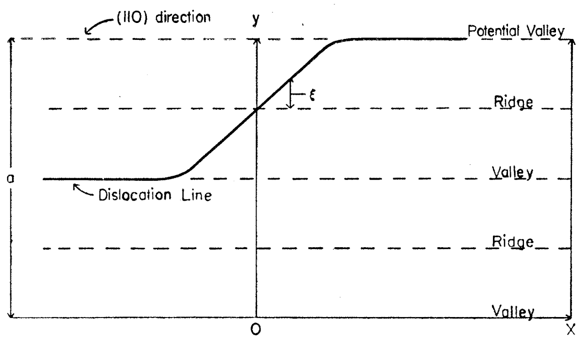

FIG. 4. Detail of a kink in a dislocation line in a {111} plane.

By insertion of Eq. (28) into (29), the energy of the kink is[8]

$$W_k=(2a/\pi^2)(2\pi ab\sigma_p S)^{\frac{1}{2}}. \tag{30}$$

Subsequently the dislocation line is described by normal mode amplitudes. Consider a dislocation of length M. Then perform the orthogonal transformation

$$\xi(x)=(2/M)^{\frac{1}{2}}\textstyle\sum_j A_j \sin[k(x-\frac{1}{2}M)],\qquad j=m\pi/M;\quad m=1,2,\cdots. \tag{31}$$

The summation over j should only be carried out up to $j_{\max}=\pi/b$, as b is the distance between neighboring atoms along the dislocation. However, such a cutoff is not consistent with the continuum model defined by Eq. (26). Fortunately it will turn out that all of the quantities of interest receive negligible contributions from short-wave amplitudes so that summations may be carried out up to $j=\infty$ without appreciable error.

Expanding the dislocation energy H to the second power, the whole segment M remaining in one potential valley,

$$H=\int_{-M/2}^{M/2}\left[\tfrac{1}{2}\rho\left(\frac{\partial\xi}{\partial t}\right)^2+\tfrac{1}{2}S\left(\frac{\partial\xi}{\partial x}\right)^2+\frac{\pi b\sigma_p}{a}\xi^2\right]dx, \tag{32}$$

and inserting Eq. (31) into (32),

$$H=\sum_j \tfrac{1}{2}\rho\dot{A}_j^2+\sum_j\left(\tfrac{1}{2}Sj^2+\frac{\pi b\sigma_p}{a}\right)A_j^2. \tag{33}$$

The circular frequencies of vibration ω_j are given by

$$\omega_j^2=\frac{S}{\rho}j^2+\frac{2\pi b\sigma_p}{\rho a}. \tag{34}$$

The kinetic energy term in H will factor out with the same amount in the partition integral in all cases to be considered, so only the potential energy term

$$Z=\int\int\cdots\int\exp\left(\frac{-H}{kT}\right)dA_1dA_2\cdots dA_m \tag{35}$$

need be treated. By Eqs. (33) and (34)

$$Z=\prod_j\left(\frac{2\pi kT}{\rho\omega_j^2}\right)^{\frac{1}{2}}. \tag{36}$$

Now consider a dislocation line of the same length M and the same total number of degrees of freedom which contains a kink. It is necessary to compute the partition integral for this system to compare with Eq. (36). In passing from the unkinked to the kinked configuration, one vibrational degree of freedom has been removed and one translational degree of freedom consisting of pure translation of the kink along the dislocation line has been introduced.

Under pure translation of the kink, the energy remains constant and a line in the m-dimensional space $(A_1, A_2, \cdots, A_m)$ is described. The contribution to the partition integral stems from a "tube" in phase space around the translational line (see Fig. 5). The cross section of the tube is determined by the vibrational modes. It is assumed that it is possible to integrate independently over the cross section and along the translational line. This procedure is rigorous only for an infinitesimal cross section.

