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Internal Friction and Defect Interaction in Germanium: Experimental

J. O. KESSLER
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

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Some aspects of the interrelation of lattice defects and impurities in single crystals of germanium have been studied by means of the internal friction method. The logarithmic decrement of Ge crystals undergoing small-amplitude longitudinal forced vibrations was measured as a function of temperature, frequency, and concentration of impurities and edge dislocations.

A peak in the curve of logarithmic decrement *vs* temperature was found at 380°C, for a frequency of 40 kc/sec. From the peak shape and from the dependence of its position on the applied vibrational frequency, it was inferred that the peak is due to an anelastic relaxation phenomenon with relaxation time $\tau=\tau_0 \exp(H/RT)$, where $\tau_0=10^{-13\pm1}$ second and $H=25\pm3$ kcal/mole. At high temperatures the logarithmic decrement was found to rise with temperature according to the equation $\delta=\delta_0 \exp(-H'/RT)$, where $H'=23\pm2$ kcal/mole.

A phenomenological interpretation of these results is given in terms of a mechanism depending on the interaction of lattice vacancies with the edge components of dislocations present in the specimens. By using this interpretation, the activation energies for the generation of lattice vacancies, for their diffusion, and for self diffusion in germanium are derived. The respective values, which are 48 ± 4, 25 ± 3, and 73 ± 5 kcal/mole, are in agreement with analogous values obtained by other observers. It is also implied that 10^{10} vacancies/cm^3 are normally forzen into Ge crystals during growth. This concentration corresponds to the equilibrium concentration in the vicinity of 550°C.

INTRODUCTION

A RELATIVELY minor fraction of the vast amount of research which has been done on germanium in recent years has been concerned with the mechanical properties of that material. Accordingly, these properties are neither as well understood nor even as well delineated as the electrical properties. It has been shown that the mechanical propertics of metal and salt crystals depend primarily on the types and concentrations of lattice imperfections present in the crystals. This dependence comes about largely through the interaction of the imperfections with each other and with chemical impurities.[1] The same is probably true in the case of germanium.

Several difficulties arise in the study of the properties of lattice imperfections in germanium. Particularly troublesome are the high temperatures at which relevant experiments must be carried out. These temperatures are sufficiently high that the danger of chemical contamination through the influx of rapidly diffusing impurities is appreciable. High temperatures are required both for the investigation of the dynamic behavior of dislocations, because of the brittleness of germanium, and for the equilibrium generation of measurable quantities of lattice vacancies. Contamination by chemical impurities may change the properties under investigation, or, if measurements are carried out electrically, may affect the meaning of the results obtained. A further and more general difficulty with the plastic deformation method, which is commonly used to study dislocation properties, is the unnaturally severe strain to which the test specimen is subjected. This high strain rapidly and effectively obscures the initial state of the crystal lattice.

Measurements of the internal friction, or rate of energy dissipation of crystals undergoing forced vibrations, circumvent some of these difficulties. Since investigations of this sort may be made at very low strain levels, they do not, in themselves, alter the state of the crystals. It is therefore possible to repeat portions of experiments on an essentially undisturbed lattice. Furthermore, in internal friction experiments it is possible to monitor results continuously and thereby to determine whether any time-dependent process, such as contamination by impurities, is affecting the results. The impurity problem in internal friction experiments is not as severe as in some others, because of the good vacua in which the experiments must be carried out. As the experiments are nondestructive, it is possible to check some characteristic electrical effects both before and after completion of the tests.

There is, of course, a drawback to this method. Experience with other materials has frequently shown that the unambiguous interpretation of internal friction data is difficult.[2] Nevertheless, in those cases where it is possible to identify the processes giving rise to the internal friction, the energy dissipation is often a very sensitive quantitative measure of certain parameters, such as diffusion coefficient or the degree of cold work.

The internal friction of a material under alternating stress is a measure of the amount of vibrational energy, ΔW, dissipated per cycle relative to W, the total stored vibrational energy at maximum strain. The logarithmic decrement, $\delta\equiv\pi/Q\equiv\Delta W/2W$, will be used in this paper to describe the internal friction.

A large number of effects may give rise to the dissipation of vibrational energy. Many of these effects may be recognized by a specific dependence of the decrement on the externally variable parameters.[2] Stress-induced viscous motion of dislocations, for instance, would be expected to give values of δ which show a pronounced dependence on the amplitude of the applied stress, whereas stress-induced diffusive motion of point defects

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[1] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, Oxford, 1953).

[2] For a review article covering this field, see A. S. Nowick, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 4, p. 1.

would be expected to yield no such amplitude dependence, but possibly large frequency and temperature effects.

