THE KINK PICTURE OF DISLOCATION MOBILITY AND DISLOCATION-POINT-DEFECT INTERACTIONS
A. Seeger

To cite this version:
A. Seeger. THE KINK PICTURE OF DISLOCATION MOBILITY AND DISLOCATION-POINT-DEFECT INTERACTIONS. Journal de Physique Colloques, 1981, 42 (C5), pp.C5-201-C5-228. <10.1051/jphyscol:1981531>. <jpa-00221073>

HAL Id: jpa-00221073
https://hal.archives-ouvertes.fr/jpa-00221073

Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
THE KINK PICTURE OF DISLOCATION MOBILITY AND DISLOCATION-POINT-DEFECT INTERACTIONS

A. Seeger

Max-Planck-Institut für Metallforschung, Institut für Physik, und Universität Stuttgart, Institut für theoretische und angewandte Physik, Postfach 800855, D-7000 Stuttgart 80, Germany

Abstract.- The paper gives a coherent account of the theory of dislocation mobility in terms of kink-pair formation and kink migration. Three levels of description arise in a natural way, namely those of the motion of straight dislocations, of kink-pair formation on dislocations, and of kink migration. The interrelationships between these levels ("hierarchies") are discussed. The interaction with phonons and foreign atoms ("impurities") is treated on the third level, that of the kink mobility.

Experimental information on the properties of kinks may be obtained from measurements of dislocation velocities, of flow stress, and of internal friction and modulus effect. The comparison between theory and experiment is illustrated by examples from valence crystals (dislocation velocity in Ge) and from body-centred cubic transition metals (γ relaxation = kink-pair formation on screw dislocations; dislocation-enhanced Snoek effect; Snoek–Köster relaxation in Nb and Ta).

1. Introduction and General Background.- The "discovery" of dislocations during the period 1929–34 provided the explanation for the observation that in many crystalline materials the critical shear stress \( \sigma_0 \) for plastic deformation by glide is several orders of magnitude lower than the theoretical shear strength \( \sigma_{th} \) as calculated from the model of perfect crystals. Already in some of the early work it was recognized that the resistance-to-glide due to the discrete nature of crystals was not completely removed by the movement of straight dislocations running parallel to one of the major crystallographic directions (this was the model used throughout in the early days of dislocation theory). Based on what is now called the PRANDTL–DEHLINGER–FRENKEL–KONTOROVA model [1,6,7] an attempt to estimate the stress required to move a straight "dislocation" in a crystal is already contained in U.DEHLINGER's "Verhakungen" paper of 1929 [1]. (A brief historical account of early dislocation models and their relationships to the problem of dissipation of mechanical energy (=internal friction) in crystals has appeared elsewhere [8].)
At the suggestion of E. OROWAN, in 1939 R. PEIERLS [9] performed the first detailed calculation of the resolved shear stress required to move a straight dislocation through a crystal in the absence of thermal fluctuations. This stress is now called the Peierls stress \( \sigma_p \). The line energy \( E_d \) of a straight dislocation on a given glide plane is a minimum in the so-called "Peierls valleys" and a maximum on the "Peierls hills" (comp. Fig. 1). The original estimate of Peierls (for a historical description see [10]) was corrected and improved by various authors; for the methods used and the results obtained the reader is referred to the review literature [11-14]. The best calculations available indicate that in many instances the observed critical shear stresses, at least at not too low temperatures, are substantially lower than the calculated Peierls stresses.

In the post-war development of dislocation theory it became soon clear that dislocation lines must be considered flexible. W. SHOCKLEY [15] pointed out that together with the existence of the Peierls potential this may lead to the formation of kinks, i.e., short segments of dislocation lines in which these cross over from one Peierls valley to a neighbouring one (comp. Fig. 1), and estimated that kinks may form in thermal equilibrium. A. SEEGER [12, 16] recognized that the thermally activated formation of pairs of kinks of opposite sign (original name "double kinks", in the following briefly called kink pairs) under the action of an oscillating applied stress might lead to a relaxation effect in internal friction. He proposed that the relaxation process observed by P. G. BORDONI [17, 18] in various deformed fcc metals below room temperature might be due to this process. This suggestion was developed further in numerous theoretical and experimental papers (see, e.g., [19, 20]) and appears now to be generally accepted as the correct explanation of the Bordoni relaxation. From a historical point of view it is interesting to note that quite a large number of alternative explanations involving dislocations have been proposed during the last twenty-five years (see, e.g., [20, 21]) but that the first explanation in terms of dislocation theory proved to be correct (BORDONI himself [18] suggested an explanation not involving dislocations).

According to the kink-pair formation model the Bordoni relaxation is an intrinsic dislocation property directly related to the existence of the Peierls potential. In most crystals it still provides the best information for estimating the numerical value of the Peierls stress \( \sigma_p \) or the height of the Peierls barriers of dislocations lying parallel to crystallographic directions. Recently, the modification of the thermally activated kink-pair formation process by atomic defects (in particular by foreign interstitial atoms) has become the subject of much interest, as is witnessed by the present conference.

In addition to kinks that are formed by thermal activation we have to consider geometrical kinks [22]. These are kinks that are present even at the lowest temperatures in dislocation lines that are approximately parallel to low-index crystallographic directions and fixed by anchoring points not lying in the same Peierls
Fig. 1: Top: The lattice-periodic Peierls potential $U(u)$ of a straight dislocation as a function of its displacement $u$. The mean value of $U(u)$ is the dislocation line energy $E_d$. The displacement $u_0$ of a straight dislocation under an applied stress $\sigma < \sigma_p$ is indicated ($b =$ dislocation strength = modulus of Burgers vector).

Bottom: Various dislocation configurations on an glide plane with Peierls valleys (full lines) and Peierls hills (dashed lines).

<table>
<thead>
<tr>
<th>hierarchy (model)</th>
<th>defect or process considered</th>
<th>overcoming</th>
<th>remaining lattice-periodic energy barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>motion of straight dislocations</td>
<td>theoretical shear strength $\sigma_{th}$</td>
<td>Peierls potential (of 1st kind)</td>
</tr>
<tr>
<td>II</td>
<td>kink-pair formation</td>
<td>Peierls potential (of 1st kind)</td>
<td>kink potential (Peierls potential of 2nd kind)</td>
</tr>
<tr>
<td>III</td>
<td>kink migration</td>
<td>kink potential (Peierls potential of 2nd kind)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table I. The three hierarchies of models and energy barriers.
valley (comp. Fig. 1). They account for the fact that dislocations approximately parallel to one of the major crystallographic directions may contribute to the modulus defect even at temperatures well below that of their Bordoni relaxation.

Theoretical reasoning analogous to that leading to the existence of the Peierls potential of straight dislocations demonstrates that the potential energy of a kink in a dislocation must be a periodic function of the kink position along the dislocation line with a period equal to that of the crystal lattice in that direction. This periodic potential is called "kink potential" or, in order to emphasize the close analogy to the Peierls potential of straight dislocation lines, "Peierls potential of the second kind".

We see that as in the classical system of the hierarchies of angels of Dionysius the Areopagite we have a division of our models into three orders, namely that of perfect crystals, that of straight dislocation lines, and that of kinks. To these three orders of models correspond three orders of barriers to be overcome (by the motion of the defects of the next lower order), namely the theoretical shear strength of a perfect crystal $G_p$, the Peierls potential (of the first kind), and the kink potential. These relationships are summarized in Table I.

The subdivision into the models and the lattice-periodic barriers listed in Table I has considerable advantages for the discussion of physical phenomena associated with dislocations, since their basic features may often be understood by referring to one of the three hierarchies of Table I only. E.g., many basic features of the deformation of crystals by glide may be explained in terms of dislocations without paying attention to the existence of the Peierls barriers. Most observations on the Bordoni relaxation are accounted for, at least qualitatively, in terms of kink-pair formation. If the kink potential is large enough, geometrical kinks may give rise to a distinct relaxation phenomenon associated with kink migration [19, 23-25].

Notwithstanding the impressive successes of the simplistic approach just outlined, a deeper understanding of the observed phenomenon can often only be achieved if it is recalled that each of the three hierarchies of Table I can at best give a partial representation of a complex physical situation.

The present paper aims at developing, in a coherent fashion, the theory of kink-pair formation and kink migration, and attempts to apply it to the interpretation of measurement of dislocation velocities and of internal-friction phenomena. We shall carefully distinguish between phenomena that may be understood be reference to only one of the models of Table I, with the aspects represented by the other models coming into play only through phenomenological parameters, and those requiring a more general ("inter-hierarchic") approach.

