Dislo.cation Relaxation at High Frequencies (*).

P. G. BORDONI

 $Istituto$ di Fisica Matematica dell' Università - Pisa $Istituto$ Nazionale di Ultracustica « O. M. Corbino » - Roma

(ricevuto il 29 Giugno 1960)

 $$ **2.** Experimental results. - 3. Theory of dislocation motion. - lI. **Fundamental parameters of dislocation relaxation and influence of different treatments.** -4 . Activation energy and characteristic frequency. -5 . Relaxation spectrum. - 6. Frequency relaxation.- 7. Subsidiary dissipation peak. - 8. Influence of anneal, cold-werk, iinpurities, strain-amplitude and neutron irradiation. -9 . Relaxation peak in alloys. -10 . Conclusions.

LIST OF SYMBOLS

- \boldsymbol{b} Burger's vector of a dislocation, taken as the distance between closest rows of atoms.
- \overline{c} Velocity of elastic waves; c_e , c_t , c_t , values for extensional, transversal and longitudinal waves; also a constant.
- \boldsymbol{d} Logarithmic decrement.
- Logarithmic constant $= 2.718...$. $\boldsymbol{\rho}$
- Vibration frequency at the temperature $T : f_m$, value at the temperature T_m $\ddot{}$ of maximum energy dissipation; f_0 , relaxed value of frequency at the temperature T ; $f_{m,0}$, limiting value of f_m at very high temperatures.
- h Planck's constant.
- l Dislocation lenght.
- Boltzmann constant. \boldsymbol{k}
- \boldsymbol{m} Linear density of a dislocation.
- t Time.

^(*) Invited paper at the Seminar on « Resonance and Relaxation in Metals » of the American Society for Metals, Chicago, Ill., November 1959. Published by the permission of the A.S.M.

- w Lenght of a kinked segment of a dislocation,
- x Axis parallel to the dislocation line.
- y Axis normal to the dislocation line.
- E Energy per unit lenght which opposes the motion of a dislocation; E_0 , constant term in the series expansion of $E(y)$.
- F_1 Function of the ratio $(H_{cr}/2H_k)$ considered in Donth's theory.
- H Computed value of the activation energy; H_M, H_W, H_s , values given by Mason, Weertman, Seeger's formulae; H_k , energy of a single kink; H_{cr} , critical energy for a couple of kinks.
- M Elastic modulus; M_R , M_U , relaxed and unrelaxed values.
- N_0 Volume density of dislocations.
- Q Coefficient of resonance (quality factor) of a solid. Usually the inverse value Q^{-1} is taken as a measure of energy dissipation; Q_m^{-1} , value of Q^{-1} at the peak.
- S Total relaxation strenght; S_{ϵ} , S_{ϵ} , values for extensional and longitudinal vibrations.
- T Absolute temperature; T_m , temperature of maximum energy dissipation.
- U Vibration energy.
- W Experimental value of the activation energy for the relaxation effect; W', value for the Niblett and Wilks peak; \overline{W} , central value of a spectrum of activation energies.
- Y Attenuation function for a single relaxation time; \overline{Y}_r , \overline{Y}_w , values computed for the centers of a time- or of an energy-spectrum.
- α Attenuation coefficient of vibration amplitude with space.
- β Temperature coefficient of frequency $=-\partial \log f/\partial T$.
- γ Parameter characterizing the width of a Fuoss-Kirkwood spectrum.
- $\delta(\tau)$ Density of relaxation strenght in a dislocation spectrum; δ_m , maximum value of $\delta(\tau)$.
- Δ Increment of some physical quantity; ΔU , increment of vibration energy; ΔW , increment of activation energy.
- Strain; ε_{el} , ε_{ao} , elastic and anelastic components. ε
- Parameter characterizing the width of a rectangular spectrum =: $\frac{1}{2} \log \tau_2 / \tau_1$: η
- 9 Debye's temperature.
- λ Wavelenght.
- μ Second Lamé's constant.
- v Computed frequency of dislocation motion; v_0 , limiting value of v at very high temperatures.
- Volume density of a solid. ϱ
- σ Stress; σ_p^0 , Feierls' stress when thermal and quantum mechanical fluctuations are disregarded.
- τ Characteristic time of a relaxation effect, at the temperature T; τ_0 , limiting value of τ at very high temperatures; $\overline{\tau}$ central value of a relaxation spectrum; τ_1 , τ_2 , values at which the density $\delta(\tau)$ is $1/\sqrt{2}$ of its maximum value δ_m ; $\bar{\tau}_0$ limiting value of $\bar{\tau}$ at very high temperatures.

1. - Introduction.

The first experimental evidence of a relaxation effect due to the dislocations was found a few years ago in some low-temperature measurements of the dissipation of elastic energy in lead, copper, aluminium and silver $[A-1]$ (1). An exhaustive investigation of the effect in copper employing both polycrystalline specimens and single crystals, was successively made by NIBLETT and WILKS $[A-4, A-8]$, by CASWELL $[A-11]$ by PARÉ $[A-13]$ by THOMPSON, GLASS and HOLMES $[A-14, A-17]$, by NUOVO, VERDINI and the A. $[A-15, A-16]$. Measurements were also made on aluminium, by HUTCHINSON, HUTTON and FILMER $[A-5, A-6, A-12]$ and by EINSPRUCH and TRUELL $[A-9]$; on lead by BOEMMEL and MASON $[A-2, A-7]$. The same effect was recently found in gold, palladium and platinum by $N\text{UVVO}$, VERDINI and the A. [A-18], and in gold-silver alloys by the same AA. and BARDUCCI [A-19].

The first attempt to give a theorethical model for the dislocation motions to which the effect is related, was made by MASON $[B-2, B-4]$ assuming that a dislocation line between two pinning points could be removed from its potential well, and that the stresses due to the elastic waves would make the potential well asymmetrical, giving rise to a macroscopic anelastic strain and producing a relaxation effect. This model lays perhaps too much emphasis on the effect of impurity content, and was discussed by WEERTMAN $[B-3, B-5]$ and by SEEGER $[B-8]$, who suggested that the dislocations may be confined to certain crystallographic directions by the Peierls' stress, and may form pair of kinks, under the combined action of the thermal fluctuations and of the applied stress. The energy required by the formation of a kink pair is an intrinsic property of dislocations, and this removes the main difficulty of MASON's model. The computation of the fundamental parameters associated with the relaxation effect has been successively improved by SEEGER, DONTH and PFAFF $[B-9, B-10]$, who have shown that the relation between the relaxation frequency and the temperature does not require any special hypothesis, but is derived from the theory of stochastic processes.

The present review of the actual knowledge on dislocation relaxation is divided in two parts. In the first the experimental evidence of a thermally activated relaxation effect due to the dislocations is discussed, together with the theoretical explanations which have been proposed for this effect.

In the second part, all the basic parameters associated with the effect are considered in detail, and their experimental values are compared with those given by the theory. The influence of thermal and mechanical treatments, of impurity content, of high energy irradiation and of strain amplitude are also examined from a quantitative standpoint. Unsolved or unexplored sides of dislocation relaxation are brought to view by this analysis and hints are derived for future investigation.

 (1) The Section A of the bibliography lists the esperimental contributions; the theoretical papers are collected in Section B.

PART I. - Evidence of a dislocation relaxation.

2. - Experimental results.

When the dissipation coefficient Q^{-1} is measured as a function of the temperature for a resonant specimen of a f.c.c. metal (2) a peak is generally

Fig. 1. - Relaxation peak in commercial and chemically pure polycrystalline lead: vibration frequency $\simeq 10$ kHz [A-1].

 (2) The anelastic behaviour of a solid may be evaluated by dinamic measurements either on standing waves or on travelling waves. The coefficient O^{-1} obtained in the first case is proportional to the ratio of the energy ΔU dissipated in half a cycle to the stored energy U

$$
Q^{-1} = \pi^{-1} \frac{\Delta U}{U}.
$$

The coefficient Q^{-1} gives also the tangent of the phase angle between a sinusoidal stress and the corresponding strain.

Experiments on travelling waves of wave lenght λ give the attenuation coefficient α which measures the decrease of vibration amplitude with space. Both types of measurements are equivalent, as far as the anelastic behaviour of solids is concerned, the parameters O^{-1} and α being related by the equation

$$
Q^{-1} = \alpha \lambda \pi^{-1}.
$$

The largest number of data on dislocation relaxation has been obtained by measurements on resonant systems: hence O^{-1} will be taken in the following as a measure of the anelastic behaviour.

ultrasonic range. The temperature T_m and the height of the peak Q_m^{-1} may differ found in the experimental curve at a temperature which is considerably lower than the room temperature when the vibration frequency is in the acoustic or

considerably from one metal to another, even when the vibration frequencies have almost the same value. For instance in lead and copper for a vibration frequency near to 10kHz the temperature T_m has the value $35 \text{ }^{\circ}\text{K}$ for the first, and $82 \text{ }^{\circ} \text{K}$ for the second (Figs. 1, 2). The difference between the values of Q_m^{-1} for the same metals is even larger, as the height of the peak is about 7.10^{-5} for the former, whilst it exceeds $400 \cdot 10^{-5}$ for the latter. Differences of the same

Fig. 2. - Relaxation peak in technically pure polyerystalline copper: vibration frequency $\simeq 10$ kHz [A-16].

order are found between the attenuation peak observed in aluminium (Fig. 3) for a vibration frequency near 40 kHz and the peaks of silver, gold, palladium

Fig. 3. - Relaxation peak in chemically pure polyerystalline aluminium (99.9%) : vibration frequency $\simeq 40$ kHz [A-1].

and platinum (Fig. 4).

A common characteristic of all the above peaks is that they are a very stable feature of the low temperature dissipation measurements, no appreciable differences being found between measurements in successive runs. Moreover the temperature T_m corresponding to each vibration frequency has a characteristic value for each metal, which is little or not affected by thermal and mechanical treatments, by impurity content, by high energy irradiation and by vibration amplitude, as it will

Fig. 4. - Relaxation peak in polycrystalline specimens of chemically pure silver (99.80%) , $f \approx 50 \text{ kHz}$; gold (99.88%), $f \approx 16$ kzH; palladium (99.91%) , $f \approx 88 \text{ kHz}$; platinum (99.89%) , $f \approx 112 \text{ kHz}$ [A-18].

be shown later. It must also be noticed that for copper, silver and gold the peaks are very high, Q_m^{-1} being many times larger than the energy dissipation measured at room temperature.

From the first experiments on lead it was evident that when

measurements are made at different frequencies, the temperature of the dissipation peak increases with frequency (Fig. 5). This result was confirmed by BOEMMEL's measurements on the same material $[A-2]$ and by all the measurements made on the other metals in which the effect has been found, as it is clearly shown by Fig. 6 in which are collected the experimental curves obtained for copper in a wide frequency range $(1.8\,\text{kHz} \div 6.4\,\text{MHz})$. The measurements are accurate

enough to show that the logarithm of the vibration frequency f_m is proportional to the inverse temperature of the peak T_m

(1)
$$
\ln f_m = -\frac{c_1}{T_m} + c_2,
$$

where c_1 and c_2 are two positive constants.

