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Dislocation Mobility in fcc Metals below 1°K

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Previous experiments have shown that the elastic moduli of pure fcc metals are lowered by the presence of mobile dislocation loops. The amount of this lowering is often called the modulus defect. Results of accurate modulus measurements from 20°K down to 0.1°K using liquid-helium and adiabatic-demagnetization techniques show that this modulus defect is temperature-dependent and decreases as the temperature approaches absolute zero. Thus the mobility of dislocations must be decreasing at these low temperatures with most of the decrease confined to temperatures below 1°K. In fact, the decrease is most rapid at 0.1°K. No attenuation changes were observed which could be directly associated with the modulus changes, thereby ruling out the possibility that the decreased mobility of dislocations arises from a thermally activated process with a unique but small activation energy. The present modulus measurements are in apparent disagreement with the often quoted statement that the elastic moduli must approach absolute zero with zero slope. However, the absolute zero of temperature has not been obtained, and there is no reason to expect that the observed dislocation effects should not ultimately approach zero with a zero slope at temperatures much below 0.1°K.

INTRODUCTION

IT is well known[1] that the temperature dependence of the elastic moduli must be such that the modulus-versus-temperature curve approaches absolute zero with a vanishing slope. This follows from the Maxwell's relation

$$\left.\frac{\partial\sigma_{ij}}{\partial T}\right|_{\epsilon_{ij}}=\left.\frac{\partial S}{\partial\epsilon_{ij}}\right|_{T}, \tag{1}$$

where σ_{ij} and ϵ_{ij} are, respectively, stress and strain, and S and T are the entropy and temperature. The third law of thermodynamics which states that isothermal entropy changes vanish in the limit of absolute zero of temperature forces the right-hand side of Eq. (1) to vanish. The left-hand side is simply the slope of the modulus-versus-temperature curve. Experiments in which the elastic moduli were measured to $\pm0.1\%$ indicate that these arguments are correct.[2] However, recent ultrasonic developments[3] have made it possible to measure modulus changes to an accuracy of one part in a million. Using such equipment, it has been observed[4] that in pure fcc metals the derivative on the left side of Eq. (1) does not tend to zero as it should and in some cases it actually becomes larger as absolute zero is approached. An example of such results is shown in Fig. 1 where changes in the shear modulus C_{44} of copper are plotted as a function of temperature down to 1°K. It can be seen that increasing the purity of the sample only serves to make the apparent deviation from the predictions of Eq. (1) worse. The work of Schultz and Chambers[5] on cold-worked niobium indicates that the effect also exists in bcc metals.

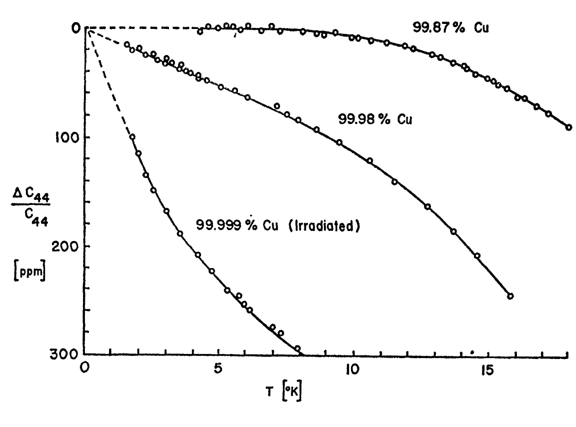

FIG. 1. Relative change of the elastic shear modulus C_{44} with temperature for copper single crystals of various purities. The zero for the ordinate was arbitrarily chosen from a linear extrapolation of each curve to zero temperature.

It is the purpose of this paper to present the experimental information available on this effect and to show that mobile dislocations are most likely responsible for it. The measurements to be described extend down to 0.1°K and show that the left-hand side of Eq. (1) is definitely not zero. However, there is no reason to believe that the dislocations will continue to contribute at even lower temperatures, so Eq. (1) cannot be considered as incorrect. The fact that dislocation motion is involved at temperatures of the order of 0.1°K is a surprising result in itself and implies that if any kind of thermal activation process is involved the activation energy must be very small.

