Ultrasonic Attenuation in Zinc Single Crystals While Undergoing Plastic Deformation*

GEORGE A. ALERS†
Department of Physics, The State University of Iowa, Iowa City, Iowa
(Received August 2, 1954; revised manuscript received November 22, 1954)

The attenuation of 7 Mc/sec ultrasonic pulses in zinc single crystals before, during, and following plastic deformation has been measured using the ultrasonic pulse technique. Simultaneous measurements of the time-dependent plastic strain at constant stress were made in order to study the correlation between this strain and the attenuation. The crystals were oriented in such a way that the applied stress was a direct shear on the slip plane, thus causing the deformation to proceed only by slip over this plane. At the same time the high-frequency sound pulses were sent through the crystal perpendicular to the slip plane.

It was found that the attenuation of transverse waves, whose stress vectors lay in the slip plane, was very sensitive to the deformation. Longitudinal waves, with stress vectors perpendicular to the slip plane, were substantially unaffected by the deformation. This indicates that the attenuation was caused by dislocations introduced with the deformation and moving only in the slip plane. The time-dependent changes in the attenuation and the strain enabled the motion of these dislocations to be studied.

For small plastic strains, the attenuation of the transverse waves rose during the loading process, but decreased again after the load was completed even as the crystal continued to deform with time. For larger strains, the attenuation continued to rise after the load was completed and was nearly proportional to the strain. Upon unloading, the attenuation recovered very rapidly toward its value before deformation. If the unloading was carried out in steps, the attenuation decreased while the crystal rested under some intermediate load. When this load was decreased still further, the attenuation rose very rapidly until the unloading was stopped, after which time the crystal again rested under constant stress and the attenuation again decreased.

INTRODUCTION

ALTHOUGH the exact relationship between internal friction and plastic deformation of solids is not very well understood, it is well known that the internal friction of a single metal crystal is very sensitive to any form of cold work. One type of experiment shows[1] that the internal friction is very large immediately after plastic deformation and falls rapidly in time as the specimen rests in the internal friction measuring apparatus. The magnitudes attained by the internal friction during the deformation and before the specimen reaches the measuring apparatus can only be imagined. Another type of experiment involves the composite oscillator technique of measuring internal friction wherein the stress amplitude of the vibrations set up in the specimen can be varied up to and beyond the static elastic limit. At these higher stress amplitudes the internal friction begins to increase,[2] indicating that the stress has introduced some nonelastic phenomenon. Since the former type of experiment indicates that during and directly following the deformation there are very marked changes in the internal friction, and the latter type of experiment effectively unloads the specimen before the plastic flow can develop, it was felt that an experiment which measured the internal friction continuously before, during, and after the deformation would be of some value.

In view of the present interest in the part dislocations play in both phenomena, such an experiment could be useful, since the deformation probably proceeds by some process involving the manufacture of dislocations or the regeneration of dislocations already present (Frank-Read mechanism). The internal friction should be related to the number and state of motion of these dislocations in the lattice. Thus one might hope to infer from a continuous plastic strain measurement the number of dislocations being introduced as the deformation proceeds, while the measurement of the internal friction should certainly be related to the existing state of the dislocation pattern.

In addition to these considerations, one might simply consider the internal friction as a highly structure-sensitive physical property of a material and use it to indicate the changes in the structure brought about by plastic deformation. For several years this laboratory has been studying the phenomenon of plastic deformation in single crystals of high purity zinc by measuring the strain as a function of time at constant stress. It has been rather well established[3] that the strain, ϵ, as a function of time at constant stress follows the law

$$\epsilon = bt^m,$$

where m, at room temperature, is approximately 0.5 and b is a constant which depends very strongly on the stress. This form of the deformation law does not immediately lead one to any picture of the atomic mechanism of the creep process. However, by measuring a highly structure-sensitive physical property like the internal friction of the crystal during the creep process, one might hope to get further information about the creep mechanism.

METHOD

There are basically three different techniques for measuring internal friction in metal crystals. At low

* This is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics of the Graduate College of the State University of Iowa.