An element of tube δB then contributes

$$\delta Z=\delta B\prod_j{}''\left(\frac{2\pi kT}{\rho\omega_j'^2}\right)^{\frac{1}{2}}x\exp\left(-\frac{W_k}{kT}\right), \tag{37}$$

where the double prime indicates that there is one less factor in the product than in Eq. (36), the single prime indicates that the frequencies are different, and

$$\delta B=[\delta A_1^2+\delta A_2^2+\cdots+\delta A_m^2]^{\frac{1}{2}}, \tag{38}$$

where δA_m are the Fourier components of the $\delta\xi$ resulting from a translation δx of the kink. From Eq. (28)

$$\delta\xi=\frac{4aG}{\pi}\frac{\exp(g)}{\exp(2g)+1}\delta x, \tag{39}$$

where $g=Gx$. Then

$$\delta A_m=\delta x\times\frac{2aG}{\pi}\left(\frac{2}{M}\right)^{\frac{1}{2}}\times\int_{-M/2}^{M/2}\frac{\exp(g)\sin[j(x-\frac{1}{2}M)]}{\exp(2g)+1}dx. \tag{40}$$

Extending the limits of integration to ±∞ and summing over the residues at $2g=(2m+1)i\pi$, $m=0, 1, \cdots$.

$$\delta A_{2m+1}=\delta x\times 2a\left(\frac{2}{M}\right)^{\frac{1}{2}}\frac{\exp(\pi\kappa/2G)}{\exp(\pi\kappa/G)+1},\qquad \kappa=(2m+1)\pi/M,\quad m=0,1,\cdots; \tag{41}$$

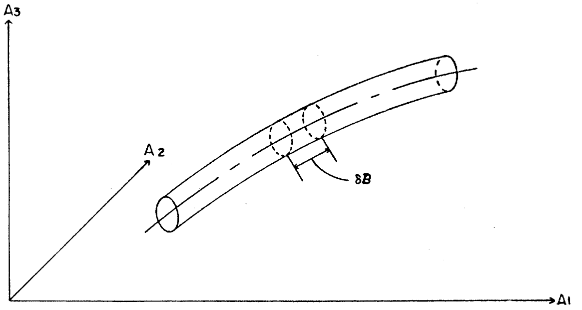

FIG. 5. A tube in phase space corresponding to translation of a kink along a dislocation.

and

$$A_{2m}=0. \tag{42}$$

Now, by Eq. (38), changing the summation into integration,

$$\delta B=\delta x\times 2a\left\{\frac{1}{\pi}\int_0^\infty\left[\frac{\exp(\pi\kappa/2G)}{\exp(\pi\kappa/G)+1}\right]^2 d\kappa\right\}^{\frac{1}{2}}, \tag{43}$$

or

$$\delta B=\frac{2a}{\pi}\left(\frac{G}{2}\right)^{\frac{1}{2}}\delta x. \tag{44}$$

The frequencies ω' are found from the differential equation resulting from linearization of Eq. (26) about the solution (28):

$$\rho\frac{\partial^2\xi}{\partial t^2}-S\frac{\partial^2\xi}{\partial x^2}+G^2S\left\{1-2\left[1-\left(\frac{\exp(2g)-1}{\exp(2g)+1}\right)^2\right]\right\}\xi=0. \tag{45}$$

Instead of the difficult (45) the frequency changes are estimated from

$$\rho\frac{\partial^2\xi}{\partial t^2}-S\frac{\partial^2\xi}{\partial x^2}-G^2S\xi=0, \quad |x|<|d|, \tag{46a}$$

$$\rho\frac{\partial^2\xi}{\partial t^2}-S\frac{\partial^2\xi}{\partial x^2}+G^2S\xi=0, \quad |x|>|d|. \tag{46b}$$