As it was pointed out by MASON [A-2, A-4] this frequency dependence of the temperature of maximum dissipation indicates a thermally

Fig. 5. - Frequency dependence of the temperature of maximum dissipation in chemically pure polycrystalline lead: frequency of the first harmonic $\simeq 10$ kHz [A-1].

activated relaxation effect, associated with a characteristic time τ which depends upon the temperature according to an Arrhenius equation

(2)
$$
\tau = \tau_0 \exp\left[\frac{W}{kT}\right],
$$

where W is the activation energy and τ_0 gives the limiting value of the characteristic time at very high temperatures. This hypothesis explains not only

Fig. 6. – Frequency dependence of the temperature of maximum dissipation in technically pure polycrystalline copper. Curve A, frequency 1.8 kHz; B, 13 kHz; C, 45 kHz; D, 550 kHz; E, 2.7 MHz; F, 6.4 MHz [A-16].

the observed dependence of Q^{-1} upon frequency and temperature, but also the temperature dependence of the resonant frequency.

In fact the theory of relaxation effects shows that the energy dissipation depends upon T and f through the product $f \cdot \tau$ according to the equation

(3)
$$
Q^{-1} = Q_m^{-1} \operatorname{sech} \left[\ln (2\pi f \tau) \right] = Q_m^{-1} \operatorname{sech} \left[\ln \left(2\pi f \tau_0 \exp \left[\frac{W}{kT} \right] \right) \right].
$$

ĩ¥ī

The dissipation reaches its maximum value when $2\pi f\tau = 1$. Then for a given vibration frequency f_m , the corresponding temperature T_m of the peak is obtained multiplying (2) by $2\pi f_m$, putting T_m instead of T and equating to unity

(4)
$$
\ln f_m = -\frac{W}{kT_m} - \ln(2\pi\tau_0).
$$

Equation (4) is the same as the experimental relation (1), provided the proper

(5)

Fig. 7. - $a)$ Temperature dependence of frequency due to thermal dilatation. b) Temperature dependence of frequency for a thermally activated relaxation effect, c) Temperature dependence of dissipation for a thermally activated relaxation effect.

values are taken for the activation energy and the limiting time λ

$$
\begin{cases} W = k e_1 \\ \tau_0 = (2\pi)^{-1} \exp \left[-e_2 \right]. \end{cases}
$$

The relaxation theory predicts also b) that the resonant frequency of a given vibration mode of the specimen must change with temperature according to the

(6)
$$
\frac{f - f_0}{f_0} =
$$

$$
\frac{Q_m^{-1}}{2} \left\{ 1 + \text{tgh} \left(\ln 2\pi f \tau_0 \exp \left[\frac{W}{kT} \right] \right) \right\},
$$

where f_0 is the relaxed value of the resonant frequency. Equation (6) does not account for the monotonic frequency changes due to the effect of thermal expansion on the size of the specimen and on the elastic moduli. When the latter variation is added to that represented by (6), an inflexion point must be found in thefrequeney-temperature curve at a temperature very near to T_m

as it may be seen by Fig. 7, adding the values of frequency given by the curves $a)$ and $b)$.

In accordance with the theory, the experimental frequency-temperature curves exhibit an inflexion point corresponding to the temperature of maximum damping. As it is required by (6) the inflexion is more pronounced in those metals which have a larger value of Q_m^{-1} , as it is the case with copper (Fig. 8).

Fig. 8. - Inflexion point in the frequency-temperature curve at the temperature of maximum dissipation for technically pure polycrystalline copper [A-16].

Fig. 9. - Inflexion point in the frequency-temperature curve at the temperature of maximum dissipation for chemically pure (99.88%) polycrystalline gold [A-20].

Fig. $10. - Inflexion point in the frequency$ cy-temperature curve at the temperature of maximum dissipation for chemically pure (99.80%) polycrystallinesilver [A-20].

The inflexion is clearly seen also in gold (Fig. 9) and in silver (Fig. 10). notwithstanding the limited temperature range covered by the experimental

Fig. 11. -- Reduction of the relaxation peak due to anneal; influence of a 2-hours treatment at 175 °C on commercial polycrystalline copper: vibration frequency \simeq 30 kHz [A-1].

data. In palladium and platinum, whose dissipation peaks are smaller and flatter (Fig. 4) the inflexion is less evident, whilst in lead and silver the peaks are so small (Figs. $1, 3$) that the measurements are not accurate enough to show a frequency relaxation which does not exceed 10^{-4} .

Fig. 12. - Dependence of he height of the relaxation peak upon the annealing temperature in high purity (99.999%) oxygen-free polycrystalline copper. Curve A, after straining 8.4%; B, after 1 h anneal at 180 °C; C, after 1 h anneal at 350 °C; vibration frequency $\simeq 1$ kHz [A-8].

To conclude the general discussion of the experimental results, it must be shown that the relaxation effect is due to the dislocations. To this purpose the influence of thermal and mechanical treatments nmst be considered

Fig. 13. - Dependence of the height of the relaxation peak upon the annealing temperature in chemically pure (99.80%) polycrystalline silver. Curve A, before anneal; B, after a 4-hours treatment at 175 °C; C, after an additional 5-hours treatment at 225 °C; vibration frequency \simeq 56 kHz [A-20]

together with the measurements which have been made on single crystals. It has been found that any treatment which reduces the number of dislocations, such as anneal, decreases the height of the peak, as it shown in

Fig. 11 for a not very pure copper specimen. The 172o0 reduction of Q_m^{-1} depends upon the annealing temperature: if this temper- $\frac{17700}{2700}$ ature is high enough, the peak may be cancelled, as it is shown by Figs. 12 $\frac{2}{8}$
and 13 for copper and $\frac{3}{8}$ ^{17,600}
silver The effect of $\frac{1}{2}$ and 13 for copper and silver. The effect of anneal can be followed through the time-changes 17,500 of frequency at constant temperature when the final temperature of the $\frac{17400}{0}$ treatment has been reached (Fig. 14). The increase of frequency shows a corresponding decrease

Fig. $14.$ - Influence of anneal on polycrystalline silver (99.80%) . Increase of the resonant frequency with time at the constant temperature of 225 °C [A-20].

Fig.. 15. - Linear dependence of tho resonant frequency upon temperature in polyerystalline silver (99.80%) , after a 5 hours anneal at 225 °C [A-20].

of the number of dislocations active in the relaxation process, and explains the reduction found in the low-temperature peak. After a complete anneal, when the peak has been cancelled, the frequency-temperature curve no longer exhibits any trace of the infleetion due to the relaxation effect (fig. 15).

On the other hand, any treatment which increases the number of dislocations, such as cold work, increases also the height of the peak, when this is already present (Fig. 16), or reintroduces it, if the material has previously

undergone a complete anneal (Figs. $17, 18$). It may be added that the annealing temperature required to cancel the peak is considerably higher than room

temperature, for all metals in which the effect has been found. 250.10^{5} As it was pointed out by SEEGER σ [B-8], this excludes that the relaxation can be due to the $re-o-$ 200 rientation of divaeaneies or similar defects created by the plastic deformation which anneal out rapidly at room temperature, 150 and suggests that the peaks arc produced by the motion of dislocation segments. ¹⁰⁰

Fig. 16. - Increase of the height 50 of the peak with the amount of cold work in polyerystalline silver (99.80%) . Curve A, after a moderate cold rolling; curve *B*, after a further $\begin{bmatrix} 0 \\ 0 \end{bmatrix}$ cold rolling to $\frac{2}{3}$ of previous thickness; cold rolling to $\frac{2}{3}$ of previous thickness; vibration frequency $\simeq 56$ kHz [A-20].

All the previous measurements were made on polycrystalline specimens. However the grain structure cannot be responsible for the dissipation peaks, owing to their low temperature. The experimental proof of this has been

Fig. 17. - Increase of the height of the relaxation peak with the amount of cold work in polycrystalline copper (99.97%). Curve A, strained 0.17%; B, strained 5.5%; vibration frequency $\simeq 0.4$ kHz [A-8].

obtained by the A. [A-1] by CASWELL [A-11] and by PARÉ [A-13] who have found the dissipation peak in copper single crystals. Within the limits of experimental accuracy, the temperature T_m corresponding to a given fre-

Fig. 18. - Increase of the height of the relaxation peak with the amount of cold work in polycrystalline silver (99.80%). Curve A, after a 5 hours anneal at 225 °C; B, after 2.7% permanent strain; vibration frequency \approx 56 kHz [A-20].

quency f_m is the same for polycrystalline specimens and single crystals and the effect of annealing treatments and cold work is also qualitatively the same for both types of materials (Fig. 19). This shows that the cause of the

dissipation maximum must be directly related to the geometrical imperfections of the crystal lattice and not to the grain structure.

Fig. 19. - Relaxation peak in copper single crystals (99.999%) for various amounts of cold work. Vibration frequency $\simeq 40$ kHz [A-11].

3. - Theory ol dislocation motion.

In order to explain how the dislocations can give rise to a thermally activated relaxation effect, some model must be found for their motion under the combined action of thermal fluctuations and mechanical stress. The

Fig. 20, - Mechanism for the dislocation motion according to Mason $[B-2, B-4]$.

next step is to relate the motion of all the dislocations with the formation of an anelastic strain. The formal theory of relaxation can be successively applied to this strain to find the frequency- and temperature-dependence of the energy dissipation.

In the model proposed by MASON $[B-2, B-4]$ a dislocation line is pinned

at points A, B by impurity atoms (Fig. 20a). The lowest-energy position corresponds to a straight segment, but other equilibrium positions may exist of somewhat higher energy, in which the disloe~tion is *kinked* (Fig. 20b). The central part of the dislocation is then displaced in the glide plane of an amount b , equal to the distance between closest lines of atoms in the same plane. Owing to the Peierls' stress, a dislocation must overcome a potential barrier H to go into the nearest equilibrium position (Fig. 20c). To compute this barrier, MASON assumed that the whole dislocation segment between the pinning points moves together. If the x axis is taken parallel to the dislocation line, and y normal to it, the potential per unit lenght $E(y)$ which opposes the motion of a dislocation may be represented between $y = -b/2$ and $y = + b/2$, by

(7)
$$
E(y) = E_0 - \frac{\sigma_p^0 b^2}{2\pi} \cos \frac{2\pi y}{b},
$$

where $\sigma_p^0 = 1/b(\partial E/\partial y)_{\text{max}}$, is the Peierls' stress required to force the dislocation through the steepest part of the potential, when thermal and quantum mechanical fluctuations are disregarded. Neglecting the changes in dislocation lenght, the height H_M of the potential barrier for this model, which is given by the maximum value of $l \cdot [E(y)-E(0)]$, that is

$$
(8) \hspace{3.1em} H_{M} = \frac{\sigma_{p}^{0}b^{2}l}{\pi}.
$$

is proportional to the dislocation lenght 1. This would lead to a strong dependence of the temperature of the peak on the parameters which control l , that.

is the dislocation density and the impurity content. As no such dependence is observed experimentally, some modification nmst be introduced in MASON's model, considering types of dislocation motions not controlled by the dislocation $length t$.