2. The Interaction between Kinks. - We consider here kinks on the same dislocation line. The simplest physical picture we may use is the description of the dislocation line as a string, characterized by the dislocation line tension $S_d$ and the dislocation...
mass per unit length, \( \gamma_d \). For additional simplicity we consider only small deviations from straight lines, measured by the displacement \( u \) of the dislocation from a Peierls valley. The motion of a dislocation line is then governed by the partial differential equation

\[
S_d \frac{\partial^2 u}{\partial z^2} - \gamma_d \frac{\partial^2 u}{\partial t^2} = \frac{du(u)}{du} + b \sigma = 0
\]  

(1)

In (1) \( z \) denotes the spatial coordinate in the direction of the Peierls valley, \( t \) the time, \( b \) the dislocation strength, \( \sigma \) the applied resolved shear stress, and \( U(u) \) the line energy of a straight dislocation line as a function of its displacement. For the purpose of calculating the line tension \( S_d \) it suffices to replace \( U(u) \) by its average value \( E_d \), the line energy of the dislocations (Fig. 1). We then have [26]

\[
S_d = E_d + a^2 \frac{dE_d}{d\theta^2}
\]  

(2)

where \( \theta \) is the angle between the Burgers vector of the dislocation line and the direction of the Peierls valleys.

For static solutions \( u(z) \) Eq. (1) simplifies to

\[
S_d \frac{d^2 u}{dz^2} - \frac{dU(u)}{du} + b \sigma = 0
\]  

(3)

Eq. (3) possesses the solution \( u_0 = \text{constant} \) corresponding to a rigid displacement of a straight dislocation line, where

\[
\left. \frac{dU(u)}{du} \right|_{u=u_0} = b \sigma
\]  

(4)

The maximum value of \( \sigma \) at which (4) still has a real solution defines the Peierls stress \( \sigma_P \) (comp. Fig. 1).

Among the solutions of (3) for \( \sigma = 0 \) is that for a single kink centred at \( z = z_0 \). In implicit form it is given by

\[
z - z_0 = \pm \left( \frac{S_d}{2} \right)^{1/2} \int_{u_0}^{u} \frac{du}{\sqrt{U(u) - U(0)}}
\]  

(5)

where the signs correspond to positive or negative kinks, respectively. For "smooth" potentials for which the maximum value \( U_{\text{max}} \) coincides with \( U(a/2) \), where \( a \) is the distance between neighbouring Peierls valleys and the height of a single kink, we may define the kink width as

\[
\omega_k = a \left| \frac{dz}{du} \right|_{u=a/2} = a \left[ \frac{S_d}{2} \left[ U(a/2) - U(0) \right] \right]^{1/2}
\]  

(6)

Within the present theoretical framework (briefly called the "line-tension model") the energy of a single kink is given by

\[
H_k = (2S_d)^{1/2} \int_{u=0}^{u=a} \left[ U(u) - U(0) \right]^{1/2} du
\]  

(7)
Under an applied shear stress \( \sigma \), Eq. (3) possesses a solution which corresponds to a pair of kinks in unstable equilibrium. The forces exerted on the kinks by the applied stress, \( \pm ab \sigma \), tend to move the kinks apart. A configuration of unstable equilibrium exists in which these forces just balance the attraction between the kinks of opposite signs. The enthalpy difference between a kink pair in this configuration and that of a straight dislocation line at \( u = u_0 \) constitutes the saddle-point enthalpy for the formation of a kink pair, \( H_{kp} \). Within the present framework we have

\[
H_{kp} = 2(2S_d)^{1/2} \int_{u = u_0}^{u = u_{\text{max}}} [U(u) - U(u_0) - (u - u_0)b\sigma]^{1/2} du,
\]

where the upper limit of the integration follows from

\[
U(u_{\text{max}}) - U(u_0) - (u_{\text{max}} - u_0)b\sigma = 0.
\]

In internal friction experiments we are particularly interested in low stresses. For \( \sigma / \sigma_p << 1 \), Eq. (7) may be written as

\[
H_{kp} = 2H_k \left\{ 1 - \frac{c_1 \sigma}{\sigma_p} \left[ 1 - \ln(c_2 \sigma / \sigma_p) \right] + \ldots \right\},
\]

where \( c_1 \) and \( c_2 \) are numerical factors that depend on the choice of the potential \( U(u) \). For the so-called Eshelby potential \(^1\) [27]

\[
U(u) = U(o) + 3^{3/2} a b \sigma_p \frac{\nu^2}{a^2} \left( 1 - \frac{u^2}{a^2} \right) - \varepsilon \leq u/a \leq 1 + \varepsilon, \quad 0 \leq \varepsilon << 1
\]

these factors are given by \([28]\)

\[
c_1 = 2c_2 = 3^{-1/2} / 2 ,
\]

the enthalpy of formation of a single kink by

\[
H_k = 3^{-1/4} a (ab\sigma_p S_d / 2)^{1/2},
\]

and the kink width by

\[
w_k = 2a^2 S_d / 3H_k .
\]

\(^1\)In contrast to the sinusoidal potential

\[
U(u) = U(o) + ab\sigma_p \left[ 1 - \cos(2\pi u / a) \right] / 2\pi
\]

the Eshelby potential (12) does not describe in an analytical way the periodicity of \( U(u) \) but is well suited for treating the effect of an applied shear stress on the interaction of a pair of close kinks. For later use (Sect. 3) we record for the sinusoidal potential

\[
H_k = (2a/\pi)(2ab\sigma_p S_d / \pi)^{1/2},
\]

\[
w_k = 2a^2 S_d / 3H_k .
\]
Eq. (1) may be used to determine the vibrational spectrum associated with a single kink or with the saddle-point configuration of a kink pair and to calculate the entropy of kink formation. For details and results the reader is referred to the literature [13, 22]. The results for isolated kinks will be used later. From (1) we may further deduce that the "velocity of sound" of small perturbations propagating along a dislocation line is

$$c_0 = (S_d / \gamma_d)^{1/2}$$

Since (1) is Lorentz-invariant, we may define the rest mass $m_k$ of an isolated kink according to

$$m_k = \rho_k / c_0^2 = \gamma_d \rho_k / S_d$$

The preceding theoretical description corresponds to line II of Table I. We have disregarded the atomistic structure of the crystal in the direction of the Peierls valleys (line III of Table I). This has the consequence that the energy of a kink is independent of its position $z_0$ along the dislocation. The fact that kinks are short segments of an otherwise straight dislocation embedded in a three-dimensional elastic continuum (line I of Table I) is taken into account only through the dislocation line tension $S_d$ and the effective mass $\gamma_d$ per unit dislocation length. For some purposes, in particular for the calculation of the kink-kink interaction at large separations, this is not sufficient, since it does not adequately describe the elastic interaction between kinks.

It is easy to show that for large separations the elastic interaction energy must vary as the inverse distance between kinks on the same dislocation [13, 22, 27, 29, 30]. For elastically isotropic media with shear modulus $G$ and Poisson's ratio $\nu$ the force between kinks of height $a$ at separations $x \gg a$ reads [13, 22, 27, 29, 30]

$$F = \frac{\pi G b^2}{4\pi} \frac{1}{1-\nu} \frac{a^2}{2x^2} [((1+\nu) \cos^2 \theta + (1-2\nu) \sin^2 \theta]$$

where $\theta$ denotes the angle between the dislocation line and the ± signs refer to kinks of equal or opposite signs, respectively. The generalization of (12) to anisotropic elasticity is [31, 32]

$$F = \pm S_0^{el} \frac{a^2}{2x^2}$$

Here $S_0^{el}$ is the prelogarithmic factor of the elastic part of the dislocation line-tension. It may be written in the form

$$S_0^{el} = b f$$

where $f$ is independent of the dislocation strength $b$. For a given glide plane $f = f(C_{ijkl}, \phi)$ depends only on the 2nd-order elastic constants $C_{ijkl}$ of the crystal and on the character of the dislocation line.
Fig. 2: The total enthalpy of two kinks of opposite sign (full line) and the interaction enthalpy $H_{\text{int}}(x)$ as a function of the kink separation $x$. The enthalpy of kink-pair formation $H_{\text{kp}}$ is indicated; the kink separation $x_1$ corresponds to unstable equilibrium.

is given by $-ab\sigma x$. The superposition of these two potential energies (full line) leads to a maximum at $x_1$

$$x_1 = \frac{(a S_o^1 / 2b \sigma)^{1/2}}{2x_1},$$

(20)

corresponding to a kink-pair formation enthalpy

$$H_{\text{kp}} = 2H_k - H_{\text{int}}(x_1) = 2H_k - \frac{a S_o^1}{2x_1} - abx_1\sigma = 2H_k - \frac{(2a b S_o^1 \sigma)^{1/2}}{2x_1}.