EXPERIMENTAL PROCEDURE

Most of the measurements to be described were made using the ultrasonic sing-around apparatus described elsewhere by Forgacs.[3] Here a 10-Mc/sec ultrasonic pulse is made to travel between flat faces on a sample in such a way that the flight time across the sample con-

[1] J. K. Galt, Phys. Rev. **73**, 1460 (1948).

[2] J. R. Neighbors and G. A. Alers, Phys. Rev. **111**, 707 (1958).
[3] R. L. Forgacs, IRE Trans. Instr. **9**, 359 (1960).
[4] G. A. Alers and D. L. Waldorf, Bull. Am. Phys. Soc. **7**, 236 (1962).
[5] J. Shultz and R. H. Chambers, Bull. Am. Phys. Soc. **9**, 214 (1964).

trols the frequency of an oscillator. By measuring the frequency of this oscillator to 1 part in 10^7, it is possible to measure the transit time, and hence the velocity of sound, to the same accuracy. Because of uncertainties in the absolute values of electronic and acoustic phases, the absolute precision is not this good, but since the uncertainties are fixed, it is possible to measure changes in velocity of 1 part in 10^7. Obviously, this technique would be sensitive to dimensional changes but precision measurements of the thermal expansion[6] show that such spurious effects are entirely negligible. The sing-around apparatus also permits the monitoring of the amplitude of the ultrasonic wave so that changes in the attenuation of the sound can be observed. Absolute attenuation values can be measured, but these are accurate to logarithmic decrement values of $\pm 0.5\times 10^{-3}$ because the pulse is shaped to optimize the velocity measurement at the expense of the attenuation measurement.

In view of the fact that the temperature dependence of the modulus near absolute zero is small and the apparatus used to detect it is rather complicated, several simpler but less accurate techniques were used to provide a check on the sing-around system. By using the usual pulse-echo technique[7] with a fast-sweep-speed oscilloscope, it was possible to detect transit-time changes of 1 part in 10^5. This system gave measurements in agreement with those obtained on the sing-around system. Another method used was the resonant-bar technique[8] in which the longitudinal resonant frequency of a bar-shaped specimen was measured to an accuracy of 5 parts in 10^6. This method provided information not only on the temperature dependence of the modulus but also on its frequency and strain-amplitude dependence. Furthermore, absolute attenuation measurements could also be made accurately.

Except for measurements below 1°K, the temperature was controlled and measured by the use of conventional techniques. The specimen was usually housed in a sealed chamber filled with helium gas which served as a constant-volume thermometer. This thermometer was calibrated against the known vapor-pressure–temperature curves for liquid helium below 4.2°K and at the normal-to-superconducting transition temperature of lead (7.175°K) above the liquid-helium range. A carbon resistance thermometer in good thermal contact with the specimen was also used to assure that thermal equilibrium was established between the gas and the specimen.

Temperatures below those obtainable by pumping on liquid helium (1.5°K) were obtained by adiabatic demagnetization of ferric ammonium alum. For these measurements, the specimen and its two transducers were mounted below the demagnetization-salt container by high-purity copper clamps which assured good thermal contact to the salt. The two coaxial rf leads to the transducers were brought to the sample along a path which maintained good thermal contact with the salt. In this way, the heat conducted down the rf leads went into the salt instead of the specimen. The heat of magnetization was conducted to the helium bath by way of a mechanical heat switch operated from outside the cryostat. Another paramagnetic salt pill made of cerium magnesium nitrate was hung below the specimen on a copper tail and was used as a thermometer since its paramagnetic susceptibility is known[9] to vary as $1/T$ in the temperature range above 0.1°K. This thermometer was calibrated against the known vapor-pressure–temperature curve of liquid helium in the temperature range from 1.2 to 4.2°K. Two separate and compact superconducting magnets in soft iron cases were installed in the liquid-helium bath around the low-temperature chamber. One magnet surrounded the ferric ammonium alum plug and was used for obtaining and controlling the low temperatures. The other magnet applied 2000 G to the specimen in order to suppress the large electron attenuation characteristic of very-high-purity copper in this temperature range. Measurements both with and without this field showed no differences in temperature dependence of the moduli. The cerium magnesium nitrate thermometer was suspended far enough away from the specimen and salt plug not to be affected by these magnets. By observing the rate at which the thermometer and specimen reached equilibrium after a complete or partial demagnetization, it was observed that the thermal contact between the various parts was very good and no corrections had to be introduced for thermal gradients. Temperatures between 0.1 and 1°K were obtained both by allowing the specimen to warm up from a lower temperature and by partial demagnetization. This latter technique proved most useful because any desired temperature could be established by simply adjusting the magnetic field applied to the salt.