It is, of course, highly desirable to correlate measurements of this sort with suitable changes in the state of the crystals under investigation. In this respect germanium is an almost ideal material, considerably superior to the metal crystals which have been examined in the past. It is available with impurity concentrations as low as $10^{13}/\mathrm{cm}^3$, and with dislocation densities ranging from none to approximately $10^6/\mathrm{cm}^2$, for the various possible types of dislocations. One's observations of the relative effects on the internal friction behavior of plastic deformation, chemical impurities, and lattice imperfection concentration may then proceed from a low base concentration of these perturbations.

In these experiments, then, the logarithmic decrement of germanium crystals with various impurity and dislocation concentrations and crystallographic directions was measured as a function of temperature, frequency, and strain amplitude.

EXPERIMENTAL

Measurements were made by the composite piezoelectric oscillator method.[3] In this method, a number of components, including two transducer crystals, all accurately cut to resonate at a multiple of some basic frequency, are cemented together and made to vibrate through the excitation of one of the transducers. A vacuum tube voltmeter is connected across the electrodes of the other transducer. The frequency of the impressed field is varied until resonance is obtained, the amplitude of vibration being detected on the gauge crystal voltmeter. The output voltage divided by the input voltage is proportional to the logarithmic decrement of the complete composite oscillator. The proportionality constant is found by photographing an oscilloscope trace of the exponential decay of the output voltage which results when the drive is shut off. From the decay time and the frequency the logarithmic decrement may be found. The transducer crystals in the present experiment are $-18.5°$ X-cut quartz, chemically plated with silver electrodes on the faces perpendicular to the electrical axis. The vibration is longitudinal.

The decrement of the specimen is found by use of a two-step process.[3,4] The decrement of the complete composite oscillator is first measured as a function of the parameters which are to be varied. Then the specimen is removed and the decrement of the remaining oscillator is measured. The decrement of the specimen is obtained by simple subtraction, using the respective masses of the components as weighting factors. In the measurements to be reported here, the complete composite oscillator consisted of the two transducers, each one-half wavelength long, a long fused silica rod, cut to a length of either four or five half-wavelengths at the resonant frequency, and the germanium specimen, which was mounted on the end of the silica rod. The purpose of the fused silica rod was to separate the transducers from the high-temperature region in which the specimen must be located for most of the measurements. The half-wavelength of both germanium and silica, for a frequency of 40 kc, is approximately two inches.

The joints between the various parts of the oscillator are located at stress nodes and thus have no effect on the decrement, as long as the components remain closely matched. Beeswax and rosin, as well as Araldite AN-101 cement, were used for the room temperature joints. The high-temperature quartz-germanium joint was made with an RCA ceramic cement similar to "Sauereisen." No differences were found, as expected, when these cements were interchanged during room temperature tests.

The high-temperature joint could be cycled without cracking between 250°C and any higher temperature, as long as very rapid changes in temperature were avoided. As the ceramic cement becomes extremely brittle after the preliminary curing, this may be taken as an indication that the germanium is still somewhat plastic at temperatures as low as 250°C. When the joint did crack, after lowering of the temperature below the 250°C limit, it always cracked within the germanium and/or quartz, rather than in the cement.

The composite oscillator was mounted upright on 8-mil phosphorbronze wires which pressed on notches ground into the transducers at the motional nodes. These wires also served as electrical contacts.

The oscillator assembly was enclosed in a long Vycor tube, evacuated to approximately 2×10^{-5} mm Hg or better, during an entire high-temperature run. The vacuum is necessary to eliminate air damping and to minimize the possibility of chemical contamination of the specimen during a run. The temperature was varied by means of a large Globar furnace, mounted immediately outside the vacuum envelope, the hot zone extending one inch or more above and below the sample. Temperatures were measured by means of a chromel-alumel thermocouple mounted very near to but not touching the specimens. The readings obtained from this thermocouple were standardized once by means of three calibrating thermocouples cemented into holes drilled at various positions into a test specimen.

The driving voltage was generated by a BC-221 frequency meter together with an associated scaling circuit and tuned amplifier. A special vernier condenser was mounted on the BC-221. Frequency changes of two parts per million could be easily obtained and reproduced with this arrangement. The BC-221 was calibrated by means of a Berkeley decimal frequency meter.

Half-wave germanium specimens 0.25 in.×0.25 in. in cross section were cut from crystals grown by the

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[3] J. W. Marx, Rev. Sci. Instr. **22**, 503 (1951).

[4] T. A. Read, Phys. Rev. **58**, 371 (1940).