(21)

Eq. (21) corresponds to the first term of a "multipole expansion". At small separations and large $\sigma$ it ceases to be valid. Then the elastic interaction between the kinks depends not only on $a$ and $b$ but in addition on the shape of the kinks (cf. [22]). In the present context, however, it is not worthwhile to work this out in detail since for small kink separations the elastic interaction is small compared with that given by Eq. (8) of the line-tension model.

The stress $\bar{\sigma}$ which separates the range of validity of (8) and (21) may be found by equating (10) and (21). The Eshelby potential (12) gives us [28]

$$\bar{\sigma} = \frac{1}{3^{1/2} 4\sigma_p} \left[ 1 + \ln \left( \frac{3^{1/2} 4\sigma_p}{\bar{\sigma}} \right) \right]^2 = \frac{S_o^1}{S_d}.$$

(22)

If we choose, e.g., $S_d/S_o^1 = 4.1$, Eq. (22) has the solution $\bar{\sigma}/\sigma_p = 0.14$, $\ln (3^{1/2} 4\sigma_p/\bar{\sigma}) = 5$. Fig. 3 shows the relationship between $\sigma/\sigma_p$ and $H_{\text{kp}}/2H_k$ for this particular case. A different choice of $S_d/S_o^1$ or $U(u)$ does not change the functional form of this relationship appreciably. For $\sigma > \sigma_p$ Eq. (8) exhibits a "quasi-universal" behaviour in the sense that

$$H_{\text{kp}} = c_3 2H_k \left( \frac{\sigma_p - \sigma}{\sigma_p} \right)^{5/4},$$

(23)
Fig. 3: The relationship between the resolved shear stress $\sigma$ (in units of the Peierls stress $\sigma_0$) and the enthalpy of formation of a kink pair $H_{kp}$ (in units of the formation enthalpy of a single kink, $H_k$) according to Eq. (10) (line-tension model) and Eq. (21) (long-range elastic interaction). The stress $\sigma$ at which the predicted relationship (full line) changes over from Eq. (10) to Eq. (21) is indicated.

where the choice of $U(u)$ affects only the numerical value of $c_3$ (for (12):

$$c_3 = \frac{6}{5}(2/3)^{5/4} \approx 0.73.$$  

For small kink separations it is not possible to define the kink separation in a unique manner. In Fig. 2 this is indicated by the dashed curve. Fortunately, the physical conclusions to be drawn from the $H_{kp}(\sigma)$ relationship are unaffected by this uncertainty.

2. The Kink-Pair Formation Rate. - The calculation of the rate of formation of kink pairs on an otherwise straight dislocation line of unit length, $\Gamma$, in the following briefly called the kink-pair formation rate, is beset by the problems of rate theory in general. A theoretical framework capable of giving practical results and being applicable under all physical conditions does not exist. The two most successful approaches are (i) an adaption of the transition state theory, originally developed for the calculation of chemical reaction rates and going back to the work of H. PELZER and E. WIGNER [34], and (ii) the diffusion theory based on the work of H. A. KRAMERS [35]. For a general discussion of the theory of kink-pair formation rates the reader is referred to A. SEEGER and P. SCHILLER [13].

The common idea behind both approaches is that the degrees of freedom of the entire crystal are treated by the usual statistical mechanics of harmonic oscillators with two exceptions: The mode describing the change in the kink–kink separation $x$ and the mode associated with the translation of a kink pair of fixed separation $x$ along the dislocation line. By well-known arguments the maximum in the energy–distance diagram of the first of these modes (Fig. 2) corresponds to the saddle-point in the many-dimensional configurational space separating a kink-free dislocation from the region containing a pair of kinks of opposite sign. The two theoretical approaches mentioned above differ in the assumptions made concerning the way in which the system crosses the above-mentioned saddle-point.

2) We take the opportunity to correct an error in ref. [28]: As pointed out by E. MANN, in Eq. (6a) the term $-3\beta^2$ must be replaced by $-3\beta^4$. This error has no other consequence for the main part of [28] but affects the Appendix of [28], in particular the exponent in the relationship (23) of the present paper. The exponent $5/4$ given above is in agreement with that recently obtained by MORI and KATO [33].
The transition state theory makes the assumption that once the system has reached the saddle point with a velocity pointing from the "no-kink" region to the "kink-pair" region, kink-pair formation takes place. The probability that the system "back-crosses" the saddle point is neglected. The kink-pair formation rate is then given by \[ \Gamma = \frac{2kT}{h^2} \sum_{n_1, n_2, \ldots} \frac{\exp\left(-\sum_{m} E_{m}^n / kT\right)}{\exp\left(-\sum_{m} E_{m} / kT\right)} \exp \left(-\frac{H_{kp}(0)}{kT}\right) \] denoting the energy eigen-values of the harmonic oscillators of circular frequency \( \omega_m \) associated with an unkinked dislocation, those associated with dislocations containing a kink pair in the saddle-point configuration. As a compensation for the two non-vibrational modes mentioned above, the sum (or product) over \( m \) contains two more terms than that over \( m' \). As mentioned in Sect. 2, within the framework of the line-tension model the frequencies \( \omega_m \) and \( \omega_m' \), which depend on \( \sigma \), may be calculated from (1). For the internal-friction phenomena to be discussed in the present paper it is an admissible simplification to disregard the stress-dependence of \( \omega \) and \( \omega' \) and hence that of the kink-pair formation entropy. The \( m' \) sums and products may then be related to the equilibrium (linear) density \( \rho_{eq}^n = \frac{(2\pi kT)^{1/2}}{h} \sum_{m} \frac{\exp\left(-\frac{\sum_{m} E_{m}^n / kT}{2}\right)}{\exp\left(-\frac{\sum_{m} E_{m} / kT}{2}\right)} \exp \left(-\frac{H_{kp}(0)}{kT}\right) \] of non-interacting kinks of a given sign, since the products in (24) are the squares of those in (27). Here \( \omega_m \) refers to an isolated kink, the product over \( m' \) containing one term less than that over \( m \). For high temperatures (characterized by \( \frac{\hbar \omega_m}{kT} \ll 1 \), \( \frac{\hbar \omega_m'}{kT} \ll 1 \) for those \( \omega \) and \( \omega' \) that differ appreciably from each other) the evaluation of the products leads to \[ \rho_{eq} = \frac{1}{\omega_k} \frac{(2\pi kT)^{1/2}}{\hbar} \exp\left(-\frac{H_{kp}/kT}{2}\right) \]
for the sinusoidal potential (11), and to
\[ \rho_{eq}^{k} = \frac{2\pi}{\pi} \frac{a_d}{w_k^2} \frac{(2\pi H_k/kT)^{3/2}}{\exp(-H_k/kT)} \]  
(28b)
for the Eshelby potential (12). In (28b) \( a_d \) denotes the interatomic distance along the dislocation line.

Insertion of (27,28) into (24) gives us for the kink-pair formation rate in the transition state theory
\[ \Gamma = \frac{1}{\pi m_k} (\pi m_k kT)^{3/2} (\rho_{eq}^{k})^2 \exp(H_{int}/kT) \]  
(29)
or
\[ \Gamma = \frac{1}{(\pi m_k kT)^{1/2}} \frac{2\pi H_k}{w_k^2} \exp[-H_{kp}(\sigma)/kT] \]  
(29a)
or
\[ \Gamma = \frac{1}{(\pi m_k kT)^{1/2}} \frac{2(3/8)^2 a_d^2 H_k}{\mu_k^3 w_k^4} \exp[-H_{kp}(\sigma)/kT] \]  
(29b)
Here \( H_{int} \) refers to the saddle-point separation of the kinks, (29a) to the sinusoidal potential, (29b) to the Eshelby potential.

(ii) The starting equation of the diffusion theory is a partial differential equation for the particle density \( \rho(p_x,x,t) \) in the phase space of the spatial coordinate \( x \) describing the kink-kink separation and the momentum \( p_x \) associated with it [35]. The theory is based on the physical picture that, in addition to the forces giving rise to \( H_{int}(x) \) (Fig.2), the kinks are subject to Brownian forces due to their interaction with lattice vibrations. The effects of the Brownian forces may be described in terms of a kink mobility \( \mu_k \) or a kink viscosity \( 1/\mu_k \). By the Einstein-Nernst relationship the kink mobility may be expressed in terms of the kink diffusivity
\[ D_k = kT \mu_k \]  
(30)
There are two limiting cases in which the number of independent variables in KRAMERS' basic partial differential equation may be reduced by one.