As it has been pointed out by WEERTMAN [B-5] it is not necessary for the whole dislocation segment to move at once in going from

Fig. 21. - Mechanism for the dislocation motion according to WEERTMAN [B-3, B-5] and to SEEGER [B-S, B-10].

one equilibrium position to another. A small kinked segment of lenght $l' < l$ may move over the potential barrier, a lower limit for l' being given by the lenght $2w$ of a kink pair (Fig. 21). Taking MASONS's estimate for w

(9)
$$
w = b \left(\frac{\mu}{\sigma_p^0}\right)^{\frac{1}{2}},
$$

and inserting 2w in equation (8) in the place of l , an approximate value is found for the energy H_w required by the formation of a kink pair

(10)
$$
H_{w} = \frac{2}{\pi} \mu b^3 \left(\frac{\sigma_p^9}{\mu}\right)^{\frac{1}{3}},
$$

where $\mu = \text{shear}$ modulus.

According to equation (10), the formation of a kink pair has an «intrinsic » character, its energy being independent of the particular lenght of dislocation lines and of their interaction with impurity atoms. Hence this model is better suited to explain the relaxation effect then the ϵ rigid motion ϵ model associated with the energy (8). However the derivation of (10) is somewhat lacking in mathematical rigour, as the maximum value of potential (7) is applied to a kinked line which is not parallel to the direction of maximum energy; moreover the approximate value (9) is taken as the lenght of a kink. and the changes in dislocation lenght are neglected.

 Λ more satisfactory computation of the energy associated with the formation of kinks has been given by SEEGEF $[B-8]$. The starting point is the differential equation for the shape of an unpinned dislocation line, whose minimum energy position is parallel to the x axis

(11)
$$
E(y) \frac{\partial^2 y}{\partial x^2} = \frac{\mathrm{d}E(y)}{\mathrm{d}y} + b\sigma + m \frac{\partial^2 y}{\partial t^2},
$$

where σ = resolved shear stress in the glide system; $m =$ density per unit lenght. The periodic potential per unit lenght $E(y)$ may be represented by (7) for any value of y , a further refinement in the representation of $E(y)$ being not significant in the present state of theory (³). As $\sigma_v^0 b^2 / 2\pi \ll E_0$, the latter value will be substituted to $E(y)$ on the left side of (11). Then in the static case, with no external stresses ($\sigma = 0$) the equation becomes

(12)
$$
\frac{\mathrm{d}^2 y}{\mathrm{d} x^2} = \frac{\sigma_p^0 b}{E_0} \sin \frac{2\pi y}{b}.
$$

 (3) All the potential minima have now the same value, the dislocation being *unpinned.* The period has been taken equal to b.

 Λ solution of (12) representing a single kink of amplitude b in the positive direction of the y axis is given by

(13)
$$
y(x) = \frac{2b}{\pi} \operatorname{tg}^{-1} \left\{ \exp \left[x \left(\frac{2\pi \sigma_p^0}{E_0} \right)^{\frac{1}{2}} \right] \right\}.
$$

The displacement y tends asymptotically to zero when x tends to $-\infty$ and to b when x tend to $+\infty$. Comparing (13) with the estimate (9) for the kink width w , it is found that the latter corresponds to a dislocation displacement differing by less then $0.04b$ from its final value (4) .

A straight dislocation line lying along one of the lines $y = nb$ ($n = 0, 1, 2, 3 ...$) has the energy E_0 per unit lenght. When the line is no longer straight, the energy is increased owing to the contemporary change in lenght and to the presence of the sinusoidal term in equation (7) . If the angles made by the dislocation with the x-axis are small, the first part of the energy increase is proportional to $(dy/dx)^2$ while the second part is proportional to $(1 - \cos 2\pi y/b)$ The energy H_k of a single kink may then be computed inserting (13) into the expression

(14)
$$
\int_{-\infty}^{+\infty} \left\{ \frac{1}{2} E_0 \left(\frac{dy}{dx} \right)^2 + \frac{\sigma_v^a b^2}{2\pi} \left(1 - \cos \frac{2\pi y}{b} \right) \right\} dx.
$$

This gives for H_k (⁵)

(15)
$$
H_k = \frac{2}{\pi} \sqrt{\frac{2}{5\pi}} \cdot \mu b^3 \left(\frac{\sigma_v^0}{\mu} \right)^{\frac{1}{2}}.
$$

To compute the energy H_s associated with the formation of a kink pair SEEGER assumes that the energies of two half-kinks corresponding to a displacement $y = b/2$, add approximately to the energy H_k of one complete kink, which is given by (15). This amounts to say that the position of maximum energy through which a dislocation segment has to pass when forming a pair of kinks is approximately reached when the central part of the kink pair is on the crest of the potential barrier, nfidway between two equilibrium positions. Moreover there is an attractive force between the kink pairs, which is particularly strong for small separations d of the kinks. This force is due to the fact the total lenght of the kinked dislocation diminishes if the kinks come together by sideways motion, and eventually annihilate each other. An opposite action is exerted by the applied shear stress; if σ is the resolved

⁽⁴⁾ It must be remembered that $\sigma_p^0 b^2 / 2\pi \ll E_0$.

⁽⁵) Following SEEGER [B-8] the value $\mu b^2/5$ is taken for E_0 .

value in the glide system, it exerts a force $\sigma \cdot b$ per unit lenght of the disloca-tion which tends to increase the slipped area in the glide plane on one side of the dislocation line. For every value of the applied stress, there is a critical separation d_{cr} corresponding to an unstable equilibrium of the kink pair under the combined action of the applied stress and of the mutual attraction. The energy associated with the attraction computed for $d=d_{cr}$ must be added to H_k to obtain the total energy barrier H_s which opposes the formation of a kink pair. An approximate computation of $d_{\rm cr}$ gives for the total energy [B-8]

(16)
$$
H_s = H_k \left\{ 1 + \frac{1}{4} \ln \left(\frac{16 \sigma_p^0}{\pi \sigma} \right) \right\}.
$$

A basic difference between the above equation and the expressions (8) and (10) is that the energy barrier given by (16) depends upon the applied stress. However σ enters the energy H_s only in a logarithmic term, and the strain value for most of the measurements is from 10^{-8} to 10^{-6} . The ratio σ/μ is of the same order as the strain, while the ratio σ_{η}^0/μ associated with relaxation measurements is generally found to be near $5 \cdot 10^{-4}$. The value of the last term in (16) is from 2.0 to 3.0 and a value 2.5 may be taken as a satisfactory average for most experimental conditions [B-11]. This gives for H_s

(17)
$$
\boldsymbol{H}_s = 3.5 \boldsymbol{H}_k = 1.25 \frac{2}{\pi} \mu b^3 \left(\frac{\sigma_p^0}{\mu} \right)^{\frac{1}{3}},
$$

which differs only by the factor 1.25 from the value (10) given by WEERTMAN (6) . It may be observed that H_s tends to infinity when the applied stress tends to zero. This does not mean that kink pairs are not formed when there is no applied stress, but that they annihilate very soon after their formation.

To compute the frequency ν of formation of kink pairs as a function of the absolute temperature T is a rather difficult problem. All the above theories avoid this difficulty *assuming* that ν may be represented by an Arrhenius equation

(18)
$$
v = v_0 \cdot \exp\left[-\frac{H}{kT}\right],
$$

where H is the energy of the potential barrier opposing the dislocation motion given by (8), (10) or (17) according to the model considered and to the anal-

 (6) In Mason's treatment of Seeger's theory the factor 1.25 of eq. (17) is replaced by 2.0 as he takes the value $\mu b^2/2$ for E_0 , instead of $\mu b^2/5$ as it is done by SEEGER; see [B-11], p. 270, eq. (9.61).

ysis of its motion; v_0 is the vibration frequency of a straigh rigid dislocation line, near its position of minimum energy.

The value of v_0 is immediately obtained for small oscillations $(y \ll b/2)$ from equation (11) putting $\frac{\partial^2 y}{\partial x^2} = 0$ and $\sigma = 0$, and substituting to the sinusoidal function its argument

(19)
$$
m \frac{\mathrm{d}^2 y}{\mathrm{d}t^2} + 2\pi \sigma_p^0 y = 0.
$$

Taking ob^2 for the linear density m, as suggested by ESHELBY (?) ($o =$ volume density) and introducing the velocity $c_t = (\mu/\rho)^{\frac{1}{2}}$ of shear waves (⁸)

(20)
$$
v_0 = \frac{e}{b\sqrt{2}\pi} \left(\frac{\sigma_\nu^0}{\mu}\right)^{\frac{1}{2}}.
$$

The frequency ν given by (18) and (20) must be interpreted as the average number of kink pairs which are formed by a single dislocation in a time interval much larger than ν^{-1} .

When no applied stress is present, on the average the same number of kink pairs will be formed on both sides of a dislocation line in its glide plane. The average dislocation position coincides then with the straight equilibrium position of minimum energy, and no macroscopic strain is originatcd. An applied shear stress, much smaller than Peierls' stress, acting in the glide system of the dislocation, will cause the kinks to get further apart on one side, and nearer to each other on the opposite side, making their statistical distribution no longer symmetrical with respect to the dislocation line. The average position of the dislocation with respect to time is no more a straight line, but it is displaced towards the side in which the applied stress favors the production of kinks. A macroscopic strain is then produced by the asymmetry of the average dislocation motion. This strain is certainly not of an *elastic* type, as a finite time of the order of v^{-1} is required by the dislocations to approach a new statistical distribution after a stress is suddenly applied.

The above remarks are of a purely qualitative type. The *anelastic* character of the strain due to the dislocations could be established on a quantitative basis showing its linear dependence on the applied stress and its exponential dependence on time, after a stress is suddenly applied. Both properties are sum-

⁽⁷⁾ See J. D. ESI1ELBY: *Proc. Roy. Soc. Lo~ulon,* A 197, 396 (1949).