† Now at the Research Laboratories of the Westinghouse Electric Corporation, East Pittsburgh, Pennsylvania.

[1] W. Koster and K. Rosenthal, Z. Metallkunde **30**, 345 (1938).

[2] C. A. Wert, J. Appl. Phys. **20**, 29 (1949).

[3] E. P. T. Tyndall, *Symposium on Plastic Deformation of Crystalline Solids*, Pittsburgh, May, 1950 (U. S. Office of Naval Research, Washington, D. C., 1950), p. 49. E. H. Weinberg, J. Appl. Phys. 24, 734 (1953).

frequencies (approximately 1 cps), a torsion pendulum is used in which the specimen forms the suspension and one measures the damping of the torsional oscillations. In order to plastically deform the specimen and measure the strain continuously while it is vibrating in torsion, one requires a longitudinal strain gauge which is not influenced by the torsional strain. Such a decoupling of the motions would not be easy to achieve for small longitudinal strains. This method has been used recently for plastic flow at large strains in polycrystalline wires.[4]

The second method involves frequencies in the kilocycle range but requires that the specimen vibrate in one of its natural modes of oscillation. It seems difficult if not impossible to apply simultaneously a static stress sufficient to cause plastic flow in such a way that the specimen could still be able to vibrate freely.

The third method is an even higher frequency method (of the order of 10 Mc/sec) and has not been used until very recently for making quantitative measurements of internal friction.[5] This is the ultrasonic pulse technique which involves using a thin wafer of quartz to introduce a short burst of high-frequency ultrasonic waves at one face of the specimen. This burst travels through the specimen and is reflected back and forth between the surfaces. A comparison of the successive heights of these echoes determines the losses in the medium. Since this method does not involve vibrating the entire body of the material being studied, it is readily applicable to the simultaneous measurement of internal friction and plastic strain. Care must be taken, however, in choosing the location of the quartz wafer on the specimen, since the plastic deformation resulting from the applied stress must not deform either the surface onto which the quartz crystal is fastened or the opposite reflecting surface. This was accomplished in the present experiment by deforming the crystal under direct shear and using a part of the surface over which the shearing stress was applied for fastening the quartz wafer. Figure 1 shows the arrangement used to obtain a shearing stress which would not tend to bend the zinc crystal. The steel plates B were held fixed and plate A

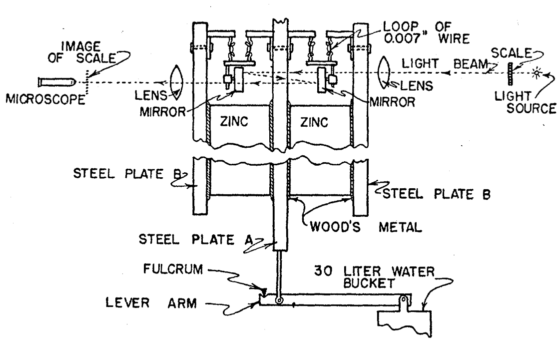

FIG. 1. Arrangement of the single crystals and optical lever system in the shearing apparatus.

[4] R. E. Maringer, J. Appl. Phys. **24**, 1525 (1953).
[5] R. L. Roderick and R. Truell, J. Appl. Phys. **23**, 267 (1952).

was pulled parallel to the plates B by means of the lever arm and water bucket. The pair of zinc crystals were two halves of the same large crystal which was grown from 99.99 percent pure zinc using the Bridgman technique. Their crystallographic orientation was determined by seeding such that the slip plane was parallel to the steel plates A and B and such that the slip direction was along the direction of the applied stress. Each crystal block was $1\frac{1}{4}$ in.$\times\frac{3}{4}$ in.$\times 3$ in. with the stress applied over the 3 in.$\times 1\frac{1}{4}$ in. surface.

Figure 2 shows the location of the quartz transducer relative to the steel plates and the zinc crystals. Holes were cut in plate B to allow the quartz crystal to be fastened directly to the zinc. The hole in plate A is necessary in order to have a zinc to air interface for reflecting the sound waves. Note that this arrangement results in propagating the sound waves down the hexagonal axis of the zinc crystal with the stress vector of longitudinal waves perpendicular to the slip plane and the stress vector of transverse waves lying in the slip plane. Consequently dislocations which are free to move only in the slip plane will respond dynamically only to transverse waves.

