PHYSICAL REVIEW B VOLUME 10, NUMBER 2 15 JULY 1974

Effects of thermal-neutron irradiation on the elastic constants of copper*†

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(Received 11 February 1974)

The three independent elastic constants of copper irradiated with thermal neutrons below 4 K have been measured. Simultaneous measurements of attenuation and resistivity were used to monitor the defect density. The elastic-constant changes during irradiation per unit concentration γ of defects, $d\ln C/d\gamma$, are -2, -15.8, and -18.1 for the bulk modulus, C_{44}, and $C'=(C_{11}-C_{12})/2$, respectively. The percentage elastic-constant changes measured at 3.6 K after pulse annealing at temperatures up to 60 K were different for the different elastic constants in the same annealing range. Also the elastic-constant changes were strongly temperature dependent. The results show that there are five different types of elastic-constant effects, each of which depends upon the type of defect involved. This analysis also helps to account for the wide variation of results found previously for measurements using different types of irradiation at different temperatures.

I. INTRODUCTION

The introduction of vacancies and interstitials by low-temperature irradiation alters many of the physical properties of solids, but most of the experiments designed to investigate the behavior of these defects have been measurements of defect-induced changes in the electrical resistivity. Although such studies have contributed much to the understanding of defect behavior, the fact that resistivity changes only measure the number of defects present in the lattice has left unanswered many fundamental questions about the nature of radiation damage. Another physical property which can be conveniently measured with high precision is a change in the elastic constant of a solid. In contrast to resistivity changes, elastic-constant effects have the advantage of being sensitive to the symmetry of the defect as well. Thus defect-induced elastic-constant changes should serve as a means for investigating the configuations assumed by various defects in the host lattice.

An early theoretical calculation by Dienes[1] indicated that irradiation with energetic particles would produce a bulk effect due to the alteration in number and strength of interatomic bonds which would increase all the ordinary elastic constants of copper by about 10% per at.% interstitials, but decrease them by approximately 1% per at.% of vacancies. If this were true, a measurement of the bulk effect would provide an empirical method for distinguishing between these two types of defects. Such a result would be very useful in the interpretation of radiation damage.

This prediction stimulated experimental studies of the effect of radiation on elastic constants.[2] The early studies showed that there was a much larger indirect effect, dislocation pinning,[3,4] which overshadowed the direct effect. A sizable literature on the pinning effects developed,[5,6] and only recently has attention been returned to the direct effect. To determine accurately the magnitude of the direct effects of point defects on the elastic constants, it is imperative to eliminate dislocation effects.

Although Dienes's calculations predict a clearcut difference in behavior for vacancies and interstitials, there are other subsequent calculations which lead to very different conclusions.[7-11] These predictions vary over two to three orders of magnitude and even differ as to the expected sign of the effect.

Hence, although elastic-constants measurements promise to be very useful for the determination of defect properties, the theoretical treatment of elastic-defect effects is uncertain, and the large dislocation contributions make the measurement very difficult. Furthermore, even in those experiments in which attempts have been made to isolate the contributions due to dislocations, large differences (which span practically the same range as the theoretical estimates) exist in the results found in the various investigations. For example, after an extended irradiation of a single-crystal copper rod at 4 K with reactor neutrons, Thompson *et al.*[3] found no change in Young's modulus of the rod, indicating an effect of less than ~1% per at.% of Frenkel defects. Dieckamp and Sosin[2] reported a decrease in the shear constant of a thin polycrystalline copper foil of (-7 ± 3)% per at.% Frenkel pairs after electron irradiation near 80 K. König *et al.*[12] also irradiated a thin polycrystalline copper foil, using α particles, and observed at 4 K, a 140% decrease in the shear constant per at.% of Frenkel pairs. Also, they gave a corrected value of the Dieckamp-Sosin results which agreed with their own work. However, Townsend *et al.*[8] obtained $(-13\pm3)\%$ per at.% Frenkel pairs after bombarding both single-crystal and polycrystalline copper foils at liquid-helium temperatures with protons. Also Nielson and Townsend[13] discovered a large relaxation-modulus effect which they associated with the reorientation of the defect responsible for either stage I_B or I_C annealing.

There are several possible explanations for the wide range of experimental disagreement. One is the uncertainty of the defect concentration in several of the experiments. The most direct measurement of concentration is furnished by electrical resistivity, but only a very few investigations have included simultaneous resistivity measurements. Another possibility is that the different elastic constants measured by the various investigators do not have the same functional dependence on defect concentration. Only one reported investigation has been made of the change in all three independent cubic elastic constants as a function of defect production; Gerlich *et al.*[14] performed the measurements on LiF at room temperature. This material is expected to give bulk-effect results similar to those computed for copper because Born-Mayer repulsion terms contribute strongly to the elastic characteristics of both solids. However, all the elastic constants were found to decrease uniformly by only a few percent per at.% of defects.

The presence of relaxation effects, which are negative and may be large, is another possible explanation. Such contributions are, in general, sensitive to the type of damage created in the lattice, the elastic constant being considered, and the frequency and temperature of measurement.

Finally, the effects on the elastic constants are probably sensitive to the nature of the defects which are generated. Isolated vacancies, interstitials, and close pairs could all produce different effects, so that irradiations with different particles or at different temperatures might be expected to produce different results. This question will be one of the principal concerns of the present investigation.

The purpose of this investigation was to determine the relative importance of all the different contributions to all the elastic constants of copper from irradiation-induced defects. The experiments consisted of measurements at 10 MHz of the irradiation-induced changes at 4 K in the three independent elastic constants, the determination of their annealing behavior through the low-temperature annealing stage I (0–50 K), and their measurement as a function of temperature. Simultaneous measurements of the attenuation and resistivity were used to monitor the defect concentration.

The use of MHz sound waves has many distinct advantages over the techniques utilizing the lower-frequency (10–10 000-Hz) range of earlier studies. Only Young's modulus can be measured by the resonant-bar technique. There is also the problem of ascertaining the effects from various clamping procedures necessary to support the cantilevered samples. In contrast, the pulse-echo method appropriate for the MHz range enables one to measure the changes in the three independent constants with high sensitivity. Since all sample dimensions are large in relation to the wavelength of the experimental frequency, the pulse-echo technique is not sensitive to surface effects. A higher frequency causes relaxation effects to be shifted upwards in temperature so that the method is also more convenient for separating low-temperature relaxation phenomena from the zero-temperature contributions.