At $x=\pm d$, it is required that ξ and $\partial\xi/\partial x$ be continuous. The distance d is chosen so that there exists a solution of Eqs. (46) of zero frequency and yielding $\xi(x)\rightarrow 0$ as $|x|\rightarrow\infty$, corresponding to the translational mode. d is then given by

$$d=\pi/4G. \tag{47}$$

Now consider the eigenfrequencies of Eqs. (46) with the boundary conditions $\xi=0$, $x=\pm M/2$. The translational mode is excluded. For $-d<x<d$,

$$\xi=A\left\{\begin{matrix}\sin(Kx)\\ \cos(Kx)\end{matrix}\right\}, \quad K^2=\frac{\omega^2}{c^2}+G^2; \tag{48a}$$

for $|x|>|d|$,

$$\xi=P\sin(Qx)+R\cos(Qx), \quad Q^2=\frac{\omega^2}{c^2}-G^2. \tag{48b}$$

The secular equations become, for uneven solutions,

$$\tan(QM/2)=\frac{1-(Q/K)\tan(Kd)\cot(Qd)}{\cot(Qd)+(Q/K)\tan(Kd)}; \tag{49}$$

for even solutions,

$$\cot(QM/2)=\frac{\cot(Qd)-(Q/K)\cot(Kd)}{1+(Q/K)\cot(Kd)\cot(Qd)}. \tag{50}$$

It can be shown that when the translational mode is excluded, only real and positive Q and K need be considered.

By some rewriting of Eqs. (49) and (50), for uneven solutions,

$$\begin{gathered}QM/2=Q_0M/2+Qd-\phi, \quad \tan\phi=(Q/K)\tan(Kd),\\ Q_0=2m\pi/M, \quad m=1,2,\cdots;\end{gathered} \tag{51}$$

for even solutions,

$$\begin{gathered}QM/2=Q_0M/2+Qd-\phi, \quad \cot\phi=(Q/K)\cot(Kd),\\ Q_0=(2m+1)\pi/M, \quad m=1,2,\cdots.\end{gathered} \tag{52}$$

To first order, from Eq. (48b),

$$\delta\omega/\omega=(Qc^2/\omega^2)\delta Q. \tag{53}$$

The sequence of frequencies ω, Eq. (34), starting with $n=2$, is to be compared with the sequence of frequencies ω' determined by Eqs. (51) and (52). This procedure secures that the total number of degrees of freedom is the same in both cases, without specification of the cutoff wavelength.

An estimate is needed of

$$\delta\ln\prod\omega=\ln\prod\omega-\ln\prod\omega'=\sum(\delta\omega/\omega). \tag{54}$$

Employing Eqs. (34), (48), (51), (52), and (53), approximating Qd by Q_0d, and turning the resulting sum into an integral, it follows that

$$\delta\ln\prod\omega=(c^2/\pi)\int_0^\infty(Q/\omega^2)(2Qd-\phi)dQ, \tag{55}$$

where

$$\tan\phi=\tfrac{1}{2}\left(\frac{Q}{K}+\frac{K}{Q}\right)\tan(2Kd). \tag{56}$$

It can be shown that ϕ must be taken in the same quadrant as $2Kd$. The integral in Eq. (55) is then rapidly convergent. By Eqs. (47) and (48), Eqs. (55) and (56) become

$$\delta\ln\prod\omega=\frac{1}{\pi}\int_0^\infty\frac{Z}{Z^2+\pi^2/16}(2Z-\phi)dZ, \tag{57}$$

where

$$\tan\phi=\tfrac{1}{2}\left[\frac{Z}{(Z^2+\pi^2/8)^{\frac{1}{2}}}+\frac{(Z^2+\pi^2/8)^{\frac{1}{2}}}{Z}\right]\tan 2\left(Z^2+\frac{\pi^2}{8}\right)^{\frac{1}{2}}. \qquad (58)$$

By numerical integration

$$\delta\ln\prod w=-0.50. \qquad (59)$$

Finally, from Eqs. (34), (36), (37), (44), and (59), and realizing that $Z'=\delta Z/\delta x$,

$$\frac{Z'}{Z}=1.05a\left(\frac{b\sigma_p}{akT}\right)^{\frac{1}{2}}\left(\frac{\pi b\sigma_p}{2aS}\right)^{\frac{1}{4}}\exp\left(-\frac{W_k}{kT}\right). \qquad (60)$$