The strain in the crystals was measured with a sensitive optical lever system attached to the crystals as shown in Fig. 1. Using this arrangement it was possible to detect shear strains of the order of 0.5 microradian. This enables one to observe elastic stress-strain curves and to detect creep at its inception. Since the mirrors were attached to the steel plate, the measured creep could include creep in the Wood's metal used to solder the zinc to the steel plates. By substituting steel blocks for the zinc crystals, it was found that the creep in the Wood's metal was negligible.

Although pains were taken to grow the crystals with surfaces so smooth and parallel that no machining would be necessary, some machining had to be done before good echoes were obtained. This machining involved either smoothing the entire surface with emery paper or smoothing only the small area onto which the quartz crystal was to be fastened. This latter was done by means of an end mill in a milling machine. For cutting the large crystal into two blocks, an electrolytic saw was used which did not introduce any strains into the crystal. After any machining, the crystal was etched in dilute HCl.

An absolute determination of the internal friction by measurements of ultrasonic attenuation is difficult because of the variety of mechanisms, in addition to the internal friction, which extract energy from the ultrasonic beam. Relative measurements of changes in attenuation can be made quite easily by simply noting the change in height of the echoes displayed on an oscilloscope. These heights, h, decrease exponentially with echo number, n, so that

$$h=h_0e^{-\alpha_0 n}$$

where α_0 is in units of nepers per echo. If the internal friction changes during time dependent creep of the specimen, the echo heights after a time, t, are given by,

$$h=h_0e^{-[\alpha_0+\alpha(t)]n},$$

where $\alpha(t)$ is the attenuation introduced by the plastic deformation alone. It is possible to obtain a value of $\alpha(t)$ from the changes in each individual echo. The flags on the measured values of $\alpha(t)$ given in Fig. 3(a) represent the spread in values of $\alpha(t)$ obtained from analyzing all the echoes.

For the present experiment, a movie camera was used to record the echo pattern on the oscilloscope once every second. The minimum observable $\alpha(t)$ was of the order of 1×10^{-3} neper per echo. In order to express this in terms of the logarithmic decrement of the decay of the stress amplitude of the sound wave as it travels through the medium, it can be shown that

$$\text{Log dec}=\frac{1}{\tau f}\alpha,$$

where τ is the time between echoes and f is the frequency of the ultrasonic burst (here 7.8 Mc/sec). For the results presented here, $1/\tau f$ is 8.1×10^{-3} for the transverse waves. Thus a change of the logarithmic decrement of the order of 1×10^{-5} could be detected.

RESULTS

The results were obtained by using the following procedure. To begin a run, the movie camera was started and water was allowed to run into the bucket which applied the load to the crystal. After about twenty seconds the water was shut off (thus ending the loading process) and the $t=0$ reading for the strain measurement recorded from the optical lever system. The camera was allowed to continue running for about one minute during which time readings were taken of the strain as a function of the time after the completion of the load. From this time on individual pictures of the echo pattern were taken and strain measurements recorded as a function of time over a period of thirty minutes. This whole procedure was repeated several times, each time increasing the load by another increment until a series of creep runs, each at a higher stress level was obtained. The unloading procedure consisted of starting a pump to remove the water from the load bucket at the same time turning on the movie camera to record the changes in the echo pattern during and after the unloading.

The results presented are taken from data obtained in several runs on three crystals. The form of the time variation of the deformation-introduced attenuation was always the same but the amount of change introduced by a given amount of stress or strain differed widely from crystal to crystal and slightly from run to run on the same crystal. This indicates that the attenuating mechanism reacts to the stress or strain in a well defined way but the degree of reaction is dependent on the previous history of the individual crystal. Such a result could be anticipated, since the magnitude of the attenuation depends in part upon the dislocation density.