⁽⁸) SEEGER [B-8], p. 660 (17), takes $(E_{\nu}/m)^{\frac{1}{2}}$ for c_t . On the other hand he gives the estimate $\mu b^2/5$ for E_0 . Then his expression for v_0 differs by a factor $\sqrt{5}$ from eq. (20). The latter coincides with Mason's value [B-11], p. 271.

marized by a stress-strain relation of the type (9)

(21)
$$
\varepsilon(t) = \frac{\overline{\sigma}}{M} \left\{ 1 + \frac{\varepsilon_{\rm an}}{\varepsilon_{\rm el}} \left[1 - \exp\left[-\frac{t}{\tau} \right] \right] \right\}, \qquad \text{for } t > 0,
$$

where $\varepsilon(t)$ is the total strain corresponding to a suddenly applied stress $\bar{\sigma}$; M is an elastic modulus; ε_{el} , ε_{an} are the elastic and anelastic fraction of the strain. No attempt is made in SEEGER's theory to derive equation (21) from the analysis of the model of dislocation motion. Such an attempt could eventually be made considering the average dislocation motion and the average equilibrium position under an applied stress. It is obvious that the formation of kink pairs is symmetrical with respect to such a position~ owing to its *average* character. This means that the effect of applied stress which favors the production of kinks on one side is counteracted near the dislocations by a distribution of *elastic* stresses due to their average displacement which must therefore be proportional to the applied stress. The exponential dependence upon time shown by (21) can also be explained observing that the average dislocations motion towards a new equilibrium position, has an entirely statistical character, being controlled by the thermal fluctuations. The average motion is therefore irreversible, and the number of dislocations which in a given time make a given step towards the new equilibrium position must necessarily be a fixed fraction of the total number of dislocations which have not yet made the same step. Hence the strain-time relation is of an exponential type, as required by (21) .

Once a relation of the type (21) has been proved or adopted, the formal theory of thermally activated relaxation effects shows that the temperature dependence of the dissipation and of the resonant frequency is represented by equations (3) and (6), and the theoretical treatment of the effect is complete from a semiquantitative standpoint. A further analysis of the anelastic strain due to the dislocations motion is however needed to find a relation between the potential barrier H (given by equations (8) , (10) and (17)) and the activation energy W of equation (2). A similar relation is also needed between the relaxation time τ_0 considered in the same equation and the frequency ν_0 of dislocation motion~ computed according to (20). This analysis is replaced in SEEGER's theory by the reasonable assumptions $[B-8]$

(22)
$$
\begin{cases} W = H \\ \tau_0^{-1} = 2\pi v_0. \end{cases}
$$

In Mason's theory some of the above difficulties were avoided making use of rate theory; a similar treatment has more recently been given by SEEGER,

760

⁽⁹) See P. G. BORDONI, *Suppl. Nuovo Cimento*, 7, 144 (1950).

DONTH and PFAFF [B-10] which do not assume the validity of the Arrhenius equation (18), but try to compute the energy exchanges between dislocations and lattice by means of the Kolmogoroff equation for diffusion processes.

The model for dislocation motion is the same that has been adopted by SEEGER, and the case of a suddenly applied stress is considered. As it has been already pointed out, when the energy of a pair of kinks exceeds a critical value, the two kinks are pulled apart by the applied stress. Owing to the statistical character of the energy exchanges between dislocations and lattice, the behaviour of the formers can be represented by the diffusion of their representative points in energy space. It may be observed that the density of such points must vanish when their energy exceeds the critical value for the applied stress. The average time required by the dislocation to reach this critical energy H_{cr} is the relaxation time. The estimation for the energy barrier H_{cr} is

(23)
$$
H_{\alpha} = 2H_k \left[1 - \frac{\pi \sigma}{8\sigma_{\nu}^0} \right] = \frac{4}{\pi} \sqrt{\frac{2}{5\pi}} \mu b^3 \left(\frac{\sigma_{\nu}^0}{\mu} \right)^3 \left[1 - \frac{\pi \sigma}{8\sigma_{\nu}^0} \right],
$$

which is near to one half of the value given by (17) .

The relaxation time of equation (2) is then given by (10)

(24)
$$
\tau = \frac{16}{\sqrt{5\pi^3}} \frac{b^4 \mu}{e_i k T} \exp \left[-F_1 \right],
$$

where F_1 is a function of the two variables $(2H_k/kT)$ and $(H_{cr}/2H_k)$. The numerical values of F_1 are given by DoNTH in a graph.

The maximum dissipation Q_{m}^{-1} is also related to the volume density N_o of dislocations of lenght l by the approximate relation

$$
(25) \t\frac{l^3N_0}{24}.
$$

From a qualitative standpoint it is quite remarkable that the temperature dependence of the relaxation time is not exponential, owing to the factor $(k \cdot T)^{-1}$ in equation (24) and to the relation between F_1 and $2H_k/kT$ which is not exactly linear. However for small stresses the ratio $H_{\alpha}/2H_k$ given by (23) is very near to unity. In this case the graph of the function F_1 is represented with good accuracy by

(26)
$$
F_1 = 1 - \frac{4H_k}{kT}.
$$

 (10) The coefficient of the exponential in eq. (24) is larger by a factor 2.4 than the coefficient $(2\pi B)^{-1}$ computed by means of the eq. (15) of the paper [A-16]. This difference is due to a different estimate for E_0 and e_t .

Moreover the variations of the function $(kT)^{-1}$ with temperature are small in comparison with those of the exponential term for all the temperatures of interest in the relaxation effect. If an intermediate temperature is chosen to compute the time factor in the right member of equation (24) (for instance $T = 100$ °K), the temperature dependence of relaxation time given by the theory of SEEGER, DONTH and PFAFF can be represented with a satisfactory approximation by the simple equation

(27)
$$
\tau = \frac{16}{\sqrt{5\pi^3 \cdot e \cdot 100 \cdot k}} \frac{b^4 \mu}{e_t} \exp\left[\frac{4H_k}{kT}\right].
$$

The above equation shows that from a numerical standpoint this theory differs very little from the simpler one formerly given by SEEGER. As far as the activation energy is concerned, the difference between the value $4H_k$ taken in (27) and that 3.5 H_k given by (17) is not physically significant, owing to the uncertainty in Peierls' stress. The same happens with the relaxation times

Metal	$ g~({\rm g~cm^{-3}}) $	b (cm)	c_t (cm s ⁻¹)	μ (dyn em ⁻²)	$\sigma_{\rm n}^0/\mu$
Copper	8.96	$2.55 \cdot 10^{-8}$	$2.26 \cdot 10^5$	$4.6 \cdot 10^{11}$	$4.2 \cdot 10^{-4}$
Silver	10.49	2.88	1.6	2.9	6.0
Gold	19.3	2.88	1.2	2.85	-8.6
Palladium	12.02	2.74	2.04	5.0	10.3
Platinum	21.45	2.76	1.7	6.1	3.2
Aluminium	2.70	2.85	3.08	2.64	5.0

TABLE I. - Physical properties of some f.e.c. metals involved in the relaxation theories.

computed for the two theories; of course in this case the comparison must be made between the logarithms, owing to the exponential character of equations (2) and (27). The values of the fundamental parameters required to compute τ_0^{-1} according to (20) and (22)₂ are listed in Table I. In the same

TABLE II. – Comparison between the values of $\ln \tau_0^{-1}$ computed by means of the Seeger's theory and of the Seeger, Donth and Pfaff's theory.

		$\ln \tau_0^{-1}$		
Metal	Seeger theory	S.D.P. theory	$\frac{0}{2}$ difference	
Copper	26.84	25.97	3.3	
Silver	26.55	25.59	3.7	
Gold	26.44	25.32	4.4	
Palladium	27.12	25.49	6.3	
Platinum	26.37	25.06	5.1	
Aluminium	27.13	26.52	2.3	

Table are also given the values of σ_{η}^0/μ computed by means of (17) and (22)₁ from the experimental value of W.

As is shown by Table II, the differences between the logarithms of τ_0^{-1} computed according to the Seeger's theory and to the S.D.P. theory are quite small. It may be added that the deviations of the exact relation (24) from the Arrhenius equation are too small to be detected with certainty even when the experiments are performed in a wide frequency range. From a numerical stand point the SEEGER's theory and the diffusion theory are equivalent, the main advantage of the latter residing in the smaller number of hypotheses required and in the possibility of evalunting the density of dislocations which give rise to the relaxation effect.

PART II. - Fundamental parameters of dislocation relaxation and influence **of different treatments.**

10

4. - Activation energy and characteristic frequency.

The validity of equation (4) may be tested plotting the logarithm of frequency against the inverse T_m^{-1} of the temperature of the peak: the experimental points must then lie on a, straight line. The metals on which the dissipation peaks have been measured on specimens having the same purity and the same history, in a frequency range wide enough to make this control physically significant are aluminium, copper, silver, gold, palladium and platinum. For all these metals no system atic deviation from a straight line has been found, the slight scattering of experimental points being of the same order of the experimental accuracy (Figs. 22,

Fig. $22.$ - Frequency dependence of the temperature of maximum dissipation in polycrystalline aluminium : activation energy 0.107 eV [A-9].

23, 24). The data obtained for copper are particularly significant, owing to the wide frequency range covered by the measurements (from 1.8 kHz to 6.4MHz) and to the fact that they were made not only on the same material, but actually on the same sample. Fig. 23 shows that the

Fig. 23. - Frequency dependence of the temperature of maximum dissipation in technically pure polycrystalline copper: activation energy 0.122eV[A-15, A-16].

parameters τ_0 and W have the same value for the flexural vibrations (lower frequencies) and for the longitudinal vibrations (higher frequencies), as

the corresponding sets of experimental points lie on the same line. In fact for each type of vibrations the distance between the experimental points is large enough to show an eventual difference in the slope or position of the straight lines drawn separately through the points belonging to each type of vibration.

When the logarithm of frequency is multiplied by k , as it is done in

Fig. $24.$ - Frequency dependence of the temperature of maximum dissipation in silver, gold, palladium and platinum. Activation energies in eV : Ag, 0.124; Au, 0.158; Pd, 0.260; Pt, 0.192 [A-18]. Figs. 23, 24 the slope of the line gives the activation energy. The values obtained in this way are listed in Table III, together with the correspond-

Metal	W (eV)	$\tau_0^{-1}/2\pi$ (s^{-1})	Debye frequency (s^{-1})	σ_p^0/μ	$\frac{2\pi e_t W}{\tau_0^{-1}b^4\mu}$
Copper	0.122 (± 0.005)	$3.8 \cdot 10^{11}$	$67 \cdot 10^{11}$	$4.2 \cdot 10^{-4}$	0.6
Silver	0.124 (± 0.005)	40	45	6.0	0.04
Gold	0.158 $(+0.002)$	0.7	35	8.6	2.2
Palladium	0.260 (-0.013)	12.0	57	10.3	0.3
Platinum	0.192 (-0.006)	0.06	47	3.2	23
Aluminium	0.107 $(\pm -)$	0.13	82	5.0	24

TABLE III. - Fundamental parameters of the relaxation effect.

ing accuracy estimated from the scattering of experimental data. In the same Table are also given the values of $\tau_a^{-1/2}\pi$ computed from the intercept of the straight lines of Figs. 22, 23, 24, with the frequency axis, according to equation (2) and to the relation $2\pi f_m \tau = 1$. Hence $\tau_0^{-1} = \lim_{n \to \infty} 2\pi f_n$, and $\tau_0^{-1}/2\pi = f_{m,0}$. For comparison purposes the frequency associated with the Debye temperature ϑ has been computed for each metal from the equation $v = k\vartheta/h$, and is given in the next columm (11).