Czochralski technique in [111] or [100] directions. The long dimension of the specimens was taken along the growth direction. Considerable care was taken to maintain the sides of the bar perpendicular to the top and bottom, and to hold taper along the length of the bar at or below two mils. The end surfaces were hand lapped to the correct length. The lateral surfaces were sometimes left as sawed, sometimes surface-ground. After completion of mechanical treatment to the surfaces, the crystals were etched in CP-4. One end was then reground to give good adhesion with the Sauereisen cement.

Several experiments showed that the state of the specimen surfaces did not affect the measured value of δ. The purpose of the etching was to remove surface impurities.

All measurements of decrements reported in this paper were made with maximum strain amplitudes, ϵ, such that $10^{-8} \leq \epsilon \leq 10^{-6}$. Within this strain range, for the temperatures investigated, the decrement proved independent of strain. Measurements at several strains were taken at each temperature. Errors indicated by vertical lines on the graphs represent the high and low decrements measured at each temperature point.

The relative accuracy of the decrement measurements from point to point and within a particular series of measurements, are as good as indicated by the vertical lines on several of the graphs. The absolute accuracy of δ from one run to the next is mainly determined by the mounting conditions and is no better than approximately $\pm 3 \times 10^{-6}$. It was therefore not possible to make a direct standard subtraction of the contribution of the quartz components of the composite oscillator to the total decrement. A standard subtraction of the temperature-dependent contributions of the quartz was made in each case. An empirical small shift of the base line was then added, for cases where the existence of a definite base line was indicated by the shape of the obtained curve. The temperature variation of the quartz components' decrement was found to be small and essentially unchanged for successive calibration runs.

In the temperature standardization runs it was found that a thermal gradient of ~15°C existed along the length of the sample. Since the contributions to δ of each segment of the sample are weighted by the local strain amplitude, this is a small effect. Allowance was made for changes of temperature at the specimen center for those cases in which a significant change in geometry was made, as for instance in going from 40 to 120 kc. The accuracy of individual temperature readings is ±1.5°C, or better.

EXPERIMENTAL RESULTS

The results for rather heavily doped crystals, containing 5×10^{15} arsenic atoms/cm^3, are shown in Fig. 1. The curves plotted here are for three specimens, cut from a large single crystal grown in the [100] direction. In all three cases, the plotted points were taken proceeding from low to high temperatures. It was found upon cycling the temperature, that for these specimens the curve of δ *vs* T was nonreversible, shifting to lower temperatures at each succeeding pass, and only returning to the normal curve at temperatures above 550°C. Figure 2 is included to show this effect. The cause of this behavior is not understood at present. It was found that various heat treatments, or anneals, did not eliminate the hysteresis. It is possible that the effect is spurious. This is unlikely, however, since the same behavior was observed in all three specimens cut from this particular parent crystal, and was not observed in any other specimens, cut from different crystals, which were subsequently investigated. It may be noted here that one effect was observed which did turn out to be an artifact. In observations of the decrement made at high strain amplitudes it was sometimes found that the decrement oscillated between normal and very high values, with a period of approximately one second. This behavior was very similar to the "gasping" reported by other observers,[5] and ascribed by them either to the existence of a dynamic yield point, or to the nonlinearity of the oscillations. It was found in the present case that this effect was simply due to poor contact between the mounting wires and the transducer electrodes. The effect was eliminated by modification of the mounting technique.

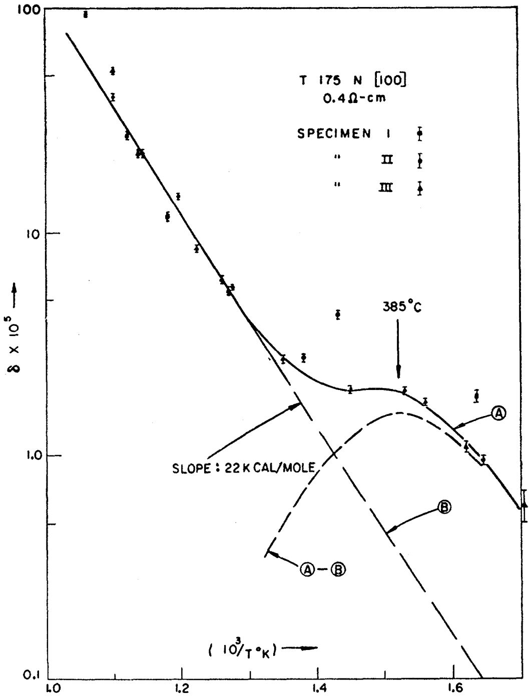

FIG. 1. Logarithmic decrement plotted against $1/T$°K, for three specimens cut from one parent crystal. Only points for increasing temperature are plotted. No temperature cycling has occured. Specimen III is copper-plated.