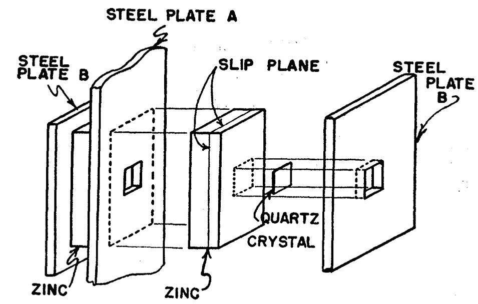

FIG. 2. Exploded view of the zinc crystal holder showing the arrangement of the quartz crystal relative to the zinc crystal and the shearing apparatus.

The most striking feature of the results is that for a crystal oriented with the slip plane exactly perpendicular to the propagation direction of the sound pulses, there was no effect of the deformation on the attenuation of longitudinal waves. On the other hand, the deformation increased the attenuation of the transverse waves to the extent that after some deformation and before unloading only the first echo remained detectable above the noise level of the amplifiers. For one of the crystals, the slip plane was tilted about five degrees away from the propagation direction and this crystal showed a small effect of the deformation on the attenuation of longitudinal waves accompanying the usual large effect on the transverse waves.

This result is exactly what dislocation theory would predict, since the dislocations move only in the slip plane and thus react only to the stresses which have components in that plane. Dislocations can give rise to an attenuation of the ultrasonic pulses only if they are in the beam of ultrasonic energy and if they are free to move under the influence of the alternating stress field of the sound wave. If they remain immobile in the beam, they would probably scatter the energy of both longitudinal and the transverse waves about equally. By moving, they can attenuate only the transverse waves by one or both of the following mechanisms. They can (1) cause a region of reduced shear modulus which would cause scattering at its boundaries due to the variation of the modulus with position in the medium, and (2) absorb energy from the sound beam to overcome "frictional" forces which tend to retard the motion of the dislocation. These two mechanisms probably both contribute but since they may well have a different frequency dependence their effects should be separable by studying the frequency dependence of the phenomenon.

The changes observed in the internal friction during loading and the subsequent time dependent creep are as follows. For loads too small to cause any nonelastic strain the attenuation of the echoes is not changed. However, as soon as the load is increased to a point where time-dependent creep begins there is a very marked increase in the attenuation. Figure 3(a) shows a typical set of curves of the quantity $\alpha(t)$ as a function of time for a series of creep curves whose log strain-log time plots are shown in Fig. 3(b). In these curves $\alpha(t)$ is taken as zero at the time the loading is started for each case. Hence all the curves pass through the origin. The vertical lines on each curve near the origin of the time axis indicate the time at which the loading was completed. The changes in $\alpha(t)$ after that time are due to the continuing plastic deformation under constant stress. The strain time curves obey the law

$$\epsilon = bt^m,$$

with m values as indicated on the curves and with t and ϵ taken as zero at the completion of the load.

A value of m from the strain-time curves which is nearly 0.3 is anomalously low when compared with the value of 0.5 usually obtained by similar experiments in this laboratory.[3] The reason for this is not completely understood. It is not because the present method involves two crystals being sheared side by side because a creep run made with only one crystal showed low m values at low stresses and m values of 0.5 at the higher stresses. The only other reason could be that all the crystals used in this experiment, probably because of their large size, were very slightly optically mosaic.[6] The effect of this mosaic structure on the form of the creep curves is not well known. Whether or not the decreasing of $\alpha(t)$ with time associated with strain-time curves with $m=0.3$ is anomalous cannot be completely settled with the present results.