It is quite remarkable that the values taken by W in different metals are nearer to each other than could possibly be expected. This seems to support the idea of WEERTMAN and SEEGER, that the dislocation motion responsible for the effects, is associated with some intrinsic property of the dislocations, the differences between the potential barriers being small in crystals having

 \sim . .

 (1) The Debye frequencies associated with the different types of waves could be computed from the theory of specific heath of crystals, taking into account the Brillouin correction for wave lenghts of the same order as the lattice constant. However the values given in Table III are accurate enough to be compared with $\tau_a^{-1/2\pi}$.

the same structure. This result shows the interest of extending the investigation to crystals with a different structure.

The experimental value of $\tau_0^{-1/2\pi}$ is in every case smaller than the Debye's value. This is quite reasonable as the latter frequency is the highest that can be propagated in a periodic lattice. It must however be remembered that long before the melting point is reached the dislocations responsible for the relaxation effect are no longer active, as it is proved by the experiments on anneal (Figs. 11, 12~ 13). To be physically significant the comparison ought to be made taking the value of the relaxation time not for an infinite temperature, but for the highest temperature that each metal can reach without cancelling the relaxation effect. To this purpose further experiments are needed on the influence of anneal on metals of known impurity content.

The ratio of the Peierls' stress to the shear modulus can be computed according to SEEGER's theory from equations (17), $(22)_1$ and from the experimental values of W. The values obtained in this way (Table III) are all higher than those obtained in static experiments. The explanation which has been given for copper, in which this difference was first noticed, can be applied to all the metals having the same structure. It has been observed [B-8] that a great portion of the dislocations dont lie along close-packed directions. Therefore their *effective* Peierls' stress which is observed in static experiments, is several orders of magnitude smaller than σ_v^0 . This explanation removes the objection made by WEERTMAN $[B-5]$, that the formation of kink pairs cannot be responsible for the relaxation effect, as the values of σ_p^0 computed by means of (10) or (17) are too large. It was suggested [A-11, A-13, B-8] to test SEEGER's theory using the values of σ_p^0/μ given by Table III to compute the dislocation frequency v_0 by means of (20); this value could then be compared with that obtained experimentally for $\tau_0^{-1/2\pi}$. However the meaning of this comparison is not quite clear, as the preceeding theoretical discussion shows that the value of ν_0 given by (20) is probably of the same order as $\tau_0^{-1}/2\pi$, but does not necessarily coincide with it. A more significant test can be obtained eliminating σ_{θ}^0/μ from (17) and (20), and observing that the expression $c_tH_s/\nu_{\theta}b^4\mu$ is an invariant for all metals. If we make the reasonable assumption that the unknown ratio between v_0 and $\tau_0^{-1}/2\pi$ has the same value for all the metals having the same structure, the above expression must also be invariant when the experimental values of W and $\tau_0^{-1}/2\pi$ are substituted to H_s and v_0 . The last column of Table III shows that this is not the case, and that the evaluation of the relaxation time is actually the less satisfactory part of the theories of dislocation motion.

A further comparison has beell made between the experimental data for copper and the theory of SEEGER, DONTH and PFAFF. A central point has been chosen on the line of Fig. 23, to compute the function F_1 and the ratio $2H_k/kT$ for the two cases $H_{cr}/2H_k = 1$ and $H_{cr}/2H_k = 0.9$. The frequency of maximum attenuation has been evaluated as a function of the temperature by means of equation (24) and of the relation $2\pi f_m \tau = 1$. The com-

parison between the average experimental line and the $2.5 \cdot 10^{-3}$ theoretical points is shown in Fig. 25. The agreement may be considered satisfactory: however the theoretical points lie on a line somewhat steeper than the experimental one.

A slight correction of the values taken by the function F_1 $\overset{\circ}{\bullet}$ A slight correction of the values taken by the function F_1 seems therefore to be required to obtain a better agreement ≤ 10 between theory and experiment.

5. - Relaxation spectrum.

If the relaxation effect were due to the sum of many elementary effects with the same values for the activation energy and relaxation time, the experimental dissipation curves would coincide with those computed by Zener for a single relaxation time (12) .

\ Cu $\overline{\mathcal{L}}$ غ ×. .
_
_ **0.5 0 0.5 1.0 1.5 2.0-10^{*}

T:** $({}^{\circ}\text{K})$ ¹

Fig. 25. - Comparison befween the experimental data and the theory of Seeger, Donth and Pfaff for technically pure polycrystalline copper. Full circles, computed values for $H_{cr}/2H_k=1$; crosses, computed values for $H_{cr}/2H_k = 0.9$. Heavy line, average of experimental data $[A-16]$.

From equations (3) and (4) the ratio of Q^{-1} to its maximum value Q^{-1}_n can be expressed in a way independent of the frequency of measurement, as a function of the variable $W \cdot k^{-1} \cdot [T_m^{-1} - T^{-1}]$

(28)
$$
\frac{Q^{-1}}{\tilde{Q}_m^{-1}} = \operatorname{sech} \frac{W}{k} \left[\frac{1}{T_m} - \frac{1}{T} \right],
$$

where T_m is the temperature of maximum dissipation for a given frequency.

Taking for W the values given by Table III, the experimental ratio Q^{-1}/Q_{m}^{-1} has been compared with the curve (28). In every case the experi-

 (12) It must also be assumed that the ratio between the dislocation frequency and the parameter τ^{-1} which characterizes the relaxation of macroscopic anelastic strain is the same for all the dislocations. However this seems rather obvious from a physical standpoint.

mental lines are much broader than the theoretical curve for a single relaxation time, as it is shown by Figs. 26, 27 for the typical cases of copper

Fig. 26. – Values of Q^{-1}/Q^{-1} as a function of $W \cdot k^{-1}$. $\cdot (T_m^{-1} - T^{-1})$ for polycrystalline copper. Open circles, experimental points; dotted line, Zener's dissipation curve for a single relaxation time [A-16].

and gold.

Since the hypothesis of a single relaxation time must be discarded, the two simplest assumptions that can be made are:

 $a)$ all the elementary relaxation effects are associated with the same value of τ_0 but their activation energies are different:

b) all the elementary relaxation effects have the same activation energy W but the values for τ_0 are different.

Owing to the exponential relation (2) between τ and W, a constant loga-

rithmic density of relaxation times between τ_1 and τ_2 corresponds to a constant linear density for energies between the values $(\overline{W} - \Delta W)$ and $(\overline{W} + \Delta W)$. As it has been shown [A-16], the value of Q^{-1} is given for an energy spec-

Fig. 27. – Values of O^{-1}/O_m^{-1} as a function of $W \cdot k^{-1} \cdot (T_m^{-1} - T^{-1})$ for polyerystalline gold. Full circles, open circles and crosses, experimental points; dotted line, Zener's dissipation curve for a single relaxation time $[A-18]$.

trum with constant linear density by

(29)
$$
Q^{-1} = \frac{S}{2 \tilde{\Delta} W} kT \operatorname{tg}^{-1} \left[\overline{Y}_{w} \sinh \frac{\Delta W}{kT} \right],
$$

where S is the total relaxation strenght $(M_v - M_{\scriptscriptstyle R})/\sqrt{M_v \cdot M_{\scriptscriptstyle R}}$, M_v , $M_{\scriptscriptstyle R}$ being the unrelaxed and relaxed values of elastic modulus; $2\Delta W$ is the width of the energy spectrum of center \overline{W} ; \overline{Y}_w is the attenuation function for a single relaxation time computed for the centre of the relaxation spectrum

(30)
$$
\overline{Y}_w = \text{sech} \left[\ln \left(2\pi f \overline{\tau} \right) \right] = \text{sech} \left[\ln \left(2\pi f \tau_0 \exp \left[\overline{W} / k \overline{T} \right] \right] \right].
$$

The dissipation given by (29) has been compared with the experimental results for copper, taking for \overline{W} the value given by Table III and choosing

Fig. 28. - Comparison between experiment and theory for a relaxation spectrum with W variable and τ_0 constant. Curves A, C, measurements on polycrystalline copper at 13 kHz and 1 MHz. Curves B, D: computed values. W and τ_0 are given by Table III; $\Delta W = 0.019$ eV [A-16].

 ΔW in order to make the theoretical curve as near as possible to the experimental dissipation values measured at about 13 kHz. The same values of \overline{W} and ΔW have been employed to compute the dissipation for the same material at a frequency of 1 MHz. Fig. 28 shows that for the high frequency vibrations the computed curve is much narrower than the experimental one, and therefore the hypothesis a) does not seems to agree with the experimental data.

 Λ more satisfactory result is obtained from the hypothesis b) of a constant logarithmic density of the values of τ_0 . This hypothesis corresponds to a constant logarithmic density of times for every temperature, and the dissipation is given by [A-16]

(31)
$$
Q^{-1} = \frac{S}{2\eta} \operatorname{tg}^{-1} \left[\overline{Y}_r \sinh \eta \right],
$$

where S has the same meaning as in the previous equation; $\eta = \frac{1}{2} \ln \tau_{2}/\tau_{1}$, τ_2 and τ_1 being the upper and lower limits of the times spectrum, and \overline{Y}_r is given by

(32)
$$
\overline{Y}_{\tau} = \text{sech} \left[\ln (2\pi f \overline{\tau}) \right] = \text{sech} \left[\ln \left[2\pi f \overline{\tau}_0 \exp \left[W/kT \right] \right] \right].
$$

As it is shown by Fig. 29 it is possible to find a value of the parameter η characterizing the band width ($\eta = 2.70$) which makes the theorethical curves to agree fairly well with the experimental ones both at low and high frequency.

Fig. 29. - Comparison between experiment and theory for a relaxation spectrum with W constant and τ_0 variable. Curves A and C are the same as in Fig. 28; curves B, D have been computed for $\eta = 2.70$ [A-16].

To complete the comparison between the hypotheses on the different types of spectra it may observed that in the case b) the ratio Q^{-1}/Q_{m}^{-1} depends only upon the variable $Wk^{-1}[T_m^{-1} - T^{-1}]$, according to equation (31), as in the case of a single relaxation time. Hence when the experimental values of Q^{-1}/Q_{m}^{-1} are plotted as a function of the above variable, the points corresponding to all the vibration frequencies must lie on the same curve as it happens with the experimental points of the Figs. 26, 27. On the other hand this property is characteristic of the time spectra with constant energy. In fact equation (29) shows that for an energy spectrum the dissipation depends not only upon $\overline{W}\cdot k^{-1}[T_{m}^{-1}-T^{-1}]$ but also directly upon T and therefore upon the frequency of measurement. It may be concluded that the elementary relaxation effects responsible for the dissipation peaks differ in the value of τ_0 but have the same value of the activation energy. To explain this result some modification is required in the present theories of dislocation motion, as τ_0 must obviously depend from a parameter which does not affect the value of the energy.