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[5] J. W. Marx, J. Appl. Phys. 23, 1406 (1952); S. Takahashi, J. Appl. Phys. 23, 866 (1952).

Specimen III of Fig. 1 was plated with copper before the beginning of the run, to see whether this impurity would modify the normal behavior. As may be seen, it did not initially change matters, although adequate time for diffusion into the germanium was allowed. The subsequent hysteresis behavior in the copper-plated crystal was found to be somewhat more erratic than usual.

It may be seen that the high-temperature part of the curve of δ *vs* T approximately follows the equation

$$\log\delta=\log\delta_0-E/RT, \tag{1}$$

where $E\simeq 22\,000$ cal/mole, and $\delta_0\simeq 67$. At lower temperatures, the exponential variation of δ with $1/T$ seems to be masked by a superimposed peak.

The next series of measurements were performed on crystals having an impurity content approximately equal to 10^{13} donors/cm^3. Specimens were cut with the major axis along growth directions which were [111] and [100]. Several examples of the curves obtained are shown in Figs. 3(a), (b), (c). In most of these cases measurements were confined to the temperature region below 500°C, in order to limit irreversible effects. It later became apparent that no appreciable hysteresis occurs in these crystals, even if they are heated as high as 750°C.

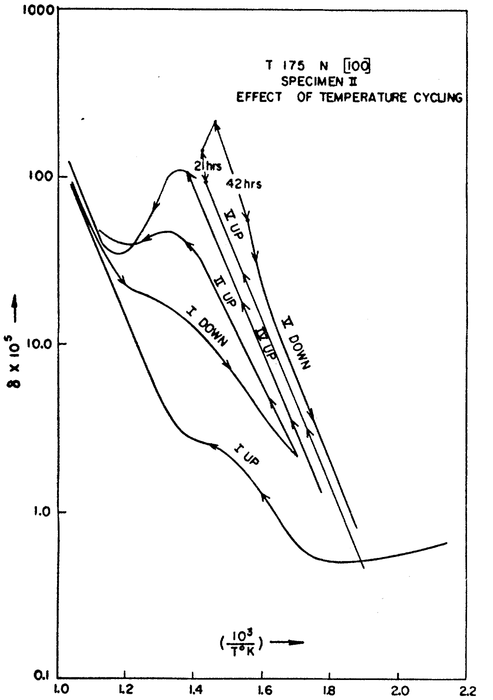

FIG. 2. Logarithmic decrement plotted against $1/T$°K. Effect of temperature cycling in heavily doped (5×10^{16} impurity atoms/cm^3) crystals. The indicated times are annealing periods within the indicated temperature range.

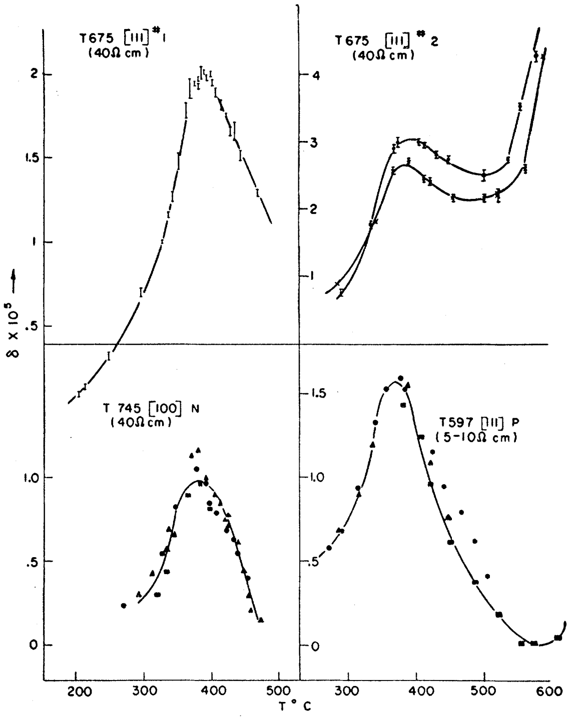

FIG. 3. Decrement plotted against T°C for four specimens cut from three different parent crystals.