EXPERIMENTAL RESULTS

The main features of the results are summarized in Fig. 1 which shows the modulus-versus-temperature variation observed in copper samples with differing purity. The ordinate is the relative change in modulus as measured on the sing-around apparatus. Here the data have been arbitrarily extrapolated to 0°K and the three curves are plotted relative to this arbitrary modulus. The sense of the modulus change is such that increasing temperature decreases the modulus value. The data shown for 99.87% Cu were obtained on a copper crystal containing 0.13-wt% gold and follow a

[6] R. H. Carr, R. C. McCammon, and G. K. White, Proc. Roy. Soc. (London) **A280**, 72 (1964).
[7] G. A. Alers and J. R. Neighbours, J. Phys. Chem. Solids **7**, 58 (1958).
[8] G. A. Alers, R. E. Condit, and J. A. Karbon, Appl. Phys. Letters. **1**, 8 (1962).
[9] J. M. Daniels and F. N. H. Robinson, Phil. Mag. **44**, 630 (1953).

curve predicted by lattice dynamics[10] (i.e., the modulus decreases as the fourth power of the temperature and its rate of decrease agrees with theoretical predictions). The linear decrease of the modulus with temperature shown on the curve labeled 99.98% copper was obtained on a crystal prepared from oxygen-free high-conductivity (OFHC) copper.[4] It is in complete disagreement with the predictions of Eq. 1. The linear variation shown was also observed in the other elastic moduli as well as in other crystals of 99.9% pure lead and gold. As a general rule, the slope of the line was largest for shear moduli and smallest for compressional moduli. Tests using conventional ultrasonic pulse-echo techniques[7] instead of the sing-around apparatus showed this same temperature variation. No changes in the ultrasonic attenuation were observed to accompany these modulus variations. A logarithmic decrement change of 5×10^{-5} could have been detected.

Samples of the highest purity copper attainable (99.999+%) showed not only a much larger temperature variation for the moduli but also a concave upward curvature. The curve in Fig. 1 labeled 99.999% Cu was actually obtained from a crystal which had received several hours of γ-ray irradiation in order to reduce the magnitude of the temperature dependence. These data were chosen for the figure only because they fit the ordinate scale suitable for the less pure samples. A well-annealed crystal with no irradiation exhibits a modulus variation more than twice as great as that shown in the figure.

In order to be sure that these apparent modulus variations did not result from the measurement technique, a series of experiments were performed on a pure gold bar driven in its fundamental longitudinal mode of vibration near 19 kc/sec. Figure 2 presents the results obtained. In the annealed state, the Young's modulus of the bar showed a linear temperature dependence of approximately 11 ppm/deg. Data obtained on the elastic moduli C_{44}, $(C_{11}-C_{12})/2$, and $(C_{11}+C_{12}+2C_{44})/2$ with the sing-around technique at 10 Mc were used to compute the anticipated temperature dependence of Young's modulus. This computed variation was 12 ppm/deg in satisfactory agreement with the measured value. Thus the anomalous temperature dependence of the moduli is not a characteristic of the method of measurement and is nearly frequency-independent. Cold-working the gold bar specimen by cold-rolling it to a 4% increase in length at room temperature increased the slope of the modulus-versus-temperature line to 155 ppm/deg. Increasing the strain amplitude at which the measurements were made did not change the slope but slightly lowered the absolute modulus value. The internal friction as measured by the logarithmic decrement of the vibrating bar did not show any very great variations. In the annealed state, the logarithmic decrement increased slightly with temperature, as would be expected from the known temperature variation of the internal friction at higher temperatures.[8]