(a) If the kink mobility is so high that the oscillations of the kinks in the attractive potential formed by the interaction of kinks of opposite sign are only little influenced by the Brownian forces, or \( p_x \) and \( x \) may be replaced by the action variable
\[ I(E) = \int p_x dx \]  
(31)
where the integral has to be taken along the closed curve in phase space corresponding to a fixed energy \( E \). As independent variable one may choose energy and time, and the physical problem may be looked upon as "diffusion and drift of energy". This is the view-point adopted by H. DONTH [36] in his theory of kink-pair formation, although as his starting point he did not use KRAMERS' paper [35] but earlier work by KOLMOGOROFF [37] and GEBELEIN [38].
E. MANN [39] has recently shown that under the condition $H_{kp} \gg kT$ the kink-pair formation rate for high kink mobilities is given by

$$\Gamma = \frac{8H_{kp} w_{kp}}{D_{kp} m_{kp}} \left( \frac{kT}{\pi H_{kp}} \right)^{1/2} \left( \rho_{eq}^2 \right) \exp \left( \frac{H_{int}}{kT} \right). \quad (32)$$

Here and later in (34) the same assumptions for the calculation of the entropy terms have been made as in the treatment (1).

For temperature-independent kink diffusivities $D_k$ the temperature dependence of (29) and (32) are the same. The results of the transition state theory and the high-mobility diffusion theory agree with each other if we make the identification

$$D_k = \frac{8w_k (H_{kp} / m_{kp})^{1/2}}{m_{kp}} = 8w_k c_0. \quad (33)$$

(b) If the effect of the Brownian forces on the kink velocity exceeds those of the "external" forces (i.e., if the kink mobility is small), Kramers’ equation simplifies to a so-called Smolukowski equation (diffusion equation with drift term), with the spatial coordinate $x$ as an independent variable. For the physical situations treated in this paper, this is the most important case. It has been discussed in detail by SEEGER and SCHILLER [13], STENZEL [40], ENGELKE [44], and MANN [39]. If the assumption $H_{kp} \gg kT$ is made the kink-pair formation rate may be expressed in terms of quadratures. The further assumption that the saddle point occurs in the regime of validity of (21) leads to the closed-form expression [39]

$$\Gamma = \left( \frac{2b \sigma_{eq}}{aS_{o}} \right)^{1/2} \left( \rho_{eq}^2 \right) \frac{1}{K_1(y)} \exp \left( \frac{H_{int}(x)}{kT} \right), \quad (34)$$

where

$$y = \frac{(2a^3 bS_{eq}^1)_{o}^{1/2}}{kT} = \frac{H_{int}(x)}{kT} \quad (35)$$

and $K_n(y)$ denotes the MacDonald (modified Bessel) function of order $n$. Important special cases are $y \gg 1$, $K_1(y) \approx (\pi/2 y)^{1/2} \exp(-y)$, leading to [13,40]

$$\Gamma = 2D_k \frac{(abc)^{1/2}}{(n\pi kT)^{1/2}} \left( \rho_{eq}^2 \right) \exp \left( (2a^3 bS_{eq}^1)_{o}^{1/2} / kT \right). \quad (36)$$

and $y \ll 1, K_1(y) \approx y^{-1}$, leading to [42, 43]

$$\Gamma = 2D_k a b \sigma (\rho_{eq}^2) / kT = 2 \mu_k a b \sigma (\rho_{eq}^2). \quad (37)$$

We note that in (36) the pre-exponential factor depends on temperature as $(kT)^{-3/2}$, whereas in (37) it depends on $T$ as $(kT)^{-2}$.

3.) The Dislocation Velocity.- The velocity $v_d$ of a dislocation proceeding perpendicular to the direction of its Peierls valleys by successive formation of kink pairs depends on the height $a$ of the kinks, the kink-pair formation rate $\Gamma$, and the
distance by which the two members of a kink pair separate before they cease to move. This may either be the case when they meet obstacles along the dislocation lines that are impenetrable to kinks, or when they annihilate with other kinks on the same dislocation line. The dislocation velocity will be determined by the shorter of the two distances, the separation $L$ of the obstacles or the separation $x_k$ of the two kinks in a pair before their annihilation with other kinks, so that we expect

$$v_d = v_d(L) = a\Gamma \frac{x_k L}{x_k + L}.$$  \hspace{1cm} (38)

The separation $x_k$ equals the distance that two kinks of opposite sign drift towards each other during the mean lifetime $t_k$ of the kinks. It is thus given by

$$x_k = 2\mu_k a\sigma t_k.$$  \hspace{1cm} (39)

In a stationary situation the mean lifetime $t_k$ of the kinks must be equal to the average time for the nucleation of a fresh kink pair on a dislocation segment of length $x_k$, i.e.

$$t_k = \frac{1}{x_k \Gamma}.$$  \hspace{1cm} (40)

Hence the final result for $x_k$ reads

$$x_k = (2\mu_k a\sigma \Gamma)^{1/2}.$$  \hspace{1cm} (41)

Insertion of (41) into (38) gives us

$$v_d = (2\mu_k a\sigma \Gamma)^{1/2} \frac{aL}{L + (2\mu_k a\sigma \Gamma)^{1/2}}.$$  \hspace{1cm} (42)

with the limiting cases ($x_k \ll L$)

$$v_d = a(2\mu_k a\sigma \Gamma)^{1/2}.$$ \hspace{1cm} (42a)

and ($x_k \gg L$)

$$v_d = aL \Gamma.$$  \hspace{1cm} (42b)

In materials on which measurements of dislocation velocities under the action of a known resolved applied shear stress $\sigma$ are available (e.g., Ge and Si, see Sect. 5) Eq. (42) may be compared directly with experiment.

3) For simplicity we disregard the fact that dislocations anchored in different Peierls valleys contain also geometrical kinks. Geometrical kinks will be treated separately at the end of Sect. 4.

4) As was pointed out to the author by E. MANN, the corresponding expression in ref. [42] is in error by a factor of two.
In internal friction experiments the acting stress is often so low that the equilibrium density of the kinks is maintained. We then have

\[ x_k = \left( \rho_k^{eq} \right)^{-1}. \tag{43} \]

Insertion of (43) into (41) gives us (37), as we expect from the assumptions made.

4.) Relaxation Strength and Relaxation Time. - The calculation of the internal friction and the modulus defect on the basis of the model developed so far is a formidable task. Under certain simplifying assumption a solution was given by H. ENGELKE [41,44,45] and reviewed elsewhere [19]. For the present purposes it suffices to derive some simple estimates capable of bringing out the dependence of the relaxation strength and relaxation time on temperature T and on the obstacle separation L.

The relaxation strength is proportional to the area A swept out by the dislocation segments. Following A. SEEGER, H. DONTH and F. PFaffen [46] the estimate (which in fact constitutes an upper limit for the area that a dislocation segment with line tension \( S_d \) may sweep out under the applied shear stress)

\[ A = l^2 b o/ 12S_d \tag{44} \]

may be obtained. If \( A \) denotes the total length per unit volume of those dislocations that participate in the relaxation process and if \( M \) denotes the elastic modulus appropriate for the mode of deformation employed, we have for the relaxation strength

\[ \Delta = A^2 b^2 b^2 M/12S_d. \tag{45} \]

We estimate the relaxation time \( \tau \) by calculating the time required by a dislocation moving with the velocity \( v_d(L') \) and sweeping out the area \( A \) in the manner indicated in Fig. 4. This gives us with the help of (38)

\[ \tau = \tau(L) = \frac{u_{max}}{v_d(L')} \int_0^l \frac{d u}{v_d(L')} = \frac{l}{v_d(L')} \int_0^l \frac{d L'}{v_d(L')} d L' = \frac{b oL}{S_d} \int_0^l \frac{L'}{v(L')} d L' \]

\[ = \frac{b oL}{a^2 S_d} \left( 1 + \frac{L}{2x_k} \right). \tag{46} \]

Fig. 4: A simple model for estimating the relaxation time. Full line: Dislocation fully bowed out under applied stress \( \sigma \). Dashed lines: Intermediate configurations corresponding to displacements \( u \) of the centre of the dislocation segment. The dislocation velocity is assumed to be given by \( v_d(L') \), with \( L'(u) \) indicated in the figure.
Among the interesting features of (45) is that the relaxation strength is predicted to be independent of temperature and (for a given total length of dislocations) proportional to $L^2$. Eq. (46) exhibits a transition from a linear dependence of the relaxation time for small $L$ to a quadratic one for large $L$. This transition is accompanied by a change in the temperature dependence of $\tau$.