A small but well defined peak in the δ *vs* T curve was observed in the neighborhood of 380°C. As the curves in Fig. 3 show, there was some variation in shape and height of the peaks obtained from different specimens, even if these originated from the same parent crystal. It was found, however, that when several of these peaks were referred to a base line, as outlined above, and when a plot of $\log\delta$ *vs* $1/T$ was made, the low-temperature side of the curve was nearly straight, the slope leading to an apparent activation energy. This energy was found to agree rather well with an energy H_w, derived from the width of the peak at half-maximum, under the assumption that the peak obeys the usual anelastic relaxation equation,

$$\delta=\Delta\omega\tau/[1+(\omega\tau)^2], \tag{2}$$

where

$$\tau=\tau_0 e^{H/RT}. \tag{3}$$

H_w is given by

$$H_w=\frac{2\cdot63R}{\Delta(1/T)_{\frac{1}{2}\max}}. \tag{4}$$

In several cases, such as that shown in Fig. 3(b), this analysis could not be performed due to the high background. The obtained values of H_w, as well as the height of the peak, the temperature at the maximum, and the high-temperature slope, H_h, are summarized in Table I. It should also be noted that a 5 ohm-cm n-type crystal, boat-grown and having low edge-dislocation density, showed a δ *vs* T curve rather similar to the atypical one of Fig. 3(b).

The data suggest that a relaxation peak obeying Eqs. (2) and (3) is located at 382°C. It may be seen

TABLE I. Observed temperatures, magnitudes, and half-width activation energies of the peak in the curve of logarithmic decrement *vs* temperature, as well as activation energy derived from the curve in the high temperature region, for all high resistivity specimens. F. D. R. [111] is the edge-dislocation-free specimen. The plastically deformed specimen is not included.

Specimen	No.	T(peak)[a] (°C)	H_w(kcal/mole)	$10^5\times\delta$(max)	H_h(kcal/mole)
T745N	1	385±15 (one run only)	...	2	...
[100]	2	386	22	1.2	...
	3	379	23	1	...
	4	380	19	1	...
T675N	1	386	23	3^b	...
[111]	2	...	...	3^b	23.8
T597P [111]		382	16–19	1.5	50–70[b]
F. D. R. [111]		382	23.7	1.5±0.5	23.4

[a] Each temperature given is the average temperature obtained from several runs with one specimen.
[b] Background subtraction uncertain.

from Eqs. (2) and (3), and from the condition for the peak maximum, $\omega\tau=1$, that a change in frequency from f_1 to f_2 should bring about a correlated change in the temperature of the peak maximum. The expected change is from T_1 to T_2, where

$$\frac{H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\log\left(\frac{f_2}{f_1}\right). \tag{5}$$

To check on this working hypothesis, one decrement *vs* temperature run was made at 60 kc/sec and several others at 120 kc/sec. The results, summarized in Table II, show that a shift in the peak position is indeed observed, corresponding to an activation energy of 25±3 kcal/mole. No accurate information regarding the peak shapes was obtainable at the higher frequencies, due to the severity of the matching conditions. The matching was arranged in such a way as to give minimum background at the peak temperature. A fairly accurate determination of that quantity was therefore possible (Table II).

The question of the underlying cause of the relaxation effect now arose. As it was felt that dislocations might play a rather major role in the process, two further experiments were performed at 40 kc/sec, using specimens with abnormal dislocation densities.

The first of these experiments employed an intrinsic Ge crystal with an edge-dislocation density $\lesssim 10/\text{cm}^2$. This crystal, one of a series grown by Rosi of this laboratory,[6] became available only after much of the previously described work had already been done. The dislocation density is obtained from a study of the pits observed upon etching a (111) face of the crystal in CP-4. It has previously been shown that these characteristic pits are associated with edge dislocation.[7,8] A different type of pit, brought out by a different etching procedure, and sometimes associated with the presence of composite dislocations,[8] was found to be present in the normal concentration of $>10^5/\text{cm}^2$.

TABLE II. Shift in the temperature of the peak in the curve of logarithmic decrement *vs* temperature with change in the vibrational frequency.[a]

Frequency (kc/sec)	40	60	120
T(peak)$_{\text{Av}}$ °C	382±2	406±8	420±6

[a] The 60-kc/sec data were taken with one specimen. The 120-kc/sec data were taken with four specimens, cut from the same parent crystals as the 40-kc specimens, in [111] and [100] directions. Temperature calibration corrections have been made.

The low-edge-dislocation-density crystal was used in order to establish what effect the removal of a substantial portion of the normally present pure edge dislocations would have on the observed phenomenon. The results of runs with this crystal are shown in Fig. 4. It is seen that the main effect of the reduction in dislocation density has been to lower the magnitude of the high-temperature portion of the δ *vs* T curve. The slope of that part of the curve, and the 380°C peak position and magnitude remained invariant. Since, in effect, the background relative to the peak has been significantly lowered, the appearance of the peak is considerably more symmetric than before. The peak