Because of the large relative size of the sample (approximately 1 cm^3) appropriate for the pulse-echo technique, only neutron irradiation is capable of creating both a homogeneous distribution and an adequate concentration of defects. However, fast neutrons create large displacement cascades in the lattice which may complicate the direct study of simple point defects. Accordingly, the irradiation in the present experiment was performed with thermal neutrons. These particles create displacements through (n,γ) capture reactions, rather than by direct knockons. Isochronal annealing studies of resistivity changes from this type of damage exhibit larger stage-I recovery and sharper annealing peaks, and therefore simpler damage is obtained for slow-neutron than for fast-neutron bombardment.[15]

There are several reasons for using copper in the investigation. High-purity samples are easily obtained and it has been the subject of much previous study. Its cross section for thermal-neutron capture is large enough to allow both resistivity and elastic-constant changes to be measured accurately in a reasonable length of time. The mean-free-path characteristic of thermal neutrons in copper is also large enough (about 3 cm) to give a homogeneous distribution of damage. Most theoretical calculations have been based on this material. A most important reason is the availability of low-dislocation-density samples[16] which permit the elimination of dislocation effects.

The measurement ot temperature-dependent defect effects requires a measurement of the temperature dependence of the three independent elastic constants of the unirradiated crystal. Recent calculations by Garber and Granato[17] have generated interest in just such low-temperature dislocation-free measurements. Their work predicts a T^4 dependence of the moduli over this range, but disagrees in magnitude with the only existing measurement which is accurate enough to be compared to the theory. The results of this comparison are of use in obtaining interatomic potentials. These measurements are also presented and discussed in this paper.

Section II of this paper contains a description of the experimental techniques and apparatus used in the investigation, and the results are given and discussed in Sec. III, along with an evaluation of the large apparent discrepancies in previously reported measurements of irradiation-induced elastic-constant changes. In Sec. IV, conclusions are given concerning the types of changes in the elastic constant produced by close pairs and isolated interstitials. A discussion of the mechanisms by which point defects alter the elastic constants and of the symmetry information which can be derived from the measurements of these effects is contained in the following paper.[18] A preliminary report has also been given elsewhere.[19]

II. EXPERIMENTAL TECHNIQUES AND APPARATUS

The single crystal of 99.999% copper was grown in a manner which has been described previously.[16] Three cubes approximately 12 mm on a side, with faces perpendicular to the [100], [011], and [01$\bar{1}$] directions, were each cut by an acid-saw technique[20] and then annealed at 1050 °C for 10 days to minimize the number of dislocations. The normal dislocation density of crystals prepared by this technique is extremely small, on the order of $10^3/\text{cm}^2$. The samples were subsequently irradiated at room temperature to an integrated dose of 10^{17} fast neutrons per cm^2 to pin the few remaining dislocations and harden the crystals. A chemical polishing technique[21] was used in order to obtain the flat, parallel, and oriented surfaces required for ultrasonic measurements without the introduction of new unpinned dislocation segments.

The measurements were taken in the low-temperature irradiation facility at Oak Ridge National Laboratory; detailed descriptions may be found elsewhere.[22] It provides a highly pure thermal neutron flux of 2.5×10^{12} $(n/\text{cm}^2)/\text{sec}$ and the liquid-helium temperatures necessary to immobilize point defects. This facility has been used extensively to investigate irradiation-induced resistivity changes in many different materials.[23]

Figure 1 shows how the crystal and resistivity samples were mounted in the capsule at the bottom of the rig. A 1-cm-diam 10-MHz quartz transducer was bonded to one polished face of each crystal. Three different samples and transducers were used: an X-cut transducer on a (100) face of sample 1 for C_{11} measurements; an AC-cut transducer on a (100) face of sample 2 for C_{44} measurements; and an AC-cut transducer, polarized in a $\langle 01\bar{1}\rangle$ direction, on a (011) face of sample 3 for C' measurements. Nonaq was used as the bonding agent. A spring-loaded aluminum plunger held the transducer and sample firmly in place and also provided an electrical contact to the transducer.

Two types of thermometry were used in the experiment. Irradiation and reference temperatures, always below 4 K, were determined by measuring the vapor pressure of the liquid helium in which the sample was immersed. A copper-constantan thermocouple was used to measure the elevated temperatures.

Small rectangular pieces, approximately 1-cm long and 10^{-2} cm^2 in cross section, were acid cut from parts of the original single crystals to be used as resistivity samples. These were etched

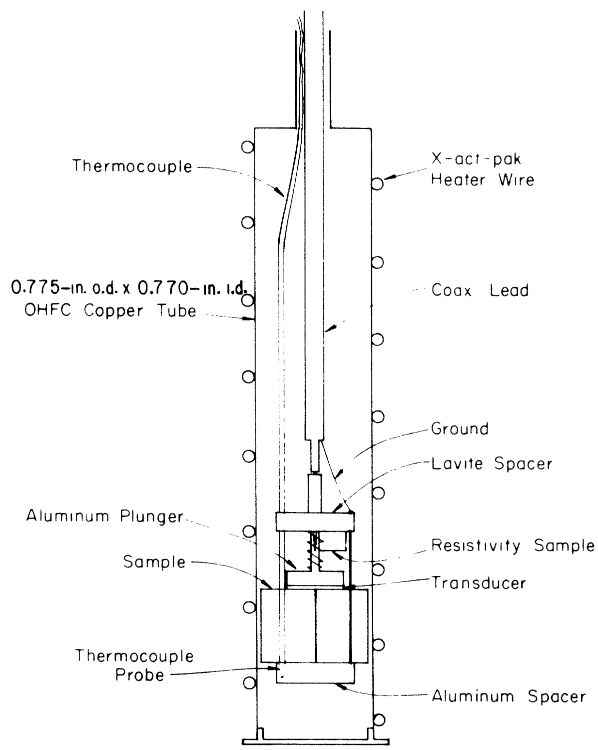

FIG. 1. Sample capsule. The location of various components has been indicated by appropriate arrows. The height of the capsule is approximately 4 in.

down with nitric acid to reduce this relatively large area-to-length ratio. One was mounted in each holder and connected with current and potential leads as shown in the figure.

The velocity and attenuation system used was that discussed previously by Holder[24] and Read and Holder.[25] The velocity measurement is based on the McSkimin pulse-superposition technique,[26] and attenuation values were obtained by periodically interrupting this interference condition and measuring the ratio of two successive pulse amplitudes. On a specimen of normal attenuation, this system has simultaneously detected velocity changes of one part in 10^7 and attenuation changes of 0.001 dB/μsec. Runs made during the experiment at helium temperature without irradiation showed the velocity as measured by the system to be stable within ±2 parts in 10^7 over a period of 2 days.