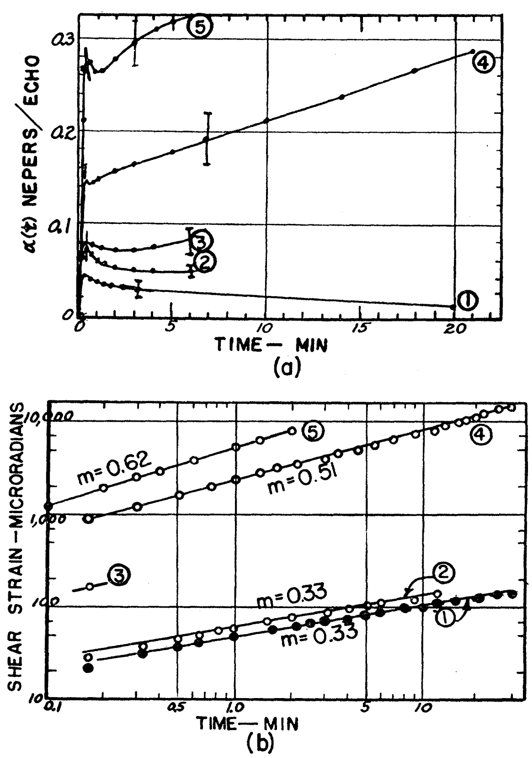

FIG. 3. (a) Attenuation *versus* time for crystal V-3 on Run I. (b) Shear strain *versus* time for Run I on crystal V-3. Shear stress: (1) 19.4; (2) 24.3; (3) 29.5; (4) 32.6; (5) 37.3 g/mm^2.

Usually the $\alpha(t)$ *versus* time curves which show $\alpha(t)$ increasing in time do not show the little maximum of $\alpha(t)$ at the completion of the load which is shown in Fig. 3(a). They are, however, smoothly increasing over the entire time range. It was found that the curves which showed this maximum were associated with strain-time curves which followed an abnormally large amount of strain during the loading process. We can interpret it as a superimposed effect which is caused by the release of a large number of dislocations which do not multiply but which move out of the crystal soon after the loading is completed.

The results imply the following features of dislocation motion and generation under a constant stress. For very small stresses (less than 10 g/mm^2), the strain is proportional to the stress and no Frank-Read sources of dislocations are activated. Hence no change is observed in the attenuation. As the stress is increased some sources become active and give rise to the nonelastic strain and the increased attenuation. At constant stress, the strain continues to increase indicating that dislocations are still being manufactured and moving toward the surface. Since the crystals used in these experiments had a mosaic structure, we may expect that the dislocation motion would be impaired particularly at low stresses. This would explain the m values of 0.3, instead of 0.5 as observed at low stresses. Apparently associated with these $m=0.3$ creep curves, the attenuation decreases with time after loading. The form of this decrease is best fitted by a relationship of the form

$$\alpha(t) = -k \log t + b \quad (t > 0.1 \text{ min}),$$

where k and b are constants. This is the same relationship which is observed to fit the decrease of attenuation with time after completely unloading the crystal. It will be shown later that this recovery mechanism probably involves the loss of mobility of the dislocations rather than their disappearance. Thus dislocations are stopped by mosaic boundaries at small stresses and they subsequently lose their ability to move in the ultrasonic beam.

For higher stresses the Frank-Read sources appear able to overcome the retarding influence of the mosaic structure and continue to manufacture dislocations. Thus we observe strain-time curves with the usual value of 0.5 for the m parameter and the lattice becomes filled with dislocations making the attenuation increase.

[6] H. K. Shilling, Physics 5, 1 (1934).

For these curves, the time dependence of the attenuation is of the same form as the time dependence of the strain. That is, for $\alpha(t)$ and t taken as zero at the completion of the load, we find that

$$\alpha(t)=At^p,$$

with A and p being constants. It must be pointed out, however, that the p values do not correspond to the m values characterizing the associated strain-time curves. Typical values of p range from 0.37 to 0.66 while the corresponding m values are 0.48 and 0.53. Thus the attenuation is not exactly proportional to the strain.