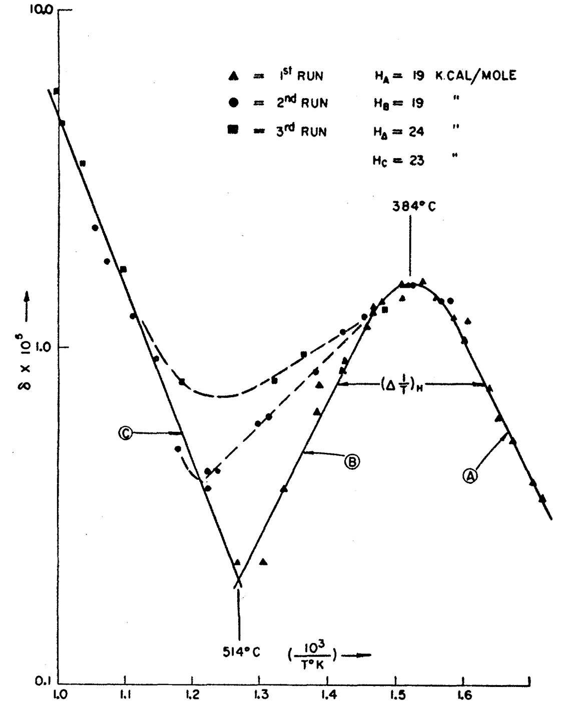

FIG. 4. Logarithmic decrement plotted against $1/T$°K. The successive runs were taken up to successively higher temperatures. This specimen had a very low density of etch pits of the kind usually associated with edge dislocations.

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[6] F. D. Rosi, Acta Metallurgica (to be published).
[7] Vogel, Pfann, Corey, and Thomas, Phys. Rev. **90**, 489 (1953).
[8] S. G. Ellis, J. Appl. Phys. **26**, 1140 (1955).

symmetry, the values of the energies derived from the slopes of the peak sides and of the width then lend further credence to the hypothesis that a relaxation effect is responsible for the peak.

From this experiment, then, one may infer that some details, but not the characteristic features of the dependence of the decrement on temperature are in part determined by the general crystal perfection.

The next, and final, experiment in this series was performed in order to test the effect of increasing, rather than reducing, the dislocation density. A germanium bar, cut approximately to sample shape from a 30 ohm-cm *n*-type crystal, was severely deformed at a temperature of 875±25°C, in a vacuum of 10^{-3} mm Hg. The deformation was carried out by placing the specimen on quartz ledges, leaving the center free, and applying a force from above the center. The crystal was first bent to an angle of 13°, the bend being distributed over a length of approximately one cm. After the initial bend, the crystal was turned and bent essentially straight again. The cooling rate was of the order of 100°C/minute. In order to establish the correct sample geometry and dimensions, the specimen was subsequently surface ground and etched in the normal manner. It was found after this treatment that the crystal had not undergone thermal conversion, except at the very ends.

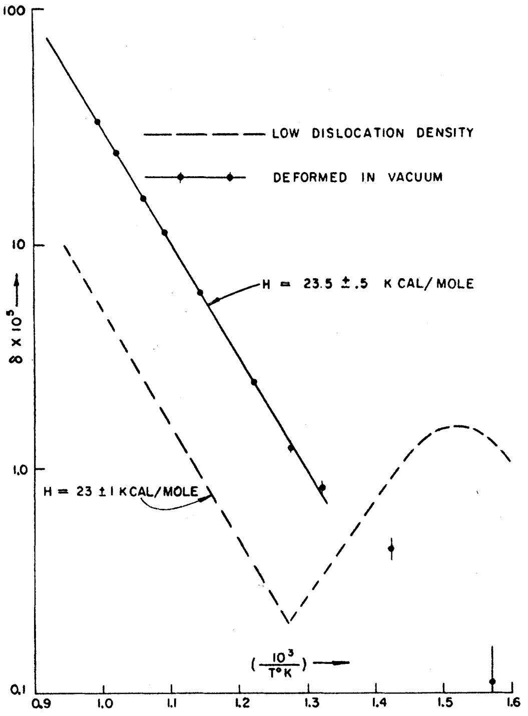

FIG. 5. Logarithmic decrement plotted against $1/T$°K. The open circles represent points taken with a plastically deformed specimen. The dashed line is the curve of Fig. 4, drawn in for comparison.

The rather striking decrement *vs* temperature curve obtained with this crystal is shown in Fig. 5. The normally present peak has almost entirely disappeared. In the high-temperature region, the dependence of δ on $1/T$ is unchanged, except for an increase in level by one order of magnitude.

From this experiment, and from the immediately preceding one, it is apparent that the behavior of the decrement does not depend on the dislocation density in any simple way. In the next section, an attempt at a phenomenological theory will be presented.