After the rigs were lowered into position, the sample chamber was slowly cooled to liquid-helium temperatures. The slow cooling (approximately 2 h) was used to lessen the risk of introducing new dislocations because of different thermal-expansion coefficients of the quartz and copper. This risk was further minimized because the bonding agent Nonaq does not solidify until well below room temperature. Readings were then made of the resonant frequency and attenuation at various temperatures between 3.6 and 45 K. These readings determine the normal temperature dependence of the attenuation and elastic constant. The absolute accuracy of the temperatures above 4 K, as determined by the thermocouple, should be ±0.1 K at the lower temperatures and even better at the higher ones. However, the reproducibility of the temperatures was to within 10 mK. Such reproducibility was essential since the temperature-dependent defect effects were found by taking the differences between these preirradiation values and the frequencies at the same temperatures after irradiation. Normally, the frequency at 40 K was found to be reproducible within ±10 cycles; at 10 K, this was ±2 cycles. Below 4 K, where the temperature was determined very precisely by the vapor pressure of the liquid helium, it was ±1 cycle.

The sample can was then filled with liquid helium, and frequency, attenuation, and resistivity were recorded at the reference temperature (approximately 3.6 K, reproducible to within a few millidegrees). The reactor was subsequently turned on and taken to full power in a period of a few minutes. The resultant heating caused the irradiation temperature to be a few tenths of a degree above the reference temperature. The attenuation and resonant frequency were monitored continuously and resistivity measurements were made periodically during the bombardment. An average irradiation was about 50 h so as to produce enough defects to permit the accurate determination of the annealing behavior.

The annealing program carried out after each irradiation consisted of pulsing the sample to an elevated temperature (usually for a period of 15 min), taking measurements of attenuation and resonant frequency at the pulse temperature, then cooling to the reference point and recording the attenuation, frequency, and resistivity. The long pulse duration was used to ensure the attainment of thermal equilibrium, which is necessary for an accurate frequency reading. These initial "at-temperature" values include both temperature-dependent and annealing effects. In order to simplify the interpretation of possible temperature-dependent effects which might be introduced by the irradiation, a number of "at-temperature" measurements were also made for temperatures below that of the annealing pulse after the pulse was completed; such readings should be free of annealing effects.

III. RESULTS AND DISCUSSION

A. Elastic-constant changes at 3.6 K

The changes in resonant frequency measured during three of the five different thermal-neutron bombardments are plotted as a function of irradiation time in Fig. 2. During every irradiation, re-

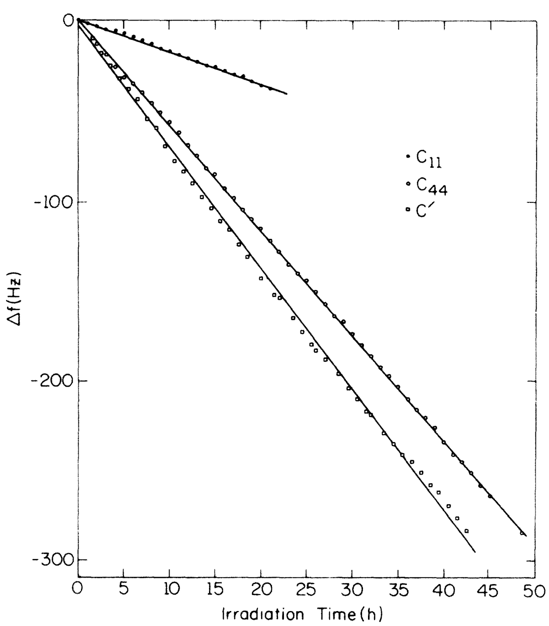

FIG. 2. Measured change in resonant frequency observed during irradiation below 4 K, plotted vs the irradiation time for three modes. The thermal neutron flux was 2.5×10^{12} (n/cm^2)/sec.

sistivity changes were observed to be a linear function of irradiation time. The marked linearity in the frequency change evident in these results demonstrates the high sensitivity attainable with the velocity-measurement system and gives good evidence that dislocation effects were not a contributing factor. Two different runs were made with the C_{44} mode; the crystal was annealed to 320 K prior to the second run. The rate of change of frequency and resistivity were within 2% of each other for the two runs. Two irradiations involving the longitudinal mode for measuring C_{11} were also made; after the first irradiation a pulse-annealing program through 45 K was carried out. These were the most difficult measurements to make. Not only was the effect small, but occasional sudden jumps of the frequency occurred during the second irradiation. The source of these jumps was not determined, but the excellent agreement between the results of the first run, and those obtained during various periods of the second irradiation where no jumping occurred, indicates that the present measurement of the effect on the C_{11} mode is a reliable one.

The change in the resonance frequency, Δf, measured in the velocity system is related to the corresponding elastic-constant change Δc by

$$\Delta C/C = 2\Delta f/f - \Delta l/l\,, \tag{1}$$

where l is the sample length. Accordingly, it is necessary to know the change in lattice parameter which results from the irradiation. Although no direct measurement is available for the lattice expansion created by thermal neutrons, we use the value obtained by various authors[27-29] using deuteron irradiation. This value, in terms of the incremental change in resisitivity, $\Delta\rho$, produced by the irradiation is $(\Delta l/l\Delta\rho) = 1.5\times10^{-3}$ $(\mu\Omega\ \text{cm})^{-1}$. This contribution to the resonant-frequency change is small compared to the total measured effects and gives only a minor correction to the elastic-constant changes.

The resulting rates of change of the elastic constants per unit concentration, γ, of Frenkel defects, $d\ln C/d\gamma$, are summarized in Table I. A value of 2.5 $\mu\Omega$ cm per at.% of Frenkel defects was used to calculate the defect concentration. The measured total resistivity and relative frequency changes and the estimated length changes for the different runs are also given. The frequency was nominally 10 MHz, and varied somewhat from one run to another.

The values for $d\ln C/d\gamma$ were computed using only 89% of the total resistivity change observed during irradiation. This value is based on a recent article by Coltman *et al.*,[30] who discussed in detail the nature of thermal neutron damage and concluded that only this portion of the resistivity change is due to the introduction of vacancies and interstitials. The remainder is due to substitutional Zn and Ni atoms which are the result of transmutations induced by certain of the capture reactions. The concentration of impurity atoms resulting from the transmutations produced during the longest irradiation was only 4.4×10^{-6}. These impurity atoms would be expected to have only a small effect on the elastic characteristics of copper since they lie adjacent to it in the Periodic Table. This contention is further supported by the observations of Köster and Rauscher[31] in which the introduction of Zn was found to produce less than $\frac{1}{2}$% decrease in the elastic constants of Cu per at.% concentration. An additional check was made by monitoring the resonant frequency for a period of almost 30 h immediately following the irradiation of sample 3. Because the conversion of Cu^{64} to Zn^{64} or Ni^{64} occurs with a half-life of 12.8 h, any significant contribution to the elastic constant from these elements should be evident here. The frequency remained constant within ±2 cycles over the entire period, indicating that no measurable contribution from this mechanism was present.