It is not surprising that the agreement between equation (31) and the experimental data becomes poorer when the distance from the peak increases. In fact the lower values of dissipation are considerably affected by the shape of the relaxation spectrum, which is only roughly represented by a constant logarithmic density. Moreover the effect of other causes of dissipation, different from dislocation relaxation, is more severely felt when the dissipution due to the latter cause is small.

It has been shown that no detailed information on the structure of the spectrum can be expected from measurements on rehxation effects, as their « resolving power » with respect to the spectral lines is comparatively poor $(^{13})$. Some additional information about the shape of the relaxation spectrum can however be obtained, observing that the experimental points of Figs. 26, 27 are not symmetrical with respect to the peak, the points on the lower temperature side being somewhat higher than the corresponding points on the other side. As the differences are not large, it may be assumed that the main peak is associated with the symmetrical part of the curve fitting the experimental points. This symmetrical curve is quite welt represented by the function

$$
(33) \quad \frac{Q^{-1}}{Q_m^{-1}} = \text{sech}\left[\gamma \cdot \frac{W}{k} \left(\frac{1}{T_m} - \frac{1}{T}\right)\right],
$$

where the parameter γ , which represents the spectrum width, is unity for

Fig. 30. - α) Comparison between the simmetrized values of dissipation in copper obtained from Fig. 26 (open circles) and the dissipation computed for a Fuoss-Kirkwood spectrum $(z=0.392,$ heavyline). $b)$ Fuoss-Kirkwood spectrum for $\gamma = 0.392$ and rectangular spectrum having the same total relaxation strenghi and a bandwidth $\eta=2.7$ [A-16].

(¹³) See P. G. BORDON1: *Theory of relaxation effects with a continuous spectrum.* Proceedings of the I1] I.C.A. Congress, Stuttgart (September, 1959).

~ single relaxation time, and vanishes for an infinite spectrum. According to the theory given by FUOSS and KIRKWOOD (14) the relaxation spectrum density $\delta(\tau)$ which gives rise to the dissipation (33) is given by

(34)
$$
\delta(\tau) = \frac{\gamma S}{\pi} \frac{\cos (\gamma \pi/2) \cosh (\gamma \ln \tau/\tilde{\tau})}{\cos^2 (\gamma \pi/2) + \sinh^2 (\gamma \ln \tau/\tilde{\tau})}.
$$

As it is shown by Fig. $30a$ the agreement between the theoretical line computed from (33) with $\gamma = 0.39$ and the experimental points obtained from the symmetrization of Fig. 26 is good, even for values of Q^{-1}/Q_m^{-1} as low as 0.3. The same computation has been made for the other metals whose dissipation measurements were accurate enough, and the values found for the parameter γ are collected in Table IV. The relaxation times τ_1 , τ_2 for which the height of the spectrum is $1/\sqrt{2}$ of the maximum height have been computed in every case, and their ratios are listed in Table IV. When the values of τ_2/τ_1 are related to the treatments undergone by the metals it is found that the wider spectra correspond to a larger amount of cold work.

Metal	Silver	Gold	Palladium	Platinum	Copper
11	0.266	0.345	0.284	0.426	0.390
τ_2/τ_1	335	57	205	18	28

TABLE IV. - Relaxation spectra.

6. - Frequency relaxation.

The experimental data concerning the temperature dependence of the resonant frequency for copper [A-16] are accurate enough to allow a comparison between the measured values of $(f-f_0)/f_0$ and those computed according to the relaxation theory. As in equation (6), f is the frequency at the temperature T, while f_0 is the relaxed value of the resonant frequency.

The above ratio can be obtained from the experimental data subtracting from the frequency measured at the temperature T , the frequency computed with a linear extrnpolation from room temperature measurements. In this way the monotonic frequency changes due to the effect of thermal expansion are cancelled and only the effects of relaxation are left $(^{15})$.

⁽¹⁴⁾ See R. M. Fuoss and J. G. KIRKWOOD: Journ. Chem. Phys., 63, 385 (1941).

⁽¹⁵⁾ For the slight errors introduced by the linear extrapolation see [A-16].

The equation (6) is no longer valid, the effect being due to a relaxation spectrum of considerable width, as it has been shown by the dissipation measurements. For a constant logarithmic density of times, the ratio $(f-f_0)/f_0$ is given by

(35)
$$
\frac{f-f_0}{f_0} = \frac{S}{2} \left[\frac{1}{2} + \frac{1}{4\eta} \ln \frac{\cosh[\eta - Wk^{-1}(T_m^1 - T^{-1})]}{\cosh[\eta + Wk^{-1}(T_m^{-1} - T^{-1})]} \right].
$$

It must be noticed that $(f-f_0)/f_0$ for vanishing T is independent of the width q_l of the spectrum, and equals $S/2$ as in the case of a single relaxation time. The same does not happen for the maximum dissipation Q_m^{-1} which is a function of the spectrum width,

and is given by

(36)
$$
Q_w^{-1} = \frac{S}{2} \cdot \frac{\text{tg}^{-1}(\sinh \eta)}{\eta} \leq \frac{S}{2},
$$

according to (31) .

The equivalent of equation (35) cannot be obtained in closed form for a Fuoss-Kirkwood spectrum; however it is easily proved that the limiting value of $(f-f_0)/f_0$ when T vanishes is still *S/2,* whilst the maximum dissipation depends upon the spectrum width as in the former case, and is given by

$$
(37) \qquad Q_m^{-1} = \gamma \frac{S}{2} \leq \frac{S}{2}.
$$

The experimental values of $(f-f_0)/f_0$ are plotted in Fig. 31. for three different types of vibrations. The corresponding dissipation curves are also plotted in the same scale for (,omparison purposes. Two facts are immediately observed: a) the total frequency relax ation is much smaller for

Fig. 31. - Frequency-relaxation and dissipation for different vibration frequencies. Abscissae $W \cdot k^{-1} \cdot (T_m^{-1} - T^{-1})$; ordinates Q^{-1} and $(f - f_0)/f_0$. Upper curves, 1.8 kHz; middle curves, 13 kHz; lower curves, 1 MHz. Polyerystalline copper. technically pure [A-16].

longitudinal vibrations (lower diagram) then for the flexural vibrations of plates and rods (intermediate and upper diagram); b) for longitudinal vibrations the total frequency relaxation is smaller than the corresponding $Q_{\rm m}^{-1}$, in contrast with equations (36) and (37).

It is not difficult to explain a) observing that the dislocation motion changes the shape of the solid rather than its volume. As it was suggested by ZENER it may be assumed that the compressibility modulus is not affected

Fig. 32. - Comparison between the experimental rolaxation of frequency, in techni cally pure copper, at 13 kHz (Curve .1) and the theoretical curves for a constant logarithmic density $(B, \eta=2.70; C, \eta=3.5)$ or for a Fuoss-Kirkwood spectrum (D, γ) .

by the relaxation effect. The elassical relations between the elastic moduli give then rise to the following equation between the relaxation strenght S_i for longitudinal vibrations and the corresponding value S_e for flexural or extensional vibrations

et (38} ,% " ' *e;ei*

where e_t, e_t, e_t are the velocities for torsionat, extensional and longitudinal waves. Taking for them the values given by the literature, the value 0.19 is found for the ratio S_i/S_e in good agreement with the experimental curves of Fig. 31. This result shows the interest of a more extended experimental investigation of this point, as the property of not affecting the compression modulus seems to be quite important for the mechanism of dislocation motion.

Point b) is somewhat less easy to explain as it is in open eontradiction with theory; it must however be remembered that the measurements were made on polycrystalline $= 0.392$ [A-16]. (opper. The stress due to the high frequency vibrations may be consid-

ered as the sum of a purely longitudinal stress and of a more complex stress changing from grain to grain, owing to the large elastic anysotropy of copper crystals and to their random orientation. The latter stress does

not correspond to any appreciable macroscopic force, because of the randomness of grain orientation, and therefore has no influence upon the vibration frequency. On the contrary the elastic energy associated with the same stress is not negligible in comparison with the energy associated with the longitudinal part, and nmst be taken into account when the total dissipation is evaluated. Hence the dissipation is larger than the value corresponding to a purely longitudinal stress, as it is found in the lower diagram of Fig. 31. The comparison between the experimental values of $(f-f_0)/f_0$ and those computed for a constant logarithmic density or for a Fuoss-Kirkwood spectrum (Fig. 32) shows that the latter type of spectrum gives a better approximation, as it is found in dissipation measurements.

7. - Subsidiary dissipation peak.

A second peak was found by NIBLETT and WILKS below the temperature of the main dissipation maximum, in high purity (99.999%) polycrystalline copper, at vibration frequencies between 0.38 and 1.1 kHz, as it is shown by Figs. 12, 17 $[A-4, A-8]$. From the original measurements the separation of the second peak from the main one does not seem to depend upon mechanical or thermal treatments, neutron irradiation or strain amplitude. The same peak is also clearly shown at somewhat higher temperatures by PARE's measurements on copper single crystals of the same purity (99.999%) for a frequency range between 3.7 and 5.6 kHz $[A-13]$. In measurements made at higher frequencies the N.W. peak is less clearly exhibited, being rather a flat «bump » on the low temperature side of the curve (Fig. 8) even when the measurements are nmde on high purity specimens (Fig. 19). In the last measurements the separation of the two peaks is snmller than in the low frequency experiments.

The above results show that the $N.W.$ peak is due to a thermally activated relaxation effect, with an activation energy W' smaller than the energy W of the main peak. To evaluate *W',* the N.Vr peak must be separated from the main maximum. This can be done computing the $(cosh^{-1})$ of the experimental values of Q_m^{-1}/Q^{-1} and plotting it as a function of $W \cdot k^{-1}[T_m^{-1} - T^{-1}]$. According to the previous remarks on the shape of the relaxation spectrum and on the Faoss-Kirkwood approximation, the curves obtained in this way are straight lines near the main maximum and on the high temperature side, where the effects of the secondary maximum are little felt. The N.W. peak can be isolated taking the difference between the straight line, obtained by extrapolation of the values near the main maximum, and the low-temperature branch of the experimental curve. The hyperbolic secant of these values multiplied by Q_n^{-1} gives the dissipation due to the N.W. peak. Fig. 33 clearly shows the increase of the temperature T'_{m} of the subsidiary peak

I'ig. 33. - Nib!ett and Wilks peak. Polyerystalline copper technically pure. Curve A, 15 kHz; B, 1.91 MHz [A-16].

with the frequency f_m . Similar computations have been made for other measurements, and the frequencies have been plotted in a logarithmic scale against $(T'_m)^{-1}$ in Fig. 34. The experimental points are placed on a straight (solid) line, and their agreement with the values obtained by other experimenters is reasonably good [A-13]. The activation energy computed from the slope of the line has the value $W' = 0.041$ eV being about $\frac{1}{2}$ of the energy found for the main peak in the same metal (Table III). The value of $(\tau_o')^{-1}$ computed from the intercept of the experimental line with the frequency axis is smaller for

the N.W. peak than for the main peak. As it is shown by Fig. 34, the vibration frequencies corresponding to the two peaks coincide at room temperature.