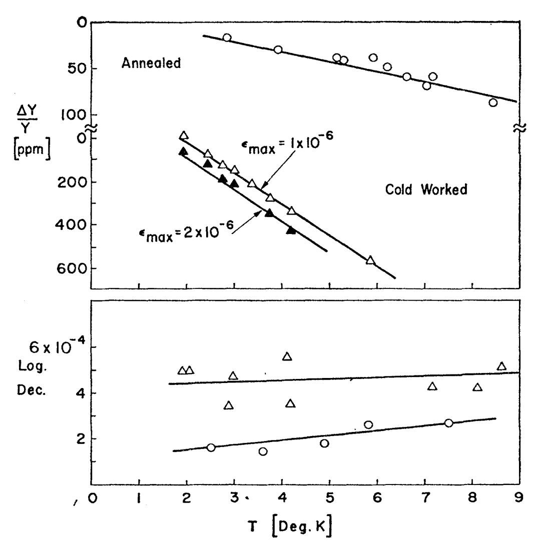

FIG. 2. Temperature variation of the Young's modulus and internal friction of a polycrystalline gold bar measured at 19 kc/sec in the annealed state and after being cold-worked.

From the foregoing observations, it can be concluded that the temperature variation of elastic moduli near 4°K can be decreased by the addition of impurity atoms (or by minor γ-ray irradiations). Its magnitude is greatest for shear moduli and least for extensional moduli and is independent of the frequency of measurement. Most important, it is increased by small amounts of cold work. All of these properties are consistent with the hypothesis that mobile dislocation lines are responsible for the effect. It is well known that dislocations can lower the elastic moduli and, in fact, it has been shown[11] that for very-high-purity copper the moduli at 4.2°K are lower than the true modulus values by nearly a percent (10 000 ppm). Thus the observed temperature dependence of the modulus may arise from a decrease in this modulus defect which implies a decrease in mobility of the dislocations as the absolute zero of temperature is approached.

In order to study this hypothesis, a series of experiments was performed on an ultrahigh-purity copper crystal in which the amount of lowering of the modulus by dislocations was controlled by γ-ray irradiation[12] in a 4000-Ci γ-ray source. Figure 3 shows how the modulus defect measured at 77°K decreased with irradiation time. The 77°K temperature was used because of its convenience. Absolute modulus data at 4.2°K are difficult to obtain because of the large acoustic absorption produced by the free electrons. The data shown in Fig. 3 were obtained by taking the difference between

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 50.

[11] G. A. Alers and D. O. Thompson, J. Appl. Phys. **32**, 283 (1961).

[12] D. O. Thompson and D. K. Holmes, J. Phys. Chem. Solids **1**, 275 (1957).

an absolute measurement of C_{44} after a certain irradiation time and a similar measurement made after 350 h of irradiation. Thus the accuracy is at best only ±0.1%. The modulus value obtained after the total irradiation was in satisfactory agreement (within less than 0.1%) of the value obtained in dilute alloy crystals where the dislocations are presumably pinned by the alloy atoms. The break in the curve at 39 h was produced by some recovery of the radiation damage brought about by a two-month "anneal" at room temperature.

Figure 4 shows the temperature variation of the modulus C_{44} which was observed on the copper crystal whose modulus defect was controlled by γ-ray irradiation as shown in Fig. 3. It is plotted as changes relative to the modulus value at 4.2°K in order to emphasize that the sing-around provides a relative measurement rather than an absolute one. The numbers labeling each curve are the number of hours of irradiation that the sample received and hence determine the modulus defect as shown in Fig. 3. These data show that, for a crystal in which the dislocations have lowered the 77°K modulus by 0.6% (6000 ppm), the process of

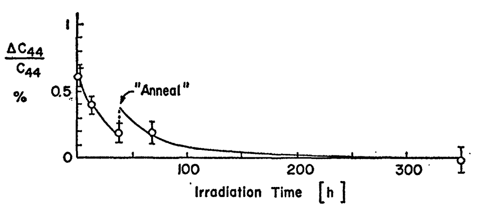

FIG. 3. Variation of the dislocation contribution to the shear modulus C_{44} at 77°K with γ-ray irradiation. The discontinuity at 39 h was produced by a two-month "anneal" at room temperature.

cooling from 9 to 0.1°K recovers almost 0.2% of this modulus defect. Furthermore, the shape of the curve is such that the modulus defect can be expected to decrease even more below 0.1°K. The effect of the γ irradiation is to make the temperature dependence of the modulus less as it makes the total modulus defect less. Thus it may be concluded that the smaller the dislocation contribution to the modulus, the smaller is the change in modulus between 9 and 0.1°K.