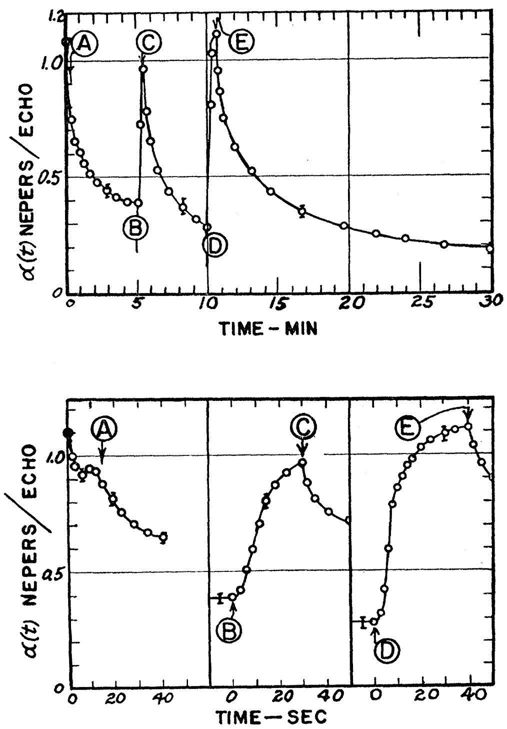

FIG. 4. (a) Recovery of the attenuation after a series of creep runs. The load is being reduced between the points $t=0$ and A, between B and C, and between D and E. (b) Changes in the attenuation during the unloading process on an expanded time scale.

During the last of a series of creep runs, the crystal is creeping under a constant stress and the attenuation is high and is increasing with time. If now the crystal is unloaded, there is a small amount of recovery of the strain and a very striking reduction in the attenuation. Figure 4(a) shows the recovery of the attenuation during and after unloading the crystal from a series of creep runs. The initial value of $\alpha(t)$ is the total attenuation accumulated during this set of runs. If or when this $\alpha(t)$ returns to zero, the crystal can be said to have returned to the value of the internal friction which it had at the start of the series of creep runs. For the case shown the load was removed in three steps, approximately one-third of the total each time. At the time

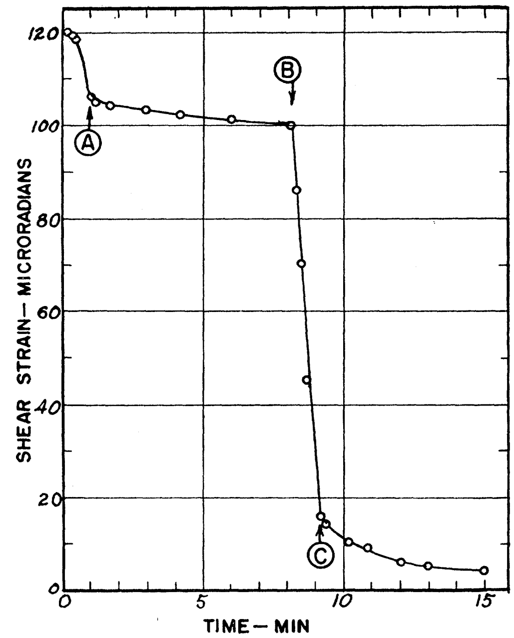

FIG. 5. Recovery of the strain when removing the load in two steps.

indicated by A on the curve, the first third of the load had been removed. The section from A to B is the change of $\alpha(t)$ under a constant load of two-thirds of the total. During the intervals of time between the zero of time and A, between B and C, and between D and E the load is being reduced. Between points C and D, $\alpha(t)$ is changing under a constant load of one-third of the total and to the right of E the changes of $\alpha(t)$ are under the condition of minimum load. Figure 4(b) shows the regions of rapidly changing $\alpha(t)$ around the points A, C, and E on a much expanded time scale.

The recovery of the strain during unloading is also affected by performing the unloading in more than one step. Figure 5 shows the strain-time curve during an unloading cycle in which the load was removed in two steps. At $t=0$ the unloading was begun. At point A the first half of the load had been removed and the curve from A to B shows the strain recovery under half the total load. At B the unloading was again begun and was complete by point C. To the right of C is the strain recovery curve for an unloaded crystal. The total amount recovered in 15 minutes is 120 microradians or about 2 percent of the total strain accumulated during the entire run. Meanwhile, the attenuation had recovered 80 percent of the amount introduced by the creep runs.