It is clear from Table I that no extremely large

TABLE I. Measured changes in relative frequency, $\Delta f/f$, and resistivity, $\Delta\rho$, estimated relative length changes, $\Delta l/l$, total irradiation time, and the calculated relative elastic constant change per unit concentration, γ, of defects.

Mode	Irradiated time (h)	$-\frac{2\times10^5\Delta f}{f}$	$\frac{10^6\Delta l}{l}$	$\frac{-10^5\Delta C}{C}$	$\Delta\rho$ (nΩ cm)	$\frac{d\ln C}{d\gamma}$
C_{11}-I	22.33	0.657 84	0.6525	0.723 09	0.435	−4.7
C_{11}-II	137.88	4.2191	3.981	4.6172	2.654	−4.9
C_{44}-I	64.62	6.5809	1.845	6.7654	1.230	−15.5
C_{44}-II	48.58	5.1009	1.374	5.2383	0.916	−16.1
C'	43.68	5.0695	1.2105	5.190 55	0.807	−18.1

effects ($d\ln C/d\gamma \approx -100$) were found in any of the elastic constants during irradiation; the magnitudes of the effect for all three constants lie intermediate in the range of previously reported values. However, the two shear constants do exhibit a significantly larger effect than does the longitudinal constant, and the relative change in the bulk modulus during irradiation, which can be calculated from the measured results, is an order of magnitude smaller ($d\ln B/d\gamma = -2$) than either of the changes observed in the two shear modes.

All possible second-order constant changes can be determined from those found in the complete set of independent constants measured here. However, previously reported values were all of Young's modulus Y. The magnitude of Young's modulus varies with crystal orientation. The magnitude of the irradiation effects, $d\ln Y/d\gamma$, calculated on the basis of the present results varies from a maximum value of -17 in a [100] direction to a minimum value of -14 for a [111] direction. Since these values fall within the range reported in Table I above, the wide spread in the previously reported results cannot be understood in terms of variations in behavior of the different elastic constants.

After each irradiation, the samples were subjected to an isochronal annealing program. Pulse durations were 5 min for the first run C_{11}I and 15 min for all subsequent runs. The results are given as the irradiation-induced relative frequency changes ($\Delta f/f$) remaining at the reference temperature of 3.6 K after the appropriate annealing pulse.

The degree of reproducibility of the results is evident from a comparison of the two different C_{44} runs. This is shown in Fig. 3, where the results from the two runs have been normalized to the same defect concentration ($\Delta\rho = 1\times10^{-9}\ \Omega$ cm) in order to allow a quantitative comparison. The agreement is excellent, particularly below 35 K, and even details of the annealing behavior are reproducible.

This comparison provides a crucial test of whether or not dislocations have contributed to the results. Since dislocation effects are not linear in defect concentration, the results from the second run would differ from those of the first if dislocations were a significant factor. More importantly, if dislocations are present in sufficient numbers to affect the low-temperature (below 35 K results, the pinning produced by defects mobile above 35 K would produce effects of a magnitude several times larger than those introduced by the bombardment. In these and all other runs the increases which resulted from the annealing of the defects in stage I were less than the decreases

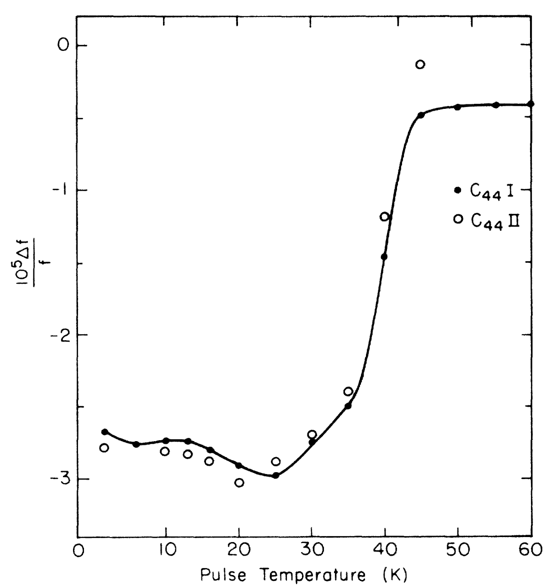

FIG. 3. Comparison of the annealing behavior found during the two C_{44} runs. The results are shown as the irradiation-induced relative frequency change which remains at the reference temperature of 3.6 K after various annealing pulses. The results from both runs have been normalized to the same defect concentration ($\Delta\rho = 1\times10^{-9}\,\Omega$cm).

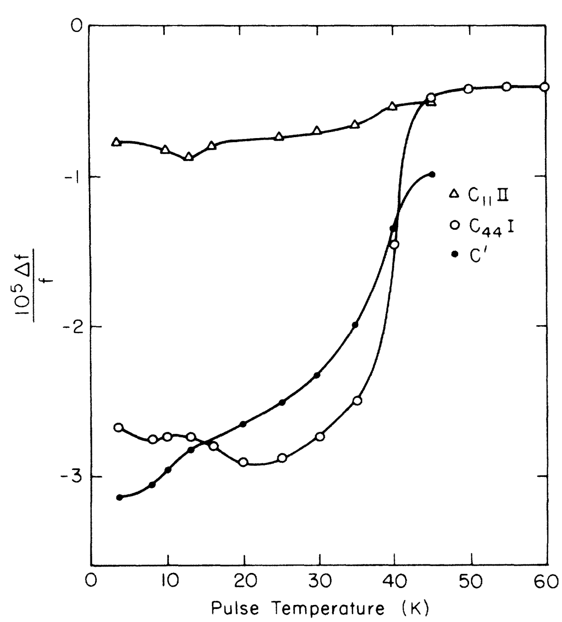

FIG. 4. Annealing of the irradiation-produced relative frequency changes measured at 3.6 K for all three elastic constants. The results from the three runs have been normalized to the same defect concentration ($\Delta\rho = 1\times10^{-9}\ \Omega$cm).

produced by irradiation.

The annealing of the irradiation produced relative frequency changes for all three modes as shown in Fig. 4. The curves indicate quite clearly that the irradiation-induced changes in the three different constants do not recover in the same fashion; the recovery of any particular constant is different in different temperature regions. The annealing results can be roughly divided into four major temperature regions.