Fig. 34. - Frequency dependence of the temperature of the N.W. peak (line Λ) and of the main peak (line B) in polycrystalline copper. Open circles $[A-16]$; crosses, (A-8, A-13). $W' = 0.041$ eV [A-16].

The comparatively low value found for W' supports SEEGER's explanation of the second peak [B-8]. In f.c.c, metals the dislocations lines which are responsible for the low temperature attenuation lie in the {111} glide planes along one of the close-packed directions, and have Burger's vectors $\frac{1}{2}$ (110). The angle between the dislocation line and the Burger's vector may then be either $+60^{\circ}$, or 0° . Theory shows that the energy for the formation of a kink pair must be different for the two cases, and according to (17) and (22) this gives rise to different values for the activation energy of the relaxation effect.

It may be added that recent investigations in silver, gold, palladium and platinum [A-18, A-20] have shown that the low-temperature side of the attenuation curves is always higher than the other side when the measured values are plotted as a function of $W \cdot k^{-1} [T_m^{-1} - T^{-1}]$, as it is shown by Fig. 27 in the case of gold.

This result seems to indicate the presence of a subsidiary dissipation maximum near to the main one. The N.W. peak is therefore a rather general, if not very evident, feature of the dissipation-temperature curves for f.c.c. metals. Further experiments at lower frequencies may consent the separation of the two peaks, as their activation energies are probably different, an it has been found in copper.

8. - Influence of anneal, cold-work, impurities, strain amplitude and neutron irradiation.

Experiment shows that the non-linear behaviour of metals is closely related to the thermal and mechanical treatments. On the other hand the effects of these treatments and of neutron irradiation are strongly dependent upon the impurity content. It is therefore convenient to consider together the influence on the relaxation effect of all the above causes, notwithstanding their apparent eterogeneity.

It has already been shown that an anneal at moderate temperatures reduces the height of the relaxation peak: in addition to this effect an increase of the room temperature dissipation is produced when the temperature of the treatment is raised. The second effect is generally not found in impure metals, as it was the case with some of the copper and silver specimens on which the first measurements were made $[A-1]$. In this case the peak can be easily cancelled by anneal, obtaining a low value of dissipation even at room temperature, as it is shown by Fig. 11 in the case of commercial copper after a 2 hours treatment at 175 °C. A similar treatment (1 hour at 180 °C) seems to be less effective in cancelling the peak in high purity (99.999%) copper (Fig. 12). If the temperature of the treatment is raised, the peak disappears but a considerable increase is noticed in the dissipation at room temperature, as it is also shown for a somewhat less pure copper (99.965%) by curve A of Fig. 17. All the above experiments were made on polycrystalline specimens; however CASWELL $[A-11]$ and THOMPSON and HOLMES $[A-17]$

Fig. $35.$ - Influence of anneal on polyerystalline technically pure copper. .1, after machining: B , after 16 hours at 138 ~C [A-16].

Fig. 36. - Influence of anneal on polycrystalline technically pure copper. A, after machining; B, after 2 hours at 225 °C; C, after an additional treatment for 1 hour at $242 °C[A-16]$.

have found that both effects of anneal are present in single crystals, and the same happens with polyerystalline 99.80% pure silver, as it shown by Fig. 13.

To get further information about the two effects of anneal, the dependence of the resonant frequency and of Q^{-1} upon temperature has been systematically investigated for polycrystalline 99.80% pure copper after different thermal treatments [A-16]. The reduction of the height of the peak is the only effect produced when the temperature of anneal does not exceed 225 $^{\circ}$ C (Figs. 35, 36, curves A, B). The same treatment reduces also the inflection of the frequency-temperature curve, without changing $\bar{\tau}_0$. The above changes in dissipation and frequency are easily explained assuming that the number of

Fig. 37. $-$ Influence of anneal on polycrystalline technically pure copper. A , after machining; B, after 5 hours at 146 °C; C, after an additional treatment for 6 hours at 243° C [A-16].

Fig. 38. - Influence of anneal on polycrystalline technically pure copper. A , after machining; B , after 1 hour at 600 °C [A-16].

dislocations active in the relaxation effect is decreased by a low temperature anneal.

When the annealing temperature exceeds 225 \degree C, a more drastic reduction of the peak is obtained, but the shape of the dissipation curve is entirely changed, and the room temperature dissipation is increased; in the same time the frequency is raised by an amount independent of temperature (Fig. 36, 37, curves C; Fig. 38, curve B). After an high temperature anneal (1 hour at $600 °C$ the frequency and the dissipation are very sensitive to the strain amplitude, even for strains of the order of 10^{-7} (Fig. 39). The same amplitude dependence produced by an high temperature anneal has also been found in copper single crystals $[A-11]$ and in polycrystalline silver $[A-20]$.

Fig. 39. - Strain amplitude dependence of frequency and dissipation at room temperature, in polycrystalline technically pure copper. A, after machining;

B, after 1 hour at $600 °C$ [A-16].

It may be observed that the curves C in the dissipation diagrams of Figs. 36 , 37 and the curve B in the same diagram of Fig. 38, were obtained for strains of the order of 10^{-8} and can therefore be considered as the limiting values of the dissipation for vanishing strain.

At the present time no theory exists which adequately describes all the effects of an high temperature anneal. From the temperature of the treatment it could be suspected that some of these effects are due to recrystallization, but it must be remembered that the high value of room temperature dissipation has been found also in single crystals. As it has been pointed out [A-11], the dissipation measured after a high temperature anneal seems to be independent of frequency, at least in the range covered by the available data $((0.5 \div 40) \text{ kHz})$. It would certainly be interesting to know if the temperature-independent increase of frequency shown by Figs. 36, 37, 38 which makes the explanation

of the effect more difficult, is also observed in single crystals.

All the available experimental data show that the peak is not only reduced by a low-temperature anneal but also slightly shifted towards the lower temperatures, as it may be seen from Figs. $11, 12, 13, 35, 36, 37$. This indicates that the relaxation effects more easily cancelled are those due to the dislocations associated with higher values of relaxation times. In fact, after the treatment, the centre of the relaxation times spectrum is lower than before, as it is shown by the slight decrease of T_m . Measurements on copper have shown that τ_0 may be reduced by a factor of 0.6; larger changes in the times spectrum can be expected in silver, in which the temperature shift of the peak is very evident (Fig. 13) according to recent experiments [A-20].

The effect of different amounts of cold work upon the height of the main and subsidiary peak has been investigated by NIBLETT and WILKS in 99.999% pure polycrystalline copper [A-8]. When the prestrain is of the order of 0.1% the peaks are hardly noticed; their height increases with the amount of the

prestrain, whilst the room temperature attenuation is reduced (Fig. 40). When the prestrain exceeds the value 2% , the amplitude of both peaks becomes approximately independent of the amount of prestrain. A similar investigation has been made by CASWELL on a 99.999% pure copper single crystal [A-11]. The results agree with the preceding ones, the amount of permanent strain required to reach the maximum height of the peak being somewhat higher in the latter ease, as it is shown by Fig. 19. Moreover CASWELL's experiments show that cross-rolling has a more pronounced effect on the height of the peak than continued rolling in one direction. This may be possibly due to the fact that cross-rolling activates different sets of slip planes.

Fig. 40. - Dependence of Q_m^{-1} upon cold work for a 99.999% pure polycrystalline copper [A-8]; curve A, strained 0.1%; B, 0.5%; C, 2.2%; **D, s.4%.**

The dependence of maximum dissipation upon prestrain, can be explained qualitatively [B-8] observing that the dislocations active in the relaxation effect are approximately parallel to a densely packed direction. This is only a small fraction of the total number of dislocations; as their number increases with increasing prestrain, the active fraction generally decreases, owing to the

Pig. 41. - Dependence of Q_m^{-1} on gold atomic $\%$, in a cross-rolled copper crystal [A-11].

elastic forces between dislocations. These forces increase with the number of dislocations and push them into directions different from the close packed ones.

For a small amount of cold work the increase in the total number of dislocations predominates, and the height of the peak increases. However the total number of dislocations parallel to close-packed directions soon reaches a saturation value under the controlling effect of the

elastic interaction, and the peak becomes independent of the amount of prestrain.

The effects of cross-rolling have also been compared for several copper crystals containing a different amount of gold [A-11]. As it shown by Fig. 41 the height of the peak is very sensitive to the presence of gold atoms, being

Fig. 42. – Dissipation in polycrystalline copper 9.699% pure, strained 6.6%, and neutron irradiated $(5 \cdot 10^{18} \text{ m.v.t.})$ [A-8].

reduced to about $\frac{1}{2}$ of its value in the 99.999% pure crystal, by 0,065% atomic $\%$ of gold, and being almost cancelled by 0.5 atomic $\%$ gold. The original measurements [A-Ill show that this reduction of the peak takes place without any change in its temperature, in complete agreement with the fundamental hypotheses of dislocation theory, which have been discussed above. The number of foreign atoms seems to control the number of dislocations active in the relaxation effect, but has little or no influence on the activation

Fig. 43.- Dissipation in polycrystatline copper 99.999% pure, neutron irradiated $(5.10^{18} \text{ n.v.t.}),$ and subsequently strained 5.1% [A-8].

energy and on the time $\bar{\tau}_0$.