In a crystal there will be in general a fairly wide distribution of $L$ values. Following G. SCHOECK [47] we may estimate the internal friction $Q^{-1}$ and the modulus defect by making the assumption (which is not quite correct) that for a fixed length $L$ we have a Debye relaxation process and integrating over the $L$-distribution. We denote by $\rho_L(L) \, dL$ the number of dislocation segments per unit volume with obstacle separation between $L$ and $L + dL$ contributing to the relaxation process, so that the dislocation length per unit volume is

$$\Lambda = \int_0^\infty \rho_L(L) L \, dL .$$

The internal friction measured at a circular frequency $\omega$ is then given by

$$Q^{-1}(\omega) = \frac{b^2 M}{12 S} \int_0^\infty \rho_L(L) L^3 \frac{\omega T(L)}{1 + [\omega T(L)]^2} \, dL$$

and the corresponding elastic modulus by

$$M(\omega) = M_u \left(1 - \frac{b^2 M}{12 S} \int_0^\infty \frac{\rho_L(L) L^3}{1 + [\omega T(L)]^2} \, dL \right) ,$$

where $\tau(L)$ is to be taken from (46) and where $M_u$ denotes the unrelaxed elastic modulus. The integral

$$I(\omega T) = \int_0^\infty \frac{\omega T \zeta^5 \exp(-\zeta)}{1 + (\omega T)^2 \zeta^4} \, d\zeta$$

which arises if $\rho_L(L) \propto \exp(-L/\bar{L})$ and $\tau \propto L^2$, has been evaluated numerically [47]. It gives a maximum value $I_{\max} = 2.2$ at $(\omega T) = 7 \cdot 10^{-2}$, where $\tau = \tau (\bar{L})$.

As remarked above, in internal friction experiments we often encounter situations where the simplifications (37) and (43) are applicable. Then (46) takes the form

$$\tau = \frac{kT}{(\frac{\rho_{eq k}}{2 a^2 S}) \frac{L}{D_k}} \left(1 + \frac{\rho_{eq k} L}{2 a^2 S} \right) .$$

Eq. (50) shows that as limiting cases the relaxation time $\tau$ may exhibit two different dependences on temperature and obstacle distance, namely in the case $\rho_{eq k} L \ll 1$ (i.e., low temperatures)

$$\tau \propto L \left(\frac{kT}{(2 H_k/kT)} \right) D_k ,$$

in the case $\rho_{eq k} L \gg 1$ (i.e., high temperatures)

$$\tau \propto L^2 \left(\frac{kT}{(2 H_k/kT)} \right)^{3/2} D_k .$$
The apparent activation enthalpies are given by
\[ H_{\text{eff}} \approx \frac{\ln \tau}{d(1/kT)} \] (53)
are given by
\[ H_{\text{eff}} = 2H_k - \frac{d\ln D_k}{d(1/kT)} - 2kT \] (51a)
in the case of \( \rho_k \text{eq} \ll 1 \), and by
\[ H_{\text{eff}} = H_k - \frac{d\ln D_k}{d(1/kT)} - \frac{3}{2}kT \] (52a)
in the case \( \rho_k \text{eq} \gg 1 \).

In those cases in which \( H_k \) is not small compared with the other terms, (51a) and (52a) show the remarkable feature that the activation enthalpy is higher at lower temperatures. The reason for this is that at low temperature the distance a newly generated kink has to travel until it is stopped at an obstacle is independent of temperature, whereas at high temperatures the kink may recombine with kinks of opposite sign, the density of which increases with increasing temperature.

Another important special case is that in which kink-pair formation may be disregarded altogether (e.g., because of low temperatures) and we have to consider only a temperature-independent density \( \rho_k \) of geometrical kinks. This case has been treated by A.D. Brailsford [23], C. Wüthrich [25], and A. Seeger and C. Wüthrich [48]. If these results are expressed in terms of the kink diffusivity, an approximate expression for the relaxation time is
\[ \tau = (L/\pi)^2/D_k, \] (54)
where \( L \) denotes again the distance between the obstacles. The relaxation strength is given by
\[ \Delta = \frac{8}{\pi^2} \frac{M b^2}{\kappa T} a^2 L^2 \rho_k \Lambda \cos^2 \phi. \] (55)
In (55) \( \phi \) denotes the angle between the direction of the Peierls valley and the average direction of the dislocation line, which is determined by the positions of the obstacles.

An \( L \) distribution may be handled as above and leads to the integral (49). In addition one has to average over the angle \( \phi \), taking into account that the density of geometrical kinks is given by
\[ \rho_k = \sin \phi/a. \] (56)

5.) The Kink Diffusivity \( D_k \).— The most important parameter in the general description of Sect. 4 of relaxation processes involving kink-pair formation is the kink diffusivity \( D_k \). It contains the "physics" of the relaxation process. Its calculation requires us to leave level II of the hierarchies of Table I. E.g., \( D_k \) may be controlled by the kink potential characteristic of level III, or it may be determined by the interaction
of kinks with foreign atoms or lattice vibrations. Such interactions can only be understood quantitatively if we take into account that a kink is a perturbation on an otherwise straight dislocation line that is endowed with a long-range strain field decreasing with the inverse second power of the distance from the kink. This means that we have to go back to level I of Table I.

An exhaustive theoretical treatment of $D_k$ would be beyond the scope of the present paper. We shall cover only some examples of (i) pure crystals and (ii) interactions with foreign interstitial atoms.

(i) Pure Crystals.- In pure crystals the diffusivity $D_k$ (or mobility $\mu_k = D_k/kT$) of kinks on dislocation lines with a large kink potential is determined by the rate by which kinks will overcome the kink potential. A complete theoretical treatment of this rate has not yet been given, but we have good reasons to believe that the analogy with the jumps of atomic defects in crystals is quite close. In the spirit of the transition state theory we may introduce the free enthalpy of kink migration

$$G_k^M = H_k^M - T S_k^M$$

as the difference between the free enthalpies when the kinks is in the saddle-point configuration and when it is in the position of stable equilibrium (excluding the degree of freedoms leading over the saddle-points in the second case). If $\nu_k^O$ denotes the attempt frequency with which the kink vibrates in its stable position towards the saddle-point and $a_d$ the period of the kink potential, the transition state theory gives us under the assumption $H_k^M >> kT$

$$D_k = a_d^2 \nu_k^O \exp\left(-\frac{G_k^M}{kT}\right).$$

A similar expression with the same temperature dependence may be obtained from the diffusion theory under the assumption that the mobility of a kink in its potential well between two neighbouring saddle-points is high.

Simple physical arguments indicate that the height of the kink potential, the kink migration enthalpy $H_k^M$, should depend very strongly on the nature of the chemical bond. $H_k^M$ is strongly related to the width of the kinks. If the kink width $w_k$ is much larger than the periodicity of the kink potential, $H_k^M$ will be small, since the contributions of the various atoms near the kink centre average out to a large extent. The kink potential can only be large if the kink width if comparable with or smaller than the period of the kink potential ("abrupt kinks" [23,30]). The kink width, in turn, is related to the periodic part of the Peierls potential (comp. Eq. (6)). This means that we expect a large kink potential only in dislocations and crystal structures with high Peierls barrier. For this reason the attempt [23] to attribute the BORDONI relaxation in fcc metals to the motion of abrupt geometrical kinks had to be refuted [13]. Estimates by G. SCHOTTKY [49] indicated that in fcc metals and in fact in most dislocations in metals the kink potential is so small that an observable relaxation due to the motion of geometrical kinks cannot be expected at temperatures above 1K.
As pointed out by A. Seeger and B. Šesták [24] there is one exceptional case
where one might expect, for theoretical reasons, a fairly high kink migration enthalpy
$H_{k}^{M}$ in metals. This exception concerns kinks in screw dislocations with Burgers vectors
$b = a_{0} <111>/2$ in bcc metals. P. B. Hirsch [50] recognized the possibility that because
of the threefold symmetry of $<111>$ axes in cubic crystals these dislocations might
not have a well-defined glide plane and that they may hence be sessile. For the pur-
pose of the present discussion this is equivalent to a high Peierls stress $\sigma_{P}$. With
certain modifications (see, e.g., [48]) the viewpoint of Hirsch has proved correct.
Computer simulation studies by Ch. Wüthrich [51] on an atomistic model for $\alpha$-Fe support
the suggestion of Seeger and Šesták [24] on the kink migration enthalpy in $a_{0} <111>/2$
screw dislocations in general terms without being able to make quantitative predic-
tions.