In the recovery range from 3.6 K through the stage-I_A peak (to about 20 K, all three modes change significantly more than would be expected on the basis of the accompanying resistivity change. Both the C_{11} and C_{44} constants experience an additional decrease of about 10% in this temperature range. This decrease was unexpected, but is reproducible (as evidenced by the two C_{44} runs shown in Fig. 3) and has been observed previously.[32] Possible explanations for this decrease could be related to the thermal conversion of defects, or the recovery of damage which gives a positive contribution to the modulus change. For pulse temperatures in the range where the I_B and I_C close pairs recover (between approximately 20 and 35 K), the fraction of the irradiation-produced change which anneals is roughly the same for all three constants. In fact, the fractional recovery of the elastic constants is also roughly equal to the fractional resistivity recovery measured in this range. Between 35 and 45 K (stage I_D), the annealing behavior is quite different for the three constants, and only C' recovers as the resistivity. More than two-thirds of the relative change in C_{44} introduced during irradiation anneals in this temperature interval, in contrast to only about one-sixth of that in C_{11}. Approximately one-third of the irradiation produced increase in resistivity recovers in this range. For the region above 45 K, where interpretation is complicated by clustering of defects, only a limited amount of data (C_{44}-I) was obtained and no further discussion will be given.

Since the different temperature regions each involve the annealing of different kinds of defects, the amount of irradiation-produced change in any given constant apparently depends upon the kinds of defects which are generated. Thus the amount of modulus change produced by an irradiation cannot be directly related to an incremental change in resistivity without regard to both the particular constant being measured and the type of damage which is created.

B. Perfect-crystal temperature dependence

Elastic constants are very sensitive functions of temperature, particularly above approximately 20K. Since these changes are larger than the temperature effects expected from irradiation, it was necessary to determine the temperature dependence of the elastic constants very accurately prior to the thermal neutron irradiation. Consequently, the frequency changes were measured up to 45 K for all three unirradiated samples. Although the principle concern of the present discussion is the effects produced by point defects, we first consider briefly a comparison of these results obtained prior to the thermal neutron irradiations, with a recent perfect-crystal calculation by Garber and Granato.[17] This comparison is important because the very precise and demonstrably dislocation-insensitive data obtained here provide the best-known experimental check presently available for the theory and lead to information useful in determining interatomic potentials.

Garber and Granato calculated the temperature dependence of the elastic constants by assuming the strain dependence of all the phonon frequencies is the same as that in the low-temperature long-wavelength region where the derivatives can be calculated on the basis of finite-elasticity theory. In this manner, they find an expression for the temperature dependence of the elastic constants in terms of third- and fourth-order elastic constants. Since short-range repulsive interactions should be increasingly more important for the higher-order constants, they further assume that only nearest-neighbor interactions will be significant in determining the fourth-order constants. Thus they were able to reduce the final expressions containing 11 fourth-order constants to ones containing only measured third-order constants and one fourth-order constant. These final expressions for the temperature dependence of the second-order elastic constants of copper for low temperatures in terms of the fourth-order constant $C_{1111}(10^{14}\ \mathrm{dyn/cm^2})$, in units of $10^2\ \mathrm{dyn/cm^2\,K^4}$, are

$$\begin{aligned}
[C_{11}(T)-C_{11}(T=0)]/T^4 &= -(5.46)C_{1111}+10.1\,,\\
[C_{44}(T)-C_{44}(T=0)]/T^4 &= -(2.73)C_{1111}+5.43\,, \quad (2)\\
[C'(T)-C'(T=0)]/T^4 &= -(1.36)C_{1111}+3.76\,.
\end{aligned}$$

Three independent determinations of C_{1111} can be made by fitting these equations to the experimental results shown in Fig. 5. The high precision of these results provides a sensitive check of the theory since the assumptions made in the calculation should be most valid in the low-temperature re-

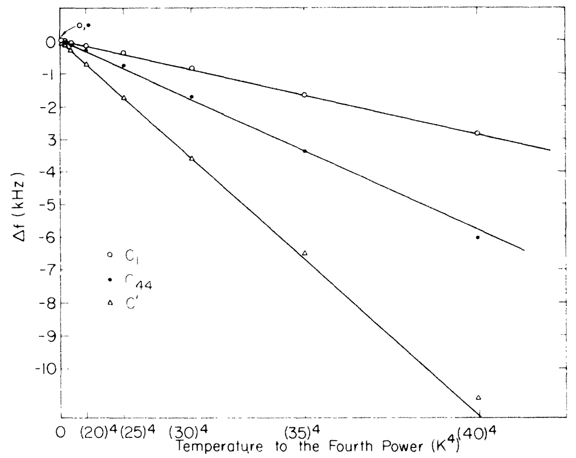

FIG. 5. Resonant frequency changes measured as a function of temperature prior to thermal neutron bombardment for all three elastic constants.

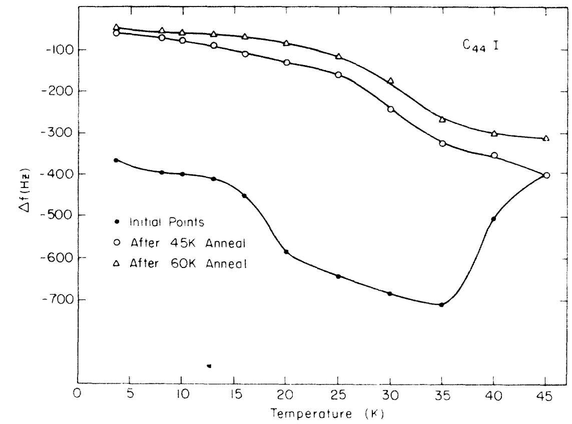

FIG. 6. Difference between the resonant frequency before and after thermal neutron irradiation which was measured at several temperatures for the first C_{44} run. The lower curve represents the values determined from measurements taken at each of the pulse temperatures near the end of the 15-min pulse. The middle and upper curves follow the results obtained after the crystal had already been annealed to 45 and 60 K, respectively.

gime. The straight lines indicative of the T^4 functional dependence of the elastic constants predicted by theory fit the experimental points quite well. The values of C_{1111} obtained using Eq. (2) are given in Table II; the length-change correction given in Eq. (1) is less than 5% in this case, and has been neglected. Also shown in the table are corresponding results found by Garber and Granato by fitting the high-temperature porton of their theory to other available data.

The three different values of C_{1111} obtained in both the high- and low-temperature regions are in good agreement with each other when account is taken of experimental uncertainties and the crude assumption made of a single fourth-order constant. This agreement is in contrast to a large discrepancy obtained with the only other previously available measurement sensitive enough to allow a comparison. The previous measurements, made by Alers[33] on C_{44} in copper from 4–21K, would require a negative value of C_{1111} and hence are in complete disagreement with the theory.