During the irradiation and the temperature-dependence runs, the ultrasonic attenuation was also monitored. At 77°K, the logarithmic decrement decreased from 6×10^{-3} to 1×10^{-3} during the 350-h irradiation treatment. At 4.2°K, the observed attenuation came largely from the electrons and did not change appreciably from a logarithmic-decrement value of 4×10^{-3} during irradiation. By applying a high magnetic field, this electron attenuation could be suppressed and the residual attenuation was measured to have a logarithmic decrement of 1×10^{-3}. As the temperature was varied to obtain the modulus data shown in Fig. 4, the attenuation was observed to change very little. The changes that were

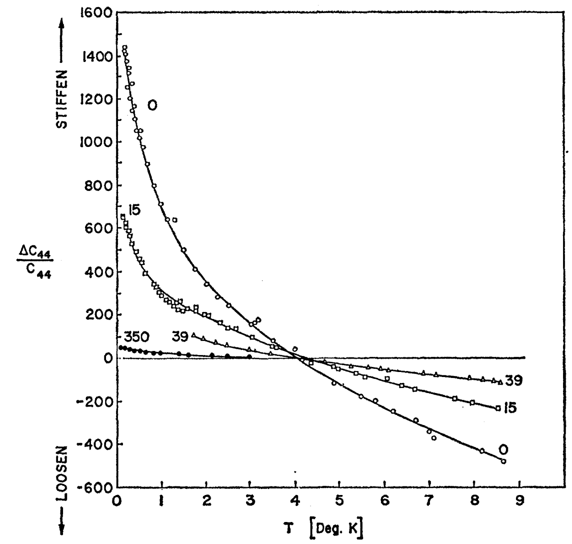

FIG. 4. Temperature dependence of the shear modulus C_{44} relative to its value at 4.2°K after various doses of γ-ray irradiation. The numbers on each curve specify the hours of exposure to a 4000-Ci γ-ray source.

observed could be described as a linear decrease in logarithmic decrement with decreasing temperature just as might be expected from an extrapolation of the dislocation attenuation at high temperatures.[11] Quantitatively, the logarithmic decrement changed by only 6×10^{-4} between 10 and 2°K in the crystal with no irradiation, and the change became much less than this after some irradiation. There was certainly no increase in attenuation greater than 1×10^{-4} in cooling to 0.1 from 4°K under any circumstances.

Since only the modulus and not the decrement varied with temperature, an attempt was made to fit a purely empirical law to the modulus curves shown in Fig. 4. By plotting the temperature derivatives versus temperature on logarithmic coordinates, it was concluded that the data could be fit by an equation of the form

$$\Delta C_{44}/C_{44}=AT^{1/4}, \qquad (2)$$

where A is a constant which depends on the irradiation dosage. This equation is such that the data should fall on a straight line when plotted against $T^{1/4}$. Figure 5 shows such a plot for all the data obtained during the radiation effect study. Since only relative changes were measured, the vertical position of each curve is arbitrary and the zero for the ordinate is arbitrary. It can be seen that the $\frac{1}{4}$ power of the temperature law satisfactorily describes the data from 0.1°K up to the temperatures at which the lattice contribution becomes appreciable. By using the measurements on the 99.87% Cu crystal (Fig. 1) to define this lattice contribution, it is possible to correct the pure-copper curves for it and show that Eq. (2) appears to remain valid to the highest temperatures of measurement (35°K). The open-circle data points below 4.2°K on the curve for the specimen with