In the case of screw dislocations in bcc metals the high Peierls barrier is due
to special circumstances related to symmetry and not to chemical bonding. (Non-screw
dislocations in bcc metals or screw dislocations with other Burgers vectors possess
"normal" Peierls stresses.) The situation is different in crystals with directional
bonds, i.e., valence crystals such as germanium and silicon.

There is considerable experimental evidence, starting with the work of Dash [52]
on dislocation lines in Si decorated with Cu and later substantiated by transmission
electron microscopy that dislocations in Ge and Si lying along $<110>$ directions possess
high Peierls barriers [53]. The origin of this is thought to lie in the covalent na-
ture of bonding in Ge and Si [54,55]. It is therefore reasonable to assume that Ge
and Si possess not only high kink formation energies but that there may also be a sub-
stantial energy barrier for the migration of kinks along dislocation lines.

If the kink migration enthalpy $H_{k}^{M}$ is large enough for the kink migration barrier
to show up experimentally, the kink diffusivity (58) will in general be small enough
for the diffusion theory of kink-pair formation to be applicable. In Si and Ge the
kink formation energy is so high that at the temperatures at which dislocation velo-
cities are measured the condition
$$\rho_{k}^{eq} \cdot L \ll 1$$
(59)
is usually fulfilled.$^5$ This means that at sufficiently low stresses (37) and (42b)

$^5$ Taking the work of H. Schauburg [56] on 60° dislocations in Ge as an example, the
highest temperature used is about 800 K. With $H_{k}^{M} = 1.3$ eV (28a) gives an equilibrium
distance between kinks of the order of magnitude of 1 cm, i.e., of the specimen di-
mensions.
hold, leading to

\[ v_d = 2 \frac{D_k a^2 b L}{\rho_k^{eq2}} \sigma/kT \quad (60) \]

The experimental results reported on Ge and Si approach indeed a linear dependence of the dislocation velocities on stress at low stresses and high temperatures. From (60) follows the effective activation enthalpy of dislocation motion

\[ H_{eff}^{(1)} = \frac{d \ln v_d}{d(1/kT)} = 2 H_k + \frac{M_k}{kT} - 2kT. \quad (61) \]

At sufficiently high stresses the rate of kink-pair formation may become so large that the kink lifetime is limited by the annihilation of kinks of opposite sign. We then have to use (42a). Together with (34) and (35) this gives us

\[ v_d = 2 a^2 b \sigma \mu_k \rho_k^{eq} \left[ y K_1(y) \right]^{-1/2}. \quad (62) \]

If \( y > 0 \) the stress dependence predicted by (62) is stronger than linear. The effective activation energy is given by

\[ H_{eff}^{(h)} = -\frac{d \ln v_d}{d(1/kT)} = H_k + \frac{M_k}{kT} - \frac{3}{2} kT - \frac{y K_0(y)}{2 K_1(y)} \quad (63) \]

For \( y \gg 1 \) Eq. (63) becomes

\[ H_{eff}^{(h)} = H_k + \frac{M_k}{kT} - \frac{3}{2} kT - (a^3 b S_o^{el} \sigma/2)^{1/2}. \quad (64) \]

Solving (61) and (64) for \( H_k \) and \( H_k^M \) gives us

\[ H_k = H_{eff}^{(1)} - H_{eff}^{(h)} + kT/2 - (a^3 b S_o^{el} \sigma/2)^{1/2} \quad (65) \]

\[ H_k^M = 2H_{eff}^{(h)} - H_{eff}^{(1)} + kT + (2a^3 b S_o^{el} \sigma)^{1/2}. \quad (66) \]

For a given type of dislocation \( S_o^{el} \) may be calculated from the elastic constants, so that from measurements of \( H_{eff}^{(1)} \) and \( H_{eff}^{(h)} \) we may determine both the formation enthalpy \( H_k \) and the migration enthalpy \( H_k^M \) of kinks. For 60°-dislocations on \(<111>\) glide planes in germanium we have \( S_o^{el} = 6 \cdot 10^{-10} \) N (A.KORNER, H.O.K.KIRCHNER, Universität Wien, personal communication). From SCHAUMBURG's [56] observations on such dislocations \( [H_{eff}^{(1)} = (3.00 \pm 0.20)eV, H_{eff}^{(h)} = (1.55 \pm 0.05)eV] \) we find for Ge \( H_k = (1.39 \pm 0.25)eV \) and \( H_k^M = (0.33 \pm 0.3)eV. \)

In crystals in which \( H_k^M \) is negligibly small the kink diffusivity must be estimated by considering the interaction between kinks and phonons explicitly [13,57,58].

At low temperatures one expects \( \mu_k \) to decrease with increasing temperature roughly as \( E_{ph}^{-1} \), where \( E_{ph} \) denotes the phonon energy density.

6) Extrapolated to \( \sigma = 0 \) with the help of Eq. (21).
At sufficiently high temperatures the theory predicts $\mu_k \propto T^{-1}$, i.e., a temperature-independent kink diffusivity $D_k$. The same temperature dependence follows from (58) for $kT > H^M$.

Calculations of the absolute magnitude of $\mu_k$ are quite difficult. The estimates of SEEGER and ENGELKE [57] indicate that the conditions for the applicability of the diffusion theory of kink-pair formation (see Sect. 2) are satisfied below about one fifth to one tenth of the Debye temperature.

(ii) Solid Solutions.- Foreign atoms in solid solution may interact with kinks in several ways. There may be an attractive interaction between kinks and immobile foreign atoms, and the latter may act as pinning points for the kinks (see, e.g. (59)). Here we consider the case that on the time scale of the internal friction or relaxation experiments the foreign atoms are mobile, i.e. that they can perform at least one diffusional and/or rotational jump during a time comparable with $T$. We are particularly interested in solid solutions of foreign atoms occupying sites with lower symmetry than the host lattice, so that the kink-foreign-atom interaction may lead to a redistribution of the symmetry axes of the foreign atoms. In order to fix the ideas, we shall refer specifically to the "heavy" interstitials oxygen, nitrogen, and carbon in bcc transition metals. In several transition metals with bcc structure, in particular in α-Fe and the Group-V metals V, Nb, and Ta, these foreign atoms have been demonstrated to occupy interstices of tetragonal symmetry. The redistribution between interstices with differently oriented tetragonal axes lead to the well known Snoek relaxation effect [60]. In this particular example the elementary atomic jumps involved in the Snoek effect and in the long-range diffusion are the same; hence the activation enthalpy of the Snoek effect, $H^S$, equals that of long-range migration, $H^M$, of the interstitial atoms.

The interaction of the strain-field surrounding a kink on a dislocation with the mobile interstitial atoms in its neighbourhood may give an important contribution to the kink viscosity $\mu_k^{-1}$. Since the situation is particularly simple for kinks on $a_0 <111>/2$ screw dislocations in bcc metals we develop the following qualitative arguments [61] for this particular case. A quantitative, more general treatment will be given in a series of papers by T.O.OGURTANI, Z.Q.SUN, and the present writer.

At a given distance from a straight screw dislocation along $<111>$ the three possible $<100>$ axes of the interstices with tetragonal symmetry are energetically degenerate. The presence of a kink on the dislocation destroys this degeneracy and leads to the development of a "Snoek atmosphere" [62], i.e., the three possible $<100>$ axes of the interstices are no longer equally populated. When a kink moves along the dislocation line this Snoek cloud exerts on the kink a restoring force which may be represented in terms of a complex compliance [63]. For a slowly moving kink this leads to a dragging force which is proportional to the kink velocity, to the inverse concentration of the interstitials near the dislocation, $C_d^{-1}$, to $D/kT$, where $D$ is the diffusivity of the interstitial atoms, and to $(\lambda_1 - \lambda_2)^{1/2}$, where $\lambda_1$ and $\lambda_2$ are the
principal components of the strain tensor (elastic dipole tensor) of the interstitials. In terms of the kink diffusivity $D_k$, this means that

$$D_k \propto (\lambda_1 - \lambda_2)^2 \exp(\frac{-GM_k}{kT}) \frac{D}{C_d}$$ \hspace{1cm} (67)

Since the diffusivity of the interstitial atoms is well represented by

$$D = D_o \exp(-\frac{H^S}{kT})$$ \hspace{1cm} (68)

with temperature-independent $H^S$ and $D_o$, the temperature dependence of kink diffusivity is described by an Arrhenius law with apparent activation enthalpy $H^M_k + H^S$.