The magnitude of C_{1111} is important in determining the parameters of a Born-Mayer potential. Based on the results given in Table II, the parameters are close[34] to those used in many defect calculations.[35-38]

C. Temperature-dependent changes in the defect contribution to elastic constants

Following thermal neutron irradiation, strong changes were observed in the temperature dependence of all three elastic constants. These changes were determined by subtracting the temperature dependence of the elastic constant prior to irradiation from its temperature dependence after irradiation. Figure 6 shows the differences in resonance frequency found for C_{44} after the first low-temperature irradiation. The lower curve represents the differences found at each of the pulse temperatures for the first pulse at each temperature after irradiation. The middle and upper curves represent the differences obtained

TABLE II. Comparison of the values of the fourth-order elastic constant C_{1111} deduced from the low-temperature T^4 region with those obtained from the high-temperature region.

	$C_{1111}(10^{14}\ \text{dyn/cm}^2)$	
Mode	Present results low-temperature region	Garber and Granato high-temperature region
C_{11}	1.2	1.05
C_{44}	0.7	0.87
C'	1.3	1.07

after the crystal had already been annealed to 45 and 60 K respectively.

A sharp dispersion is quite evident near 18 K, which has disappeared by the time the middle and upper curves were obtained. Also, a much broader dispersion around 30 K is apparent in both these latter two curves. During the second C_{44} run, the temperature dependence was measured subsequent to a 35-K pulse. The measurements showed that the sharp dispersion had not completely disappeared after this pulse. Hence the defect responsible for the 18-K dispersion anneals somewhere in the 30–45-K temperature range.

Measurements for the C' mode are presented in Fig. 7. A much more detailed annealing program was undertaken with this sample. Pulses were first made, and readings taken, at the indicated temperatures (curve A) up to and including 25 K. Measurements were then performed at all temperatures indicated by the points of curve B. After a hold at 30 K for 15 min the sample was returned to the 3.6-K reference point, and the temperature region to 35 K was traversed in a similar fashion. These results are represented by curve C and the corresponding results after the anneal to 35 K are represented by curve D. Then the crystal was pulsed to 40 K, and finally 45 K. Subsequent to the 45-K pulse, all points were then sampled again, and these are represented by curve E. No evidence of the sharp dispersion at 18 K which occurred in the C_{44} runs is evident in these results, although the broad dispersion around 30 K is again present. (The limited C_{11} data were insufficient to indicate the presence or absence of the dispersion.)

The sharp dispersion in C_{44} is characteristic of a relaxation process, and is the expected Nielson-Townsend relaxation effect.[13] Nielson and Townsend (NT) attribute this effect to the stress-induced ordering of the interstitial member of either the I_B or I_C defect. Their observation that the effect occurs in the Young's modulus of a [111]-oriented single crystal and not in a [100]-oriented single crystal agrees with the present measurement of a modulus defect in the C_{44} and not the C' mode.

They found that the relaxation in their kilohertz measurements was centered about 10 K. The center of this relaxation should occur as the frequency of the applied stress nears the jump frequency of the defect, so the temperature dependence of the resonant frequency ν_R is given by an Arrhenius expression:

$$\nu_R = \nu_0 e^{-E/kT}. \tag{3}$$

Here E is the activation energy of relaxation for the defect and ν_0 is an effective frequency. Using the value found by NT for E, 0.015 eV, this ex-

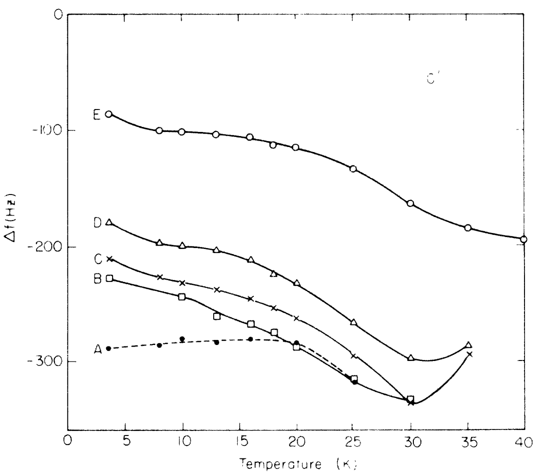

FIG. 7. Difference between the temperature dependence of the C' resonant frequency before and after thermal neutron irradiation, during various stages of the annealing program. (See text for description.)

pression indicates the process should be shifted upwards in temperature to approximately 18 K for 10-MHz measurements, in excellent agreement with the present results.

Besides the temperature dependence introduced by the relaxation process, further changes in the temperature dependence of all three elastic constants were found. The changes at 40 K were large (on the order of the changes at 3.6 K) and were unexpected. We can separate the temperature-dependent contributions from particular stage I defects by looking at the change in the temperature dependence of the elastic constants which occurs between appropriate annealing pulses. The difference between the measured temperature dependence after an anneal to temperature T_1, and that measured after an anneal to temperature T_2, gives the elastic constant temperature dependence which is introduced during irradiation by the defects which anneal between T_1 and T_2. The results obtained with the C' mode (Fig. 7) permit separation of the temperature-dependent contributions from the I_B, I_C, and I_D defects, since the temperature dependence of the elastic constants of the irradiated samples was measured after anneals to 25, 30, 35, and 45 K. The results from the C_{44} mode only allow separation of the contribution from the I_E defects, since measurements were made only after 45- and 60-K anneals. No separation is possible with the limited C_{11} data.

The change in the temperature dependence of the resonant frequency which occurs during various annealing intervals for the C' mode is given in Table III. Very little temperature-dependent contribution to the C' elastic constant is evident from

TABLE III. Change in the temperature dependence of the resonant frequency of the C' mode introduced by the defects which anneal in three different temperature regions.

Temperature (K)	Δf (Hz) annealing region 25–30 K	Δf (Hz) annealing region 30–35 K	Δf (Hz) annealing region 35–45 K
3.6	...	...	...
8		+2	−2
10	+5	−1	−6
13	−6	−3	−9
16	−5	−3	−16
18	−3	+1	−17
20	−9	+1	−22
25	−4	+2	−37
30		−7	−48

the defects which anneal between 25 and 30 K (I_B region) and none between 30 and 35 K (I_C region). However, a strong temperature-dependent contribution to this elastic constant does arise from the defects which anneal in the temperature interval 35–45 K (stage I_D). In fact, the temperature-dependent part of the contribution at 30 K is about half of the zero-temperature effect. A similar temperature-dependent change in the C_{44} modulus is also produced by the defects which anneal between 45 and 60 K, as seen from Fig. 6. Neither this nor the I_D temperature-dependent effect is characteristic of a relaxation process; a mechanism for the effect involving defect-induced changes in the vibrational spectrum is proposed and discussed in a subsequent paper. We note that the measurements obtained with the C_{44} mode subsequent to a 60-K annealing pulse (Fig. 6), and with the C' mode subsequent to a 45-K pulse (Fig. 7), indicate that a significant portion of the irradiation-induced temperature dependence is due to defects which remain after stage-I annealing.