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Effect of Oxygen on the Work Function of Barium

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While a high sensitivity of the work function to gaseous contaminants is generally characteristic of metals which adsorb the common gases strongly, barium combines outstanding work function stability with an exceptional affinity for these gases. The paradox is investigated by administering measured quantities of oxygen to vapor-deposited barium surfaces at known rates, with concurrent monitoring of the work function. It is found (1) that when clean barium is exposed suddenly to a massive dose of oxygen, its work function is lowered by 0.32 ev; (2) that the work function of the heavily oxygenated surface remains constant for 5 days and then drifts very slowly toward the clean-metal value, and (3) that when oxygen is administered to a barium surface slowly (2×10^{13} molecules per cm^2 per hour) no change of work function occurs during or after the absorption of a quantity of oxygen equivalent to 100 complete monolayers of the oxide.

The results are interpreted as stemming from two processes which compete for control of the surface; the expected surface oxidation and a restorative process involving engulfment of oxygen ions. The mechanism of engulfment is discussed.

It is well known that a high sensitivity of the work function to gaseous contaminants is generally characteristic of metals which adsorb, or absorb, the common gases strongly. The tungsten-oxygen system is the common prototype of this class; when a tungsten surface is cleaned by momentary flashing in a vacuum of the order of 10^{-8} mm, its work function drifts upward rapidly as a monolayer of oxygen builds up on it. In another group of metals, epitomized by silver, zinc, and cadmium, the work function of an initially clean surface is unaffected by prolonged exposure to residual gases at pressures of the order of 10^{-8} mm.[1] It is thus possible to classify many of the common metals in two mutually exclusive groups, the gas-sorbing, work-function-sensitive metals and the nonsorbing, insensitive metals. Against this background, the behavior of barium stands out as highly anomalous. Barium is an excellent "getter"; it combines stoichiometrically with oxygen and is an effective absorber for hydrogen, nitrogen and water vapor. But if a clean barium surface is prepared by vapor deposition at a residual gas pressure of the order of 10^{-8} mm and if the fresh surface is measured before contamination can occur, i.e., so quickly that the total number of gas molecules which strike the surface within the deposition-measurement interval is small with respect to the gas content of a monolayer, the initial work function shows no drift with time.[2,3] We have the unusual spectacle of a metal surface absorbing gas continuously while showing no measurable change in work function.

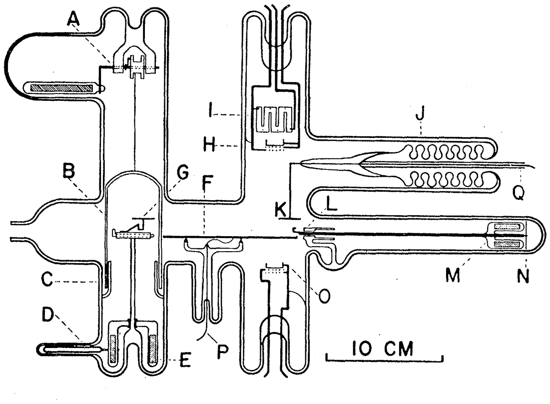

FIG. 1. Tube for massive dose experiments. Barium vaporized by ovens *O* and *H* and re-vaporizer *I* (1-mil Ta, 45° mounting) is deposited to form reference surface *K* and test surface *G*. *G*, moved on track *F* (parallel 60-mil W wires) by armature *M*, is exposed to oxygen by breakage of glass capsule *D*. *C* is molten tin seal, external heater not shown. Glass sylphon *J* transmits motion for Kelvin measurements. *K*, *G*, spun cups *O*, *H*; disk *N*: 5-mil Ta. Winch *A* for glass bell *B*: 2-mil W wire on Pyrex drum.

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