The appearance of the factor $(C_d)^{-1}$ requires some comments. Eq.(67) clearly becomes invalid when $C_d$ tends towards zero. Then other mechanisms limit $D_k$, e.g. those discussed for pure crystals. As a first approximation we may superimpose the kink viscosities due to different mechanisms, so that in the region where one mechanism replaces another reciprocal diffusivities should be added.

We treat the temperature dependence of $C_d$ by means of a simple model used in a similar context by R.deBATIST [64]. The model assumes that we may divide the sites available to the foreign atoms into bulk sites and dislocation sites with a free enthalpy of binding $G^B_d$. We denote the number of available or occupied bulk sites by $n_b$ or $N_b$, and the number of available or occupied dislocation sites by $n_d$ or $N_d$ (say, per unit volume). Straight forward statistical thermodynamics gives us [64]

$$\frac{n_d}{N_d - n_d} = \frac{n_b}{N_b - n_b} \exp(\frac{G^B_d}{kT})$$ \hspace{1cm} (69)

or, since for dilute solutions $n_b << N_b$,

$$C_d = \frac{C_b}{C_b + \exp(-\frac{G^B_d}{kT})}$$ \hspace{1cm} (70)

Here $C_b = n_b/N_b$ denotes the bulk concentration, $C_d = n_d/N_d$ the concentration of dislocations. Eq.(70) is particularly useful if the foreign-atom concentration is so high that $C_b$ may be considered as constant. Important limiting cases are $C_b \exp(G^B_d/kT) >> 1$, corresponding to a high binding enthalpy and high concentrations, and $C_b \exp(G^B_d/kT) << 1$, corresponding to small binding enthalpies and small concentrations. In the first case $C_d$ reaches its saturation value and is independent of temperature, in the second case $C_d$ shows a temperature dependence according to

$$C_d = C_b \exp(\frac{G^B_d}{kT})$$ \hspace{1cm} (71)

There may be situations (high dislocation density, high binding enthalpy, low concentration of foreign atoms) where it is not allowed to treat $C_b$ as a constant. We then have to solve

$$n_d = (N_d - n_d) n_b \exp(\frac{G^B_d}{kT})$$ \hspace{1cm} (72a)
under the auxiliary condition

\[ n_d + n_b = N \]  \hspace{1cm} (72b)

with the solution

\[ n_d = \frac{1}{2} \{ N + N_d + N_b \exp(-G^B_d/kT) - (N + N_d + N_b \exp(-G^B_d/kT))^2 - 4NN_dN_b^2 \} \hspace{1cm} (72c) \]

6. Application to Relaxation Processes and Comparison with Experiments.

(i) The Bordoni Relaxation.—The classical field of application of the theory of kink-pair formation is the Bordoni relaxation in fcc metals (comp. Sect. 1). Here \( H^M_k \) is negligibly small. According to the discussion of Sect. 5 (i) the kink diffusivity is either temperature independent or decreases with increasing temperature. This means that, depending on the length of the dislocation segments, the relationship between the effective activation energy derived from Arrhenius plots of the relaxation time are given by either (51a) or (52a)\(^7\) with a negligible or small positive value of \( d \ln D_k/(1/kT) \). A detailed comparison with experiments is beyond the scope of this paper. The reader is referred to the work of ENGELKE [44, 45] and of FANTOZZI et al. [20].

(ii) The \( \gamma \)-relaxation in pure bcc metals.—Following R.G.CHAMBERS [65] the \( \gamma \)-relaxation is defined as being related to the long-range motion of dislocations in plastic deformation. According to SEEGER and ŠESTÁK [24] the \( \gamma \)-relaxation in bcc metals is due to the formation of kink pairs on \( a_o<111>/2 \) screw dislocations. This interpretation has recently been confirmed in considerable detail.

There is a large body of evidence that at low and intermediate temperatures the flow-stress of bcc metals is controlled by the motion of the above-mentioned screw dislocations [66]. Recent measurements by ACKERMANN [67] on the temperature and strain-rate dependence of the flow stress of high-purity niobium have confirmed the kink-pair formation theory of the flow stress [68] in great detail. E.g., the temperature and strain-rate dependence following from the expressions derived of Sect. 2 including the transition between the different \( H^M_{k,p} (\sigma) \) laws at \( \sigma = \tilde{\sigma} \) could be verified and the quantities \( 2H_k + H^M_k = (0.67 \pm 0.02)\text{eV} \) and \( a^3 b S^L_0 \) could be derived from the data.

The \( \gamma \)-relaxation in high-purity Nb was studied by deLIMA and BENOIT [69] by means of internal friction experiments. After plastic deformation they found a maximum at about 250 K with an effective activation enthalpy of \( H_{\text{eff}} = (0.61 \pm 0.02)\text{eV} \), which they identified as a dislocation relaxation. Application of (51a) gives us

\[ 2H_k + H^M_k = (0.65 \pm 0.02)\text{eV} \], in excellent agreement with the value obtained from

\(^7\)Since the Bordoni relaxation is rather stable against annealing internal friction measurements may be carried out at high frequencies (in the MHz range) and high temperatures. In general such measurement will pertain to the regime \( \epsilon_k^{eq, L} >> 1 \).
ACKERMANN's flow stress measurements[67] and thus providing strong experimental evidence that the two experiments pertain indeed to the same basic process.

Since the quantity $S_0^{e1}$ may be calculated from the elastic constants, the assignment of the $\gamma$-relaxation to kink pairs on screw dislocations may be tested further by comparing experimental and theoretical values of $a^3b S_0^{e1}$. It turns out that the experimental value is eight times that calculated for kinks of height $a = (2/3)^{1/2}a_0$. This in turn is surmised to be a consequence of the particular atomic structure of screw dislocations in bcc metals, which may exhibit a symmetry-breaking effect and acquire a new property named "polarity" [48]. The occurrence of "double kinks", i.e. kinks of lowest energy with twice the height expected from the periodicity of the perfect crystal structure, is thought to be directly related to the "polarity" of $a_0<111>/2$ screw dislocations in bcc metals and to be without analogue in other dislocations.\(^8\)

(iii) The Snoek-Köster relaxation. Following A.S. NOWICK and B.S. BERRY [71] we denote by "Snoek-Köster relaxation" a relaxation process first discovered by SNOEK [60] on cold-worked iron containing nitrogen at a temperature above that of the Snoek effect. It was studied in detail by W. KÖSTER, L. BANGERT, and R. HAHN [72], who showed that the process involves an interaction between dislocations and foreign interstitial atoms (nitrogen and carbon in the case of \(\alpha\)-Fe). More specifically, according to SCHOECK [47] the relaxation effect is due to the motion of dislocations that are dragging the interstitial atoms. However, the activation enthalpy of the Snoek-Köster relaxation, $H_{SK}$, exceeds substantially the migration enthalpy $H_{MK}$ of the foreign interstitial atoms involved. One of the key questions in the interpretation of the Snoek-Köster relaxation is the origin of the difference between $H_{SK}$ and $H_{MK}$.

A. SEEGER [73] has recently proposed that the basic process of the Snoek-Köster relaxation is the formation of kink pairs in the presence of mobile interstitial atoms. This theory provides us with a classification of the Snoek-Köster relaxation according to the dislocations on which the kink pairs are formed and according to the foreign interstitial atoms involved. The "classical" Snoek-Köster relaxation is attributed by SEEGER [73] to $a_0<111>/2$ screw dislocations interacting with the "heavy" interstitials (C, N, O) but there may be analogous relaxation processes involving non-screw dislocations (with a lower kink-pair formation enthalpy) and hydrogen atoms (with a lower migration enthalpy).

The main difference between the theories of SCHOECK [47] and SEEGER [73], which give essentially the same expressions for the relaxation strength [comp.(45)], is that in the latter theory the expression for the relaxation time contains the kink

\(^8\) The use of the expression "double kink" for the kink configuration described above requires to drop "double-kink generation", originally coined by the present writer [16], as a synonym for "kink-pair formation".
formation enthalpy on specific dislocations. The kink–foreign-atom interaction is usually strong enough for the conditions for the application of the diffusion theory of kink-pair formation to be fulfilled, so that the temperature dependence of the Snoek-Köster relaxation may be obtained by inserting (34) and (67) into (36). Since the general expression for $\tau(T)$ is rather complicated, we treat a number of special cases.