The presence of these temperature-dependent effects, which differ for different constants and different types of defects as do the 3.6-K changes, may be very important for comparisons between elastic-constant changes measured at different temperatures. This is discussed further in Sec. III E.

TABLE IV. Comparison of the theoretical and experimental results for the change in electronic attenuation due to the irradiation-produced resistivity change.

Mode	Attenuation α (dB/μsec) Theoretical (free-electron model)	Experimental
C_{11}	−0.005	−0.006
C'	−0.046	−0.031

D. Attenuation changes

The simultaneous-attenuation measurements for two of the modes, C_{11} and C', exhibited a linear decrease as a function of irradiation time. The results for C' are shown in Fig. 8. The initial attenuation of the C_{44} mode was considerably higher, and no systematic change was evident.

The observed decreases are in agreement with the expected reduction of the electron-phonon contribution to the attenuation. This reduction arises from a decrease in the electron mean free path

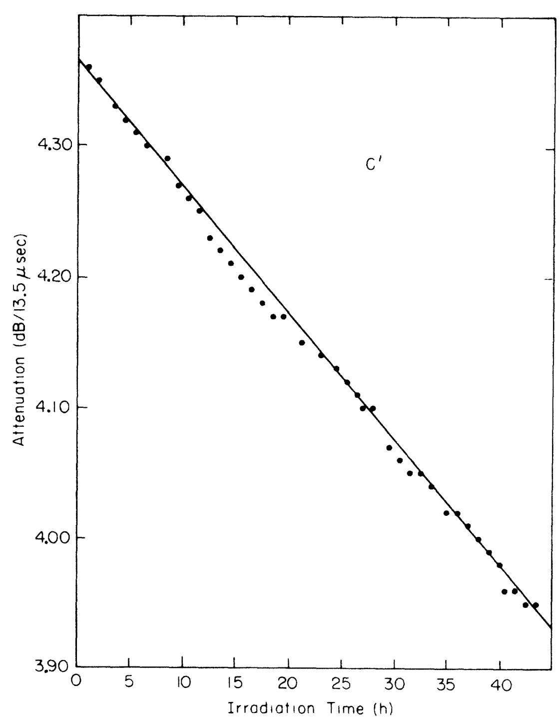

FIG. 8. Measured change in the attenuation of the C' mode during irradiation below 4 K.

due to the additional scattering centers created by the irradiation. Electronic attenuation is discussed in detail by Pippard[39] and Mason,[40] who use a free-electron approximation to calculate the magnitude of attenuation, $\alpha(Np/\text{cm})$, to be expected for a sample with resistivity ρ. The results are different for longitudinal (L) and shear (S) modes, and depend upon the frequency f and velocity v of the sound wave as well as the density ρ_d of the sample:

$$\alpha_L = \frac{2f^2}{15\rho_d v_L^3} \; \frac{\hbar^2(3\pi^2 N)^{2/3}}{e^2\rho} , \tag{4}$$

$$\alpha_S = \tfrac{3}{4}(v_L/v_S)^3\alpha_L . \tag{5}$$

In the above, N is the number of electrons per unit volume and e is the charge carried by one electron. Hence the change in α is related to the corresponding change in resistivity.

A comparison of the experimental results with the values obtained from these equations and the resistivity results from Table I is given in Table IV, and the agreement is considered good. The theoretical estimate for C_{44} indicates that it is smaller than the experimental uncertainty of the present measurements, and is consistent with the fact that no systematic change of attenuation was observed in either of the two C_{44} runs. This theory also accounts for the observed agreement between the attenuation and resistivity recovery during annealing (Fig. 9).

This is believed to be the first such measurement of the change in electronic attenuation produced by irradiation. The results indicate that attenuation measurements can provide a reliable measurement of defect concentrations in the same sample in which elastic-constant changes are measured. This is a very useful technique, especially for MHz elasticity measurements where sample dimensions are too large for ordinary resistivity measurements to be made.

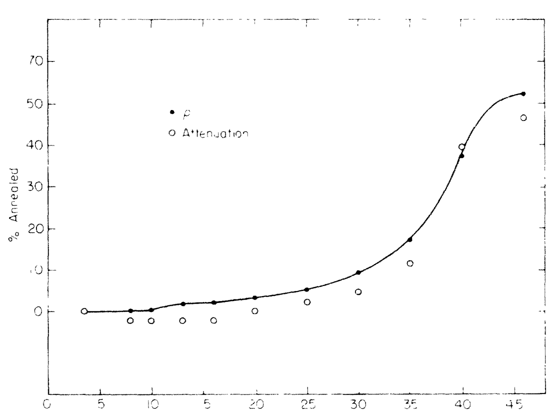

FIG. 9. Annealing of the resistivity and attenuation changes produced during irradiation below 4 K in the C' mode.

E. Comparison with other results

We now turn to one of the original questions posed in Sec. I: Why is there such a wide range in the values reported by different investigators for the magnitude of the change in elastic modulus as a function of Frenkel pair damage? The present results indicate that some difference is to be expected between measurements on different elastic constants, and with different types of irradiation, but the large differences in reported magnitudes cannot be explained by these effects. However, some of the other results obtained here are helpful in explaining many of the apparent discrepancies.

A brief description of each of the reported measurements of irradiation-induced changes in the elastic modulus is given in Table V and VI. The first table (V) is included for the sake of completeness, and lists the studies on materials other than copper. No comparison of these results will be attempted. The results for copper are shown in Table VI.

Two of these studies, by Dieckamp and Sosin,[2] and Roth and Naundorf,[41] were conducted at liquid-nitrogen temperatures, and both report large effects. These large effects might have resulted at least in part from the strong change in the temperature dependence of the elastic constants which was observed here after stage-I annealing.