After a crystal has been deformed and unloaded, the phenomenon of static hysteresis can be observed in the stress-strain curve for very small stresses. With the stress kept well below the elastic limit observed before the deformation was introduced, the stress-strain curve labeled II in Fig. 6 was obtained. The curve labeled I

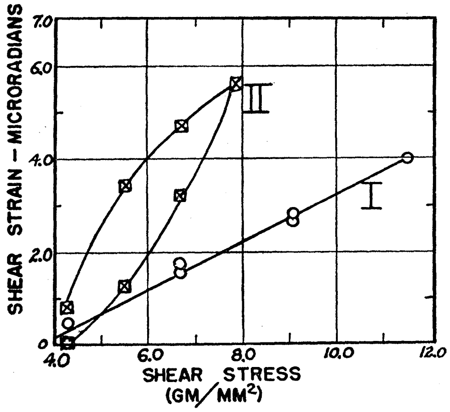

FIG. 6. Stress-strain curves before (Curve I) and after (Curve II) plastic deformation.

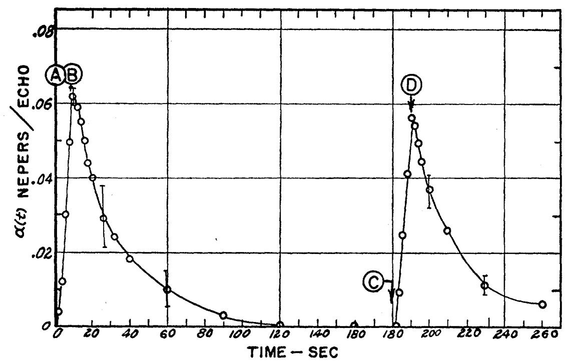

FIG. 7. Changes in the attenuation accompanying elastic hysteresis.

in the same figure is the stress-strain curve obtained before the deformation. Before the deformation there were no changes in the attenuation for loads small enough to give only elastic strains. After the creep runs and accompanying the elastic hysteresis, a very marked effect in the attenuation is observed when the crystal is loaded and unloaded. In Fig. 7 between points A and B is shown $\alpha(t)$ as a function of time during the addition of 3 g/mm^2. The variation of $\alpha(t)$ under this constant load is shown between points B and C. The unloading of the 3 g/mm^2 is shown between points C and D and is followed by the variation of $\alpha(t)$ under no load. No creep greater than 0.1 microradian/min was observed during this operation.

An interpretation of these unloading effects in terms of dislocations is that after the crystal has been run through a series of creep runs, the dislocations which have been manufactured but which did not get completely to the surface are still in the lattice and make the attenuation high. If the static stress is removed, these dislocations collapse back toward their sources where they can disappear if they do not get held up against some lattice imperfection. Upon the first partial unloading not all of the dislocations are released but some are held in place by the remaining load. The attenuation stays nearly constant during the unloading because as many dislocations move out of the beam as move into it. At the completion of this first part of the unloading, no more dislocations are released and the attenuation decreases with time. This decrease is due to either the disappearance of the dislocations or their becoming tied down so that they can no longer vibrate in the ultrasonic stress field. If the load is now further reduced, new dislocations are released as well as the ones which were tied down in the static stress field existing before this second unloading. This puts an increased number of dislocations moving in the lattice which causes great decreases in the strain and great increases in the attenuation. As soon as a static load is again reached there is no more releasing of dislocations and the attenuation decreases. This decrease is probably due to the dislocations becoming tied down rather than their complete disappearance because the phenomenon of static hysteresis still exists in the crystal and forces us to say that there are still movable dislocations in the lattice even though the attenuation may be very nearly back to the value it had before there was any deformation. The time variation of $\alpha(t)$ observed when there is static hysteresis in the crystal is explained by dislocations moving between trapping points as they readjust themselves to the new static stress conditions.

CONCLUSIONS

All of the above results apply to transverse waves whose propagation vectors lie along the normal to the slip plane. This means that their stress vectors lie in the slip plane. The polarization of these waves relative to the applied static shear stress and hence the direction of slip had no obvious effect on the results. The attenuation of the longitudinal waves was affected by the deformation only when the slip plane was not perpendicular to the propagation direction. Thus attenuation due to plastic deformation is observed only when the ultrasonic wave has a component of its stress vector in the slip plane.