DISCUSSION

It appears from the experiment that the most interesting feature in the curve of decrement *vs* temperature, the peak observed at 380°C, is apparently due to an anelastic relaxation. The relaxation time, which is determined from the vibrational frequency and the peak position is given by $\tau = \tau_0 \exp(H/RT)$, where $\tau_0 = 10^{-13\pm1}$ sec, and $H = 25\pm3$ kcal/mole. The magnitude of $1/\tau_0$, which corresponds to a jump frequency, is strongly suggestive of a stress-induced atomic diffusion process.

There exist in the literature several examples of well understood systems in which anelastic relaxation is caused by an atomic migration.[2] The basic mechanism in all these cases depends on the existance of impurity sites which are normally equivalent, but which, under uniaxial stress, become nonequivalent, thus inducing a rearrangement of impurity atoms until statistical equilibrium between high- and low-energy sites is established. Under these circumstances, if the temperature is such that the jump time for the diffusion is of the order of the inverse of the applied frequency, a relaxation effect will occur.

Several difficulties present themselves if one attempts to interpret the present data in this way. It has been found empirically in a number of other cases that the constant Δ, which determines the height of the peak, Eq. (2), is of such a magnitude that the concentration of impurity atoms, in weight percent, is given approximately by the height of the relaxation peak.[9] In the present instance, this would imply an impurity conconcentration $\geqslant 10^{16}/\text{cm}^3$. In several of the specimens showing the peak, resistivity and lifetime were measured before and after the high-temperature experiment. The resistivity was found to be of the order of 40 ohm-cm, while the lifetime of minority carriers was 1 millisecond. Thus the presence of a high concentration of any impurity having normal characteristics may be ruled out. A further objection to the interpretation of the data in terms of a relaxation process which depends on the migration of impurities between sets of inequivalent lattice sites may be derived directly from the results of internal friction measurements. The symmetry of the available interstitial lattice sites, in conjunction with

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[9] For instance, W. Köster and L. Bangert, Acta Metallurgica 3, 274 (1955).

the fact that the intensities of the relaxation peak observed for application of longitudinal stress in both the [111] and [100] directions are essentially the same, rules out the possibility that intersitials randomly distributed in an otherwise perfect lattice cause the observed effects.

It is nevertheless possible to construct a model which explains the data and which is not inconsistent with the known properties of germanium. For this model, one may consider the stress-induced diffusion of impurity atoms located at sites which are inequivalent, not by virtue of the basic crystal structure, but by strains which are built into the crystal during growth. In particular, one may consider the strain field surrounding a dislocation with an edge component. Such a field attracts impurities in order to relieve the strain and hence to reduce the energy. Under equilibrium conditions, the impurities form a Maxwellian distribution, known as a Cottrell atmosphere, around the dislocation.[10] Any motion of the dislocation due to externally applied stress, subsequent to the establishment of the equilibrium, would then result in a concomitant motion of the impurities. The motion is in such a direction as to re-establish the equilibrium conditions.[11] The magnitude and phase of the motion of the impurities is expected to depend on the amplitude of the applied stress moving the dislocations, on the frequency of the applied stress, and on the diffusion coefficient of the impurities. In this model, the energy dissipation implicit in the decrement is brought about by the effective force exerted by the dislocations on the impurities in "dragging" them from one equilibrium position to the next.[12]

It now again becomes necessary to inquire into the nature of the impurities taking part in the process. The magnitude of the impurity concentration for the newly proposed mechanism is not established. It is therefore possible that a very small impurity concentration would suffice to give the observed effects, and that hence no particular impurities may be ruled out on account of the electrical properties of the germanium. There is, however, one "impurity" the choice of which is not only reasonable, but also allows a complete explanation of the relaxation peak as well as the exponential rise of the decrement which occurs at high temperatures. This impurity is the lattice vacancy.

It has been shown[13–15] that the equilibrium concentration of vacancies at a temperature T is given by

$$n_1(T)=n_0e^{-K/RT}, \tag{6}$$

where K is the activation energy for vacancy formation and n_0 is approximately equal to the number of lattice sites. It may be assumed that there exists a temperature T_q below which the vacancies have insufficient mobility to come to equilibrium at the rates of cooling encountered in normal crystal growth and in the present experiment. The vacancy concentration at low temperatures is then given by $n_1(T<T_q)\simeq n_1(T_q)$. The concentration of vacancies at an arbitrary temperature may therefore be written

$$n(T)\simeq n_1(T_q)+n_1(T), \tag{7}$$

the first term predominating at low temperatures, and the second at high temperatures.