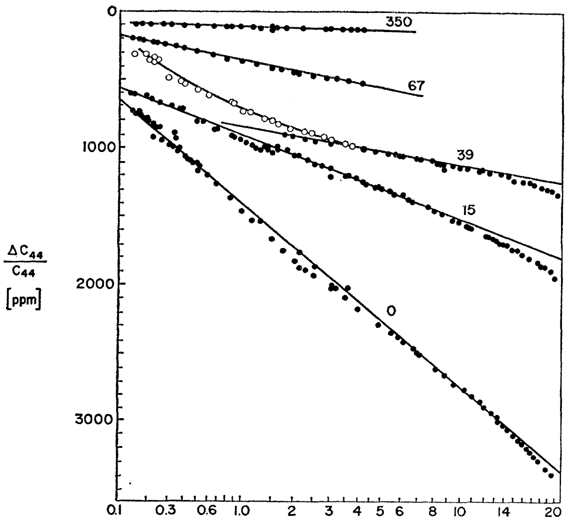

FIG. 5. Relative changes in the elastic modulus C_{44} plotted against the $\frac{1}{4}$ power of the temperature. The open-circle data points were obtained after 39 h of irradiation and a two-month "anneal" at room temperature. The numbers associated with each curve refer to the total irradiation time in hours.

39 h of irradiation deviate from the empirical law because they were obtained after a two-month "anneal" at room temperature. These annealing results show that Eq. (2) is not very universal even though further irradiation (67-h and 350-h curves) restores it. The data obtained after 350 h of irradiation are also fit by Eq. (2) and are significant because the magnitude of modulus change involved is comparable with that which was observed on the OFHC copper. This enables a comparison between the two crystals to be made, as is shown in Fig. 6. Here it can be seen that the modulus variation of the crystal in which the dislocations are pinned by grown-in impurities is somehow different from that in which the pinning is accomplished by defects introduced by γ-ray irradiation.

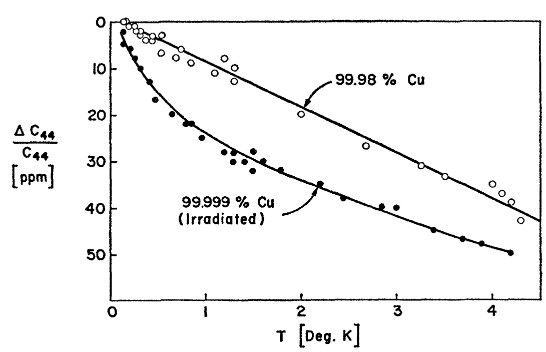

FIG. 6. Comparison of the temperature dependence of C_{44} observed on a heavily irradiated high-purity copper crystal with that observed on a crystal of OFHC copper.

DISCUSSION

These measurements show that when elastic moduli are measured to an accuracy of greater than 0.01% (100 ppm), the thermodynamically anticipated disappearance of temperature dependence near absolute zero is not observed. The observed temperature dependence appears to arise from thermally induced changes in the mobility of those dislocations which produce a lowering of the absolute modulus value. Two possible descriptions of this apparent loss of mobility can be considered. One is associated with the entropy of a dislocation line and would use Eq. (1) to explain the observations by showing that a long dislocation line has a large strain dependence of its entropy at low temperatures. The other explanation uses the more common idea that dislocation motion is a thermally activated process. From this point of view, the present observations would show that pure fcc metals possess a finite but very small activation energy for dislocation glide. If this activation energy had a particular value, the modulus variation would be very rapid and would be accompanied by an easily observed internal friction variation. The experimental results, however, show that there must be such a wide distribution of activation energies that the temperature dependence of the logarithmic decrement remains less than 10^{-4} per degree and the modulus variation is spread from 0.1°K to beyond 20°K. Since the choice between these two possible explanations can be settled only by detailed calculations based on specific models, no further discussion will be carried on here.

It must be emphasized that the present measurements do not contradict the thermodynamic arguments expressed in Eq. (1) but simply show that where dislocations are concerned much lower temperatures (less than 0.1°K) must be reached before the temperature dependence of the elastic moduli will vanish. Certainly the empirical equation (2) cannot be expected to apply all the way to absolute zero.

ACKNOWLEDGMENTS

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