 300 $\left(\begin{array}{ccc} 1 \ 1 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ $\left(\begin{array}{ccc} 20 & 0 \ 0 & 0 \end{array}\right)$ investigated on a 99.999% pure polycrystalline copper for a radiation flux of 5.10^{18} n.v.t. [A-8]. A substantial reduction of the height of the peak is found, together with a slight shift towards the lower temperatures, as after an anneal. This may be seen comparing the peak height of Fig. 42, which is of the order of $35 \cdot 10^{-5}$, with the peak for the same specimen (poly-

crystalline copper 99.999 % pure) before the irradiation, whose height, given by Fig. 12, is about $240 \cdot 10^{-5}$. When the sample is strained after irradiation, the height of the peak may be larger than for the unirradiated material (Fig. 43). Other measurements made on a polycrystalline specimen of commercial copper (purity not stated) for a smaller irradiation flux $(5.10^{17} \text{ n. v. t.})$ are in qualitative agreement with those of Fig. 42 [A-17]. However the peak reduction is only of 20% , and no temperature shift is found when the two curves are superposed, as it may be seen from Fig. &4. The neutron bombardment seems to have a larger effect on high purity copper crystals which have previously undergone a complete anneal at $650 °C$. The high attenuation found at room temperature after

Fig. 44. - Dissipation in technically pure polycrystalline copper. The unirradiated values have been reduced by a factor of about 20% [A-17].

anneal is reduced to $1/10$ of its value by an irradiation flux on only $2 \cdot 10^{12}$ n. v. t. while a small relaxation peak is faintly shown (Fig. 45). At the

Fig. 45. - Influence of neutron irradiation upon frequency and dissipation of a 99.999% pure copper crystal, previously annealed $[A-17]$.

same time the room temperature frequency is increased by an amount of about 2% . This result supports the hypothesis that high energy irradiation can reduce the number of active dislocations, as it is done by anneal and by increasing impurity content, but does not affect the basic parameters W and W' . Moreover the influence of irradiation seems to be strongly dependent upon the presence of foreign atoms, being rather small for impure metals.

9. - Relaxation peak in alloys.

The experimental investigation of the relaxation effect has been recently extended to a complete system of gold-silver alloys, which has been chosen owing to the complete solubility in the solid phase, due to the favourable ratio of the atomic diameters (1.0014 for silver-gold).

To make the results more easily comparable, all the specimens have undergone the same thermal and mechanical treatments, and their size has been

Fig. 46. - Dissipation in silver-gold alloys: resonant frequency $\simeq 20$ kHz [A-18].

chosen in such a way the aU their resonant frequencies are near to 20 kHz. As it is shown by Fig. 46 the peak is clearly exhibited by the systems with a small concentration of foreign atoms, and reduces to a flat bump when the atomic concentration approaches 50% . This may be clearly seen in Fig. 47, where the height Q_m^{-1} of the peak is plotted as a function of the atomic percent of gold.

On the silver side the values of Q_m^{-1} have a maximum for a concentration of about 2 atomic $\%$ of gold, the height of the peak for this alloy being more than twice that for pure silver. This result shows that a small concentration of impurities may favor the formation of active dislocations by cold work. This explanation agrees with the fact that the room temperature velocity of extensional waves c_e has a minimum for the same alloy (Fig. 48), owing to the larger number of dislocations which can move freely at that temperature. It must also be noticed that the temperature coefficient of frequency shows an anomalous behaviour for the same concentration.

Fig. 47. - Values of Q_m^{-1} and T_m as a function of gold atomic $\%$, in silver-gold alloys. Open circles, computed values of T_m [A-18].

For small concentrations of gold it is quite interesting to compare the $Q_{\rm m}^{-1}$ -concentration curve of Fig. 47, with the similar curve of Fig. 41, for a small concentration of gold in copper crystals. It is not surprising that a maximum for Q_m^{-1} is not found in the second curve. In fact owing to the less favorable ratio of the atomic diameters (1.1283 for gold-copper), corresponding to a stronger lattice distortion for the same atomic concentration, the maximum for gold-copper alloys can eventually be expected for gold concentrations smaller than 0.065 atomic percent, and therefore may have escaped the notice of the experimenters. On the other hand, it is also possible that the maximum in the Q_{m}^{-1} -concentration curve may only be found for atomic ratios very near to unity. For this reason it would be interesting to extend the investigation to small concentrations of silver-gold on the gold side, between the last alloy considered in Fig. 45 (80 atomic $\%$ gold) and the pure metal.

The temperature T_m of the peak for a vibration frequency of about 20 kHz rises gradually with the gold concentration from the value 71.5 K for pure silver to $135 \text{ }^{\circ}\text{K}$ for pure gold. This is an additional proof of the intrinsic character of the activation energy and of $\bar{\tau}_0$ which are very little influenced

Fig. 48. - Values of the extensional velocity c_e and of the frequency-temperature coefficient $\beta = -\partial \ln f/\partial T$ measured at room temperature, as a function of gold atomic %, in silver-gold alloys [A-18].

by the presence of foreign atoms. These atoms seem to be effective only in controlling the number of active dislocations and therefore the height of the peak, as it is shown by the Q_m^{-1} -concentration curve of Fig. 47.

Fig. 49. - Dependence of W on the gold atomic O_0 , in silver-gold alloys. Dotted line, linear dependence: heavy line, assumed dependence [A-18].

The activation energies for the different silver-gold alloys have not yet been measured directly. An estimate for the values of W has been obtained assuming that the energy-concentration curve turns the concavity towards the concentration axis as it happens with the velocity c_{n} of Fig. 46, and as it is suggested by the negative deviations from the Vegard's law shown by the lattice constant $(^{16})$.

The values of W obtained in this way are given in Fig. 49 as a function of the atomic concentration of gold. It will be interesting to check these values with the direct measurements of the activation energies for the same alloys.

10. - Conclusions.

The theoretical and experimental investigation on the relaxation effect, althought limited to f. c. e. metals, has given substantial contributions to the knowledge of the dislocation behaviour.

The intrinsic character of the mechanism which gives rise to the motion of dislocations near their equilibrium positions has been established beyond doubt by the experiments on the influence of anneal, cold work impurity content and neutron irradiation. This result has suggested a very satisfactory model for dislocation motion: the formation of kink pairs, whose potential barriers and characteristic frequency depend *only* upon the physical parameters of the *single* dislocations, and *not* on their density or on the presence of foreign atoms.

Conversely, the last two parameters have been found very effective in controlling the *number* of active dislocations, as it is shown by the influence of thermal and mechanical treatments, of impurity content and of neutron irradiation on the height of the relaxation peak.

Another general property which has been established is that the volume of the specimens is independent of dislocation motion. It may be added that the dislocations of a given metal have been found to differ between them rather in their characteristic frequencies than in their potential barriers.

The dislocation relaxation in f. c. c. metals has not yet been completely explored. Further information on the effect in single crystals will be helpful in defining the *types* of dislocations responsible for the two dissipation peaks. It would also be interesting to relate the relaxation effect to some direct evidence of the presence of the dislocations, such as can be obtained from X-rays or electron diffraction experuneats. Additional infor-

^{(&}lt;sup>16</sup>) C. S. BARRETT: *Structure of Metcls* (London, 1953), p. 222.

mation is required to explain the influence of high temperature anneal upon **dissipation and frequency.**

However the present review points out the opportunity of focussing the attention on the entirely unexplored field of non-f.e.c, metal crystals. It is felt that a systematic investigation of the effect in this field can be as effective as was the previous investigation on the f. c. c. metals in improving our knowledge of the dynamical behaviour of dislocations.

* * *

The Author is very grateful to Prof. M. Nuovo and Dr. L. VERDINI of the Istituto « O. M. Corbino » for their valid contribution to the present paper.

REFERENCES

A. Experimental.

- [1] P. G. BORDONI: *Journ. Acoust. Soc. Am.*, **26**, 495 (1954).
- [2] H. E. BOEMMEL: *Phys. Rev.*, **96**, 220 (1954).
- [3] H. E. BOEMMEL, W. P. MASON, A. WARNER: *Phys. Rev.,* **99**, 1894 (1955); 102, 64 (1956).
- [4] D. H. NIBLETT and J. W~LKS: *Phil. Mag.,* t, 415 (1956).
- [5] T. S. HUTCHISON and G. J. HUTTON: *Can. Journ. Phys.*, **34**, 1498 (1956).
- $[6]$ T. S. Hutchison and A. J. Filmer: *Can. Journ. Phys.*, **34**, 159 (1956).
- [7] W.P. MASOn," and t{. E. BOEMMEL: *Journ. Acoust. Soc. Am.,* 28, 930 (1956).
- [S] D. **H.** NIBLETT and **J. WiLKS:** *Pbyl. Mag.,* 2, 1427 (1957).
- [9] N. G. EINSPRUCH and R. TRUELL: *Phys. Rev.,* **109**, 652 (1958).
- [10] P, G. BORDOM and M. Nvovo: *E]]eet o] Crystal Dislocations upo~ Vibrations* (Contribution to the Paints de la Science of the Exposition Universelle de Bruxelles, 1958).
- [11] H. L. Caswell: *Journ. Appl. Phys.*, **29**, 1210 (1958).
- [12] A. J. FILMER, G. J. HUTTON and T. S. HUTCIIISON: *Journ. AppI. Phys.,* 29, 146 (1958).
- [13] V. K. PARÈ: *Experimental and Theoretical Study of low-temperature internal Friction in Copper* (Cornell University, Dept. Eng. Phys., Techn. Rep., n. 4, July 1958).
- [14] D. Thompson and F. H. Glass: *Rev. Sci. Instr.*, **29**, 1034 (1958).
- [15] P. G. BORDONI, M. NUOVO and L. VERDINI: *Phys. Rev. Lett.*, **2**, 200 (1959).
- [16] P. G. BORDONI, M. Nuovo and L. VERDINI: *Nuovo Cimento*, **14**, **273** (1959).
- [17] D. O. Thompson and D. K. Holmes: *Journ. Appl. Phys.*, **30**, 525 (1959).
- [18] P. G. BORDONI, M. Nuovo and L. VERDINI: *Relaxation of Dislocations in facecentered cubic Metals* (to be published in the Proceedings of the III I.C.A. Congress Stuttgart, September 1959).
- [19] I.]~ARDUCCI, ~I. NUOVO and L. VERDINI: *Bordotd Peak in Silver-gold Alloys* (to be published in the Proceedings of the III I.C.A. Congress Stuttgart, September 1959); *Nuovo Cimento*, (to be published).
- [20] P. G. BORDONI, M. Nuovo and L. VERDINI: *Dislocation Relaxation in Silver, Gold, Palladium and Platinum* (to be published).

B. Theoretical.

- [1] P. G. BORDONI: *Ric. Scient.*, **19**, 851 (1949).
- [2] W. P. Mason: *Phys. Rev.*, **98**, 1136 (1955); *Bell System Tech. Journ.*, **34**, 903 (1955).
- [3] J. WEERTMAN: *Journ. Appl. Phys.*, **26**, 202 (1955).
- [4] W.P. Mason: *Journ. Acoust. Soc. Am.*, **27**, 643 (1955).
- [5] J. WEERTMAN: Phys. Rev., **101**, 1429 (1956).
- [6] W.P. Mason: *Phys. Rev.*, **101**, 1430 (1956).
- [7] P. G. BORDONI: Proc. II I.C.A. Congress, 101 (1956).
- [8] A. SEEGER: *Phil. Mag.*, **1**, 651 (1956).
- [9] H. DONTH: Zeits. *f. Phys.*, **149**, 111 (1957).
- [10] A. SEEGER, H. DONTIt ~nd P. PFAFF: *Discussions Far. See.,* 23, 19 (1957).
- [11] W.P. MASON: *Physical Acoustic and the Properties of Solids* (New York, 1958) p. 266-271.