The remaining measurements were all at or near liquid-helium temperatures. The two investigations which represent the extremes of all the reported values, Thompson *et al.*[3] and König *et al.*,[12] are not consistent with the present results or with any other similar measurement. The failure of Thompson *et al.* to observe any effect is the most difficult to understand, especially since the experiment by Wenzl *et al.*[42] is so similar in nature. Possibly, some cancellation due to dislocation-pinning effects occurred during the measurement. The difficulties in the König *et al.* experiment have been discussed elsewhere, in terms of both the inhomogeneity of damage in their sample,[13] as well as the uncertainty in the assumed Frenkel-pair-production rate.[43]

Wenzl *et al.*[42] report a value of −39 using reactor irradiation, which is about two to three times as large as would be expected on the basis of the present results if the type of damage was the same. However, the damage introduced by reactor irradiation is more complex than that created by thermal neutrons, and is characterized by large displacement cascades. It is quite possible that these cascades may contribute significantly to the measured modulus changes, and thus account for the larger observed value. In fact, the annealing studies by Ehrensperger[44] show that only about 20% of the observed shear-modulus change in copper produced by fast neutron irradiation anneals in stage I. This indicates that studies of fast-neutron-induced changes in the elastic moduli of copper may be primarily measurements of defects other than those which anneal in stage I. Since the findings of Okuda and Nakanii[45] give only an upper limit on the magnitude of the effect (−80), they are not inconsistent with the present findings.

Excellent agreement is obtained with the Townsend *et al.* results[8] of -13 ± 3. Excellent agreement was also obtained previously with their values for the parameters associated with the relaxation process. Since deuteron- and thermal-neutron damage are quite similar in nature, this high degree of agreement should be expected.

TABLE V. Brief description of the reported measurements of irradiation-induced changes in the elastic modulus of various materials other than copper.

	$\frac{d\ln C}{d\gamma}$	Material	Radiation type	Radiation temperature (K)	Measurement temperature (K)	Simultaneous resistivity	Measurement frequency (Hz)
Gerlich *et al.*[a]	Few percent decrease for all 3 constants	LiF	Reactor neutrons	300	300	No	10^7
Muss and Townsend[b]	−0.44	W	13.7-MeV deuterons	300	300	No	10^3–10^4
DiCarlo and Townsend[c]	−(0.2–1)	W	13-MeV deuterons	78–90	78	No	10^3–10^4
DiCarlo *et al.*[d]	−11	W	2.5-MeV electrons	≤20	≤20	Yes	600
Townsend *et al.*[e]	-13 ± 3	W	10-MeV protons	< 15	4.2	No	$(5-20)\times10^2$
Hillairet *et al.*[f]	Large decrease	Mg	Reactor neutrons	80	80	No	⋯
Likhter and Kikoin[g]	No effect on bulk modulus	Mg Al	Reactor neutrons	300	300	No	⋯
Folweiler and Brontzen[h]	−10	Al	Quench (only vacancies)	Quench from 800	300	No	10^5
Wenzl *et al.*[i]	−47 −67	Al Pt	Reactor neutrons	4	4	Yes	50–300
Chountas *et al.*[j]	-39 ± 9	Ag	Reactor neutrons	25	10	Yes	44 140
Soulie *et al.*[k]	−70	Ni	2-MeV electrons	11–21	11–21	Yes	350

[a] Reference 14.
[b] D. R. Muss and J. R. Townsend, J. Appl. Phys. 33, 1804 (1962).
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TABLE VI. A brief description of the reported measurements of irradiation-induced changes in the elastic modulus of copper.

	$\frac{d\ln C}{d\gamma}$	Material	Radiation type	Radiation temperature (K)	Measurement temperature (K)	Simultaneous resistivity	Measurement frequency (Hz)
Present experiment	C_{11}-4.8 C_{44}-15.8 C'-18.1	Cu	Thermal neutrons	<4	3.6	Yes	10^7
Dieckamp and Sosin [a]	-140 ± 60	Cu	1-MeV electrons	78–206 (gradient)	78	No	500
Roth and Naundorf [b]	-75 ± 20	Cu	3-MeV electrons	120	78	Yes	2.5×10^3
Thompson *et al.* [c]	none (<1)	Cu	Reactor neutrons	21	21	No	10^4
Konig *et al.* [d]	−130	Cu	5.3-MeV α particles	~30	4	No	10^2
Okuda and Nakanii [e]	<−80	Cu	Reactor neutrons	<15	4	No	4×10^2
Wenzl *et al.* [f]	−39	Cu	Reactor neutrons	4	4	Yes	50–300
Townsend *et al.* [g]	-13 ± 3	Cu	10-MeV protons	<15	4.2	No	$(5-20) \times 10^2$

[a] Reference 2.
[b] Reference 41.
[c] Reference 3.
[d] Reference 12.
[e] Reference 45.
[f] Reference 42.
[g] Reference 8.

IV. SUMMARY AND CONCLUSIONS

The elastic-constant changes during irradiation are −2% −15.8%, and −18.1% per atomic percent of defects for the bulk modulus C_{44} and C', respectively. The percentage elastic-constant changes measured at 3.6 K after pulse annealing tc different temperatures are different for different elastic constants in the same annealing range, and for different annealing regions for the same elastic constant. Also, the elastic-constant changes are strongly temperature dependent. This shows that there are several different types of effects occurring, each of which depends upon the type of defect involved (close pairs or isolated defects).

Five different effects are separated. (i) The indirect dislocation-pinning effect is eliminated in these measurements. (ii) The bulk-modulus change is small ($d\ln B/d\gamma \sim 1$), both with irradiation below 4 K and an annealing through state I_D, showing that the bulk effect first considered by Dienes, is small. (iii) The shear modulus changes during irradiation are large ($d\ln C/d\gamma \sim -15$ to -20), and cannot be a bulk effect. (iv) The relaxation effect discovered by Nielson and Townsend is confirmed. (v) The temperature dependence of the elastic constants is also changed by point defects, and the temperature-dependent part of the change at 40 K is of the same order of magnitude as the 3.6-K change.

The strong dependence of the elastic-constant changes on the type of defect involved and on the temperature helps to account for the wide variation of results found previously for measurements using different types of irradiation at different temperatures.

The agreement found between experiment and theory for the magnitude of the temperature dependence of the elastic constants in the low-temperature T^4 region, gives support for the interatomic potential most used for defect calculations in copper.

The fact that the attenuation changes observed are proportional to the electrical conductivity and in good agreement with theory shows that attenuation measurements, made simultaneously with elastic-constant measurements, can be used to measure defect densities in bulk specimens.

ACKNOWLEDGMENT

The authors wish to thank J. S. Koehler for support in this undertaking, R. Schwarz for help in polishing the specimens, C. E. Klabunde for help with the irradiations, and W. Schilling and P. H. Dederichs for discussion of their work.

*Research supported in part by the National Science Foundation under Grant No. GH-33634 and by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198.

†Research sponsored in part by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

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