This dependence of the attenuation on the stress component of the sound wave in the slip plane requires dislocations to explain the results. Even though the stress amplitudes involved in the ultrasonic sound waves are very small, it appears that dislocations are activated and can contribute to the internal friction in the megacycle range of frequencies. The ultrasonic pulse technique can thus be used to study the damping caused by dislocations.

In the ultrasonic pulse technique, the relative heights of the echoes gives information about the internal friction. In addition to this, the distance between the echoes on the time scale is directly related to the velocity of the sound in the medium which in turn is related to the elastic constants. Thus the elastic constants can be measured. During the plastic deformation process no change in the positions of the echoes on the time axis could be detected. Hence, one concludes that if the deformation introduced changes in the elastic constants C_{33} or C_{44} these changes must be less than one or two percent for strains up to 10^{-2} radian. Such a result is to be expected since the appearance of slip bands on the surface indicates that the deformation was confined to numerous very narrow bands. Within these bands one might expect very different elastic modulii but since their total thickness is small compared to the total thickness of undisturbed crystal, the sound wave spends most of its time traveling in an undeformed lattice.

The author is particularly indebted to Professor E. P. T. Tyndall for his encouragement and valuable suggestions throughout the development and performance of this experiment.

PHYSICAL REVIEW VOLUME 97, NUMBER 4 FEBRUARY 15, 1955

Motion of Electrons and Holes in Perturbed Periodic Fields

J. M. LUTTINGER* AND W. KOHN†
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received October 13, 1954)

A new method of developing an "effective-mass" equation for electrons moving in a perturbed periodic structure is discussed. This method is particularly adapted to such problems as arise in connection with impurity states and cyclotron resonance in semiconductors such as Si and Ge. The resulting theory generalizes the usual effective-mass treatment to the case where a band minimum is not at the center of the Brillouin zone, and also to the case where the band is degenerate. The latter is particularly striking, the usual Wannier equation being replaced by a set of coupled differential equations.

I. INTRODUCTION

In recent years, there has been a renewed interest in the problem of motion of charge carriers in perturbed periodic fields. The principle tool has been the so-called "effective mass" theory, which replaces the effect of the periodic field by a mass tensor, the elements of which are determined by the unperturbed band structure.[1] The rigorous theory has so far been limited almost entirely to the case where the relevant band is simple and has its lowest point at the center of the first Brillouin zone. In this form it is not directly applicable to the treatment of semiconductors such as Si and Ge. For these substances, recent "cyclotron" resonance experiments[2] indicate that both the conduction band and the valence band are not of this simple form. The conduction band for Si does not have its minimum at $\mathbf{k}=0$, but has six equivalent minima along the (100) directions of the first Brillouin zone. Similarly the conduction band in Ge consists of eight equivalent minima along (111) directions. In both these cases the principal curvatures —which determine the effective mass tensor—are known with some accuracy. For the valence band, the situation is rather more complex. The top of the valence band is at $\mathbf{k}=0$, but this is also a degeneracy point, i.e., there are several eigenfunctions with the same energy at this point. The theory of band structure in the neighborhood of such a degeneracy is due to Shockley.[3] There is in addition the complication that for such degenerate functions the spin-orbit coupling must be taken into account.[4]

We have investigated the form of the effective mass theory for these more complicated situations. For clarity, we begin with a new treatment of the case of a simple band with its lowest point at $\mathbf{k}=0$. This treatment, we believe, expresses the results of the effective mass theory in particularly compact form, and also has the advantage of being easily generalized to more complicated cases. (An alternative derivation more closely related to the work of Adams[1] is described in Appendix A. This derivation is perhaps simpler for impurity states in nondegenerate bands but is not as easily generalized for the cases of cyclotron resonance and degenerate bands.) In Sec. II, this theory will be developed for the discussion of impurity centers and "cyclotron" resonance. In Sec. III, the changes necessary for the "many-valley" case (i.e., the conduction band of Si or Ge) will be discussed. Section IV then extends the treatment to degenerate bands without spin-orbit coupling, and finally in Sec. V the modifications brought about by spin-orbit coupling are introduced.

* Permanent address: University of Michigan, Ann Arbor, Michigan.
† Permanent address: Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

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