(a) If the kink-formation enthalpy is very small compared to the migration enthalpy of the interstitials involved, the condition $\rho_k^{eq} L >> 1$ will be fulfilled. The temperature dependence of the relaxation time is then given by (52). Since for $H_k$ the factor $(kT)^{3/2} \exp(H_k/kT)$ is only weakly temperature dependent, the temperature dependence of the relaxation time of the Snoek-Köster effect becomes virtually the same as that of the dislocation-enhanced Snoek effect [62,74]. This is reasonable, since the lower the kink formation enthalpy and the higher the temperature, the less these two mechanisms are distinguishable. A possible example for this situation may be a relaxation effect recently studied by U. RODRIAN and H. SCHULTZ [75] on plastically deformed high-purity Ta containing fairly low concentrations of oxygen.

When the relaxation times associated with this process were represented in an Arrhenius plot:

$$\tau = \tau_\infty \exp(H_{eff}/kT)$$  \(73\)

$H_{eff} = (1.12 \pm 0.04) eV$ and a pre-exponential factor $\tau_\infty = 8 \cdot 10^{-15} s$ were obtained. Comparison with the corresponding quantities of the Snoek effect of oxygen in Ta, $H^S = 1.105 \pm 0.01 eV$, $\tau = 8.6 \cdot 10^{-15} s$ [76] shows that during the relaxation process the O atoms perform only about one jump. Thus $C_d$ may indeed be considered as temperature-independent and the above description appears appropriate.

(b) Another simple case is that of dislocations saturated with foreign atoms, realized at high interstitial concentrations and high free enthalpies of binding to the dislocations, $\rho_d^B$. Then $C_d$ is temperature independent even under equilibrium conditions. The temperature dependence of the relaxation time of the Snoek-Köster effect is given by either

$$\tau \propto T^2 \exp[(2H_k + H^M)/kT]$$  \(74\)

(if $\rho_k^{eq} L << 1$) or

$$\tau \propto T^{3/2} \exp[(H_k + H^M)/kT]$$  \(75\)

(if $\rho_k^{eq} L >> 1$). A noteworthy feature of (74) and (75) is that the expression (75) valid at higher temperatures shows the lower activation enthalpy.

For a given kink-formation enthalpy and a given length distribution of the dislocation segments the temperature of which the relaxation process is observed will be the lower the smaller the migration enthalpy $H^M$ of the interstitials. In the bcc transition metals the migration enthalpy of hydrogen is very much smaller than that of the "heavy" interstitial atoms. This means that in torsion-pendulum or after-effect measurements the Snoek-Köster relaxation associated with hydrogen is likely to occur in the regime of validity of (74) (see, e.g., [77]).
Eq. (74) represents the case treated by SEEGER [73] and found to be in reasonable agreement with the experiments on the Snoek-Köster relaxation of N and C in α-Fe. Another example which might be covered by (74) is that of O in Ta. Here RODRIAN and SCHULTZ [75], working at frequencies of about 1 Hz, observed a Snoek-Köster relaxation with an effective activation enthalpy $H_{\text{eff}} = (2.25 \pm 0.16)$ eV. The $\gamma$-relaxation, which they find in pure Ta at about 390 K, possesses an effective activation enthalpy $H_{\text{eff}} = 1.24 \pm 0.05$ eV. If we allow for a kink-migration enthalpy of $H_k = (0.08 \pm 0.04)$ eV, we find from this $2H_k = (1.23 \pm 0.09)$ eV. Together with the above-mentioned value for the migration enthalpy of oxygen in Ta this gives us $2H_k + H^M = (2.33 \pm 0.10)$ eV, in good agreement with the value of $(2.35 \pm 0.16)$ eV following from the $H_{\text{eff}}$ of RODRIAN and SCHULTZ [75]. A corollary of this interpretation is that the free enthalpy of binding oxygen to dislocations in Ta is at least 0.6 eV, in agreement with the conclusions of RODRIAN and SCHULTZ [75]. At the temperature of the Snoek-Köster relaxation the preceding analysis gives $\exp(\frac{H_k}{kT}) = 1.5 \times 10^5$ so that it is indeed plausible that the experiments pertain to the regime $\rho^\text{eq}_L \gg 1$ as assumed.

(c) Finally we treat the case $C_d \exp(\frac{H_d}{kT}) \ll 1$ and assume, following deBATIST [64], that during the determination of the effective activation enthalpy thermal equilibrium between dislocations and bulk is maintained. We then have

$$\tau = T^2 \exp \left( \frac{(2H_k + H^M + H^B_d)/kT}{\Delta} \right)$$

(76)
in the case of $\rho^\text{eq}_L \ll 1$ or

$$\tau = T^{3/2} \exp \left( \frac{(H_k + H^M + H^B_d)/kT}{\Delta} \right)$$

(77)
if $\rho^\text{eq}_L \gg 1$. ($H^B_d$ denotes the foreign-atom-dislocation binding enthalpy.)

Let us compare (76) and (77) with the Snoek-Köster relaxation of oxygen in niobium. Here we have accurate experimental values $2H_k + H^M = (0.66 \pm 0.02)$ eV [comp. subsection (ii)] and $H^M = (1.154 \pm 0.009)$ eV [75]. J.DIEHL, T.S.KE, Z.L.PAN, M.WELLER, J.X.ZHANG, and the present writer have recently studied in considerable detail the Snoek-Köster relaxation in this system and compared it with the results reported in the literature (for these see [73]).

Two distinct relaxation processes with the attributes of the Snoek-Köster relaxation are observed, viz. a rather stable process at about 725 K (measuring frequency $f = 1$ Hz) with an effective activation enthalpy $H_{\text{eff}} = (1.69 \pm 0.04)$ eV and one at about 545 K with $H_{\text{eff}} = (1.99 \pm 0.2)$ eV, which, however, is less stable against annealing. The smaller of these two effective activation enthalpies would be in excellent agreement with (74), but not the larger one. An interpretation which explains quantitatively the occurrence of two distinct "Snoek-Köster relaxations" not only in this work but also in the literature can be given by assuming that the stable (and more precisely studied) Snoek-Köster relaxation is described by (77). From this follows a binding enthalpy $H^B_d \approx 0.35$ eV. This binding enthalpy accounts then for the higher activation enthalpy in terms of (76). The interpretation implies that after
cold-work there are dislocations anchored so that $p_{eq}^k L << 1$ holds, and that subsequent annealing changes the anchoring points in such a way that at the temperature of the stable Snoek-Köster peak the condition $p_{eq}^k L >> 1$ is fulfilled. This hypothesis is clearly an interesting subject for further investigation.

(iv) Relaxation by migration of geometrical kinks. - The relaxation time is given by (54), the relaxation strength by (55). If (58) is obeyed one expects the frequency $v_k^0$ to be of the order of magnitude of the Debye frequency. This means that if there is an observable relaxation strength (i.e., the $L$ values are sufficiently large) the pre-exponential factor $\tau_\infty$ will be several powers of ten larger than the reciprocal Debye frequency. This feature allows one to distinguish the kink-migration relaxation fairly easily from the other relaxation processes discussed in this paper, since these give $\tau_\infty$ comparable with or smaller than the reciprocal Debye frequency.

Acknowledgement

The author is indebted to a large number of collaborators for discussions and help. He should like in particular to acknowledge the support by Dr. E. Mann and Dr. M. Weller.

References

[16] A. Seeger, Phil. Mag. 1, 651 (1956)
[25] Ch. Wüthrich, Scripta metall. 9, 641 (1975)
[37] A.N. Kolmogoroff, Mat. Ann. 104, 425 (1931); 108, 149 (1933)
[38] H. Gebelein, Ann. Physik (5) 19, 533 (1934)
[40] G. Stenzel, Beiträge zur Theorie der Kinken, Diplomarbeit, Technische Hochschule Stuttgart, Stuttgart 1965
[49] G. Schottky, phys. stat. sol. 5 697 (1964)
[51] Ch. Wüthrich, Phil. Mag. 35, 337 (1977)
[56] H. Schaumburg, Phil. Mag. 5, 1429 (1972)
[60] D.L. Snoek, Physica (Utrecht) 8, 711 (19417)
[61] A. Seeger, phys. stat. sol. 55, 457 (1979)
[66] B. Sesták and A. Seeger, Z. Metallkde. 69, 495, 355, 425 (1978)
[69] F. de Lima and W. Benoît, phys. stat. sol., to be published
[70] A. Seeger, submitted to Scripta metall.
[73] A. Seeger, phys. stat. sol. (a) 55, 457 (1979)
[74] A. Seeger and F.J. Wagner, phys. stat. sol. 9, 583 (1965)
[75] U. Rodrian and H. Schultz, Z. Metallkde, to be published