If one now further assumes that the relaxation strength, Δ/π, is directly proportional to the number of defects present, the equation for the logarithmic decrement becomes

$$\delta(T)=\gamma n(T)\frac{\omega\tau_0 e^{H/RT}}{1+(\omega\tau_0)^2e^{2H/RT}}, \tag{8}$$

where ω is the applied angular frequency, $\gamma n(T)=\Delta(T)$, and $[T_0\exp(H/RT)]^{-1}$ is the jump frequency for the diffusion of vacancies. Substituting Eqs. (6) and (7) in Eq. (8), it is found that, for $T\ll T_q$,

$$\delta(T)=\gamma n_1(T_q)\frac{\omega\tau_0 e^{H/RT}}{1+(\omega\tau_0)^2e^{2H/RT}}. \tag{9}$$

For high temperatures, where

$$T\gg T_q \quad\text{and}\quad \omega\tau_0\exp(H/RT)\ll 1,$$
$$\delta(T)=\gamma n_0\omega\tau_0 e^{-(K-H)/RT}. \tag{10}$$

Equation (9) is that of a characteristic relaxation peak of height $\delta(T_m)=\gamma n(T_q)/2$, for the position determined by the condition that $\omega\tau_0\exp(H/RT)=1$. Equation (10) gives an exponential rise, as observed.

All but one of the constants entering into these relations are determined by the experiment. It has already been noted that $\tau_0=10^{-13\pm1}$ sec, and that $H=25\pm3$ kcal/mole. $K-H$ was found to be 23 ± 2 kcal/mole, whence $K=48\pm4$ kcal/mole. This activation energy is in very close agreement with that found by the direct quenching of vacancies.[13,14] Moreover, it is expected that the activation energy for self-diffusion, if this proceeds by a vacancy mechanism, should be $K+H$. From the present experiment, $K+H=73\pm5$ kcal/mole, which again agrees well with the value of 68.5 kcal/mole found by Letaw *et al.*[16]

Three constants remain to be evaluated. As the experiment only gives two additional ratios amongst these, it is necessary to assume the value of one. The only quantity for which a theoretical estimate may be made is n_0.[15] It will be assumed that it is approximately $10^{23}/\text{cm}^3$. From the ratios of Eqs. (9) and (10), in the appropriate temperature ranges, and from the experi-

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[10] A. H. Cottrell, *Report on Strength of Solids* (The Physical Society, London, 1938), p. 30.

[11] A. H. Cottrell and M. A. Jaswon, Proc. Roy. Soc. (London) **199**, 104 (1949).

[12] This mechanism is similar to that proposed in reference 9.

[13] S. Mayburg, Phys. Rev. **95**, 38 (1954).

[14] R. A. Logan, Phys. Rev. **101**, 1455 (1956).

[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1940), Chap. II.

[16] Letaw, Portnoy, and Slifkin, Phys. Rev. **102**, 636 (1956).

mental data, one may show that $n(T_q)/n_0 \simeq 10^{-13}$, which implies, together with the assumption for the value of n_0, that $n(T_q) \simeq 10^{10}/\text{cm}^3$. The "freezing in" temperature calculated from $n(T_q)$ and Eq. (6) is $T_q \simeq 550°\text{C}$, which is quite reasonable. The value of the remaining constant, γ, may be determined from n_0, from the definition of the decrement, and from some average value of the stored vibrational energy. Taking an average value of 1 erg/cm^3 for the latter, the derived value of γ is approximately 10^{-15} (ergs dissipated/cycle)/defect.

The explanation of the data observed with the plastically deformed crystal follows from the present hypothesis. It is known that germanium crystals which have been subjected to severe bending exhibit intersecting slip bands, which, in their turn, cause the formation of many jogs in the dislocation lines. Vacancies precipitate on the jogs until these are essentially "grown out" of the dislocation line. If the plastic deformation results in the production of a large concentration of such jogs, it would be expected that the number of vacancies quenched into the crystal would be greatly reduced.[14,17] With the sensitivity of the present experiment, i.e., peak height above background, a tenfold reduction in the vacancy concentration could easily cause the apparent vanishing of the peak.

From the data obtained with the edge-dislocation-free crystal it must be inferred that the postulated process takes place in the neighborhood of the composite dislocations[8] present in the crystals. Since the concentration of composites is nearly constant and generally as high or higher than the concentration of edge dislocations, one would expect a nearly constant peak height, as observed, even if the vacancies surrounding both types of dislocations contributed to the effect. In addition, it will be shown in the theoretical treatment which follows that the relaxation strength is proportional to both the loop length and the dislocation density, and that one would therefore not expect a simple proportionality between the relaxation strength and the dislocation density.

The reasonableness of the proposed model and of the numerical values derived from it have been investigated theoretically. The results of that investigation, upon which the validity of the model rests, will be presented in the succeeding paper.

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