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Low Temperature Release of Stored Energy in Cold Worked Copper*

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Pure polycrystalline copper and alpha-brass specimens were deformed in compression at temperatures near −185°C. The release of stored energy was observed during subsequent warmups to room temperature and above. The annealing spectrum of pure copper shows prominent peaks at −25°C and −90°C, and smaller resolvable peaks at lower temperatures. The total energy release was about 0.17 cal/g for a specimen strained to 0.65. In contrast to pure copper, the spectrum for brass shows only one clearly resolvable peak at −10°C and extends to higher temperatures. The energy release was almost three times that of pure copper for comparable strains.

The sensitivity of the experimental method is about 10^{-4} cal/g per degree centigrade, and the results are believed to be accurate to about thirty percent. The apparatus was calibrated by measuring the known heat-of-fusion of mercury.

A tentative theory of the multiple peaks in the rate of energy release below −70°C is given. This theory supposes that the moving imperfections in this temperature range are divacancies and that the energy of motion of a divacancy is different depending on its orientation in the internal stress field.

I. INTRODUCTION

WHEN a metal has been deformed plastically it contains many structural defects which were not present in the unstrained lattice. These defects are responsible for observable changes in many of the physical properties of the metal such as electrical resistivity, elastic constants, and internal friction. They also increase the total energy content of the deformed metal. This additional energy, of course, results from the work done in the deformation process and represents only a part of that work, the remainder being directly converted into heat. When possible, the lattice moves towards states of lower free energy releasing the stored energy as heat. Many of the effects of the deformation can thus be annealed out by raising the temperature of the metal sufficiently to allow thermally activated processes to proceed with appreciable velocities.

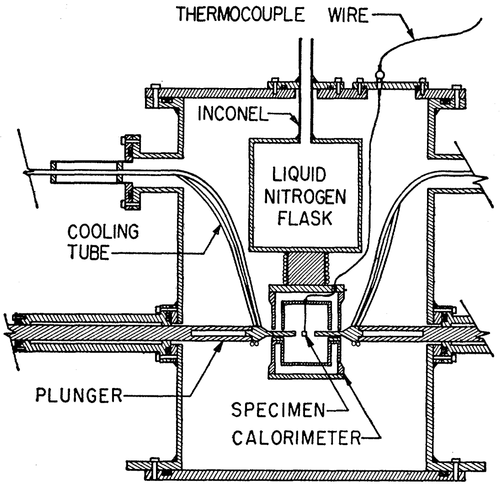

FIG. 1. Schematic diagram of the experimental apparatus. The unit has cylindrical symmetry about a vertical axis. The external hydraulic system which supplies the working force is not shown.

It is generally believed that the principal defects produced by plastic deformation are dislocations, interstitials, vacancies, and clusters of vacancies or of interstitials. In many metals, such as copper, the annealing spectrum includes processes observed below room temperature. In fact, investigations of copper in the related area of radiation damage where only interstitials and vacancies are thought to be produced show that these defects are largely removed by annealing at temperatures below 20°C. Previous studies[1–8] of the release of the stored energy of cold work have all been carried out at room temperature and above, and give no information about the processes which occur at lower temperatures. It is evidently desirable to supplement these studies with measurements of the stored energy released below room temperature.

In the present investigation, 99.999% pure polycrystalline copper specimens were deformed in compression at temperatures near that of liquid nitrogen. They were then allowed to warm up at a controlled rate of about 2°C per minute to temperatures somewhat above room temperature. The stored energy released during the warmup was measured as a function of

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[1] G. I. Taylor and H. Quinney, Proc. Roy. Soc. (London) **A143**, 307 (1934); **A163**, 157 (1937).

[2] T. Suzuki, Science Repts. Research Inst. Tôhoku Univ. **1**, 193 (1949).

[3] H. Kanzaki, J. Phys. Soc. Japan **6**, 90 (1951); **6**, 456 (1951).

[4] Borelius, Berglund, and Sjoberg, Arkiv Fysik **6**, 143 (1952).

[5] Clarebrough, Hargraves, Michell, and West, Proc. Roy. Soc. (London) **A215**, 507 (1952).

[6] Clarebrough, Hargraves, and West, Phil. Mag. **44**, 913 (1953).

[7] W. Boas, *Bristol Conference on Defects in Crystalline Solids* (Physical Society, London, 1954), p. 212.

[8] P. Gordon, J. Metals **7**, 1043 (1955).

temperature. The differential technique employed for these measurements is an adaptation of the method used by Overhauser to measure the release of stored energy due to radiation damage in a similar temperature range.[9] Briefly, this technique consists of a measurement of the temperature difference between a specimen containing stored energy and a similar dummy specimen containing no stored energy as they move through a temperature interval in which one or more annealing processes occur. Quite obviously the method is neither isothermal nor adiabatic. Copper was chosen for this study because of the existence of related information and because it is believed that dislocations play a secondary role in the low-temperature annealing processes.

II. DESCRIPTION OF THE APPARATUS

The experimental apparatus is shown schematically in Figs. 1 and 2. The outer vacuum jacket is a steel cylinder with cover plates. It supports a pair of plungers which are used to compress the specimens, and has vacuum ports for admitting the copper cooling tubes shown. In addition, it has other ports which are not shown in the figure and which connect to the vacuum pumps, the vacuum gauges, and to a line used to admit dry nitrogen gas to the system. The top cover plate supports a liquid nitrogen flask which in turn supports the calorimeter. The solid copper cylinder which connects the flask to the calorimeter is wound with a nichrome heater which is used to control the warmup rate of the calorimeter. The remaining volume within the vacuum jacket is filled with glass wool.

The calorimeter was machined from copper bar stock. When assembled as in Fig. 2 it consists of two concentric cylindrical tubes with closed ends. The inner tube is connected to the outer by an annular ring just below the midpoint. The upper and lower parts of the calorimeter may be separated at this point to give access to the inside. All bolts used to fasten the calorimeter are spring-loaded with lock washers so that thermal expansions cannot loosen the joints. Holes necessary to admit the plungers are drilled perpendicular to the axis of the calorimeter.

Although the measurements are made under a gas pressure of one atmosphere, it is necessary to remove gases such as carbon dioxide and water vapor from the system. Such gases would condense on the specimens and cause spurious signals during the data-taking warmups. The system is therefore evacuated to a pressure lower than one micron before cooling. This moderately good vacuum was found to be adequate for the purpose.

The plungers used to compress the specimens are stainless steel rods fitted with tips machined from drill stock. They are each free to move parallel to their common axis so that they may be withdrawn from the calorimeter. As shown in the figure, a turn of copper tubing is soldered to each plunger near the tip. Liquid nitrogen is forced through these tubes before and during the compression so that the specimens are cold worked at a temperature of about $-185°C$. The tips of the plungers which engage the specimens are lubricated with graphite to allow the area of the specimen ends to increase as their length decreases and to prevent the specimens from adhering to the tips. When the plungers are withdrawn from the calorimeter after the compression, a gate consisting of a copper ring drops to cover the openings necessary to admit the plungers. A hydraulic ram is used to supply the force which is applied to the plungers during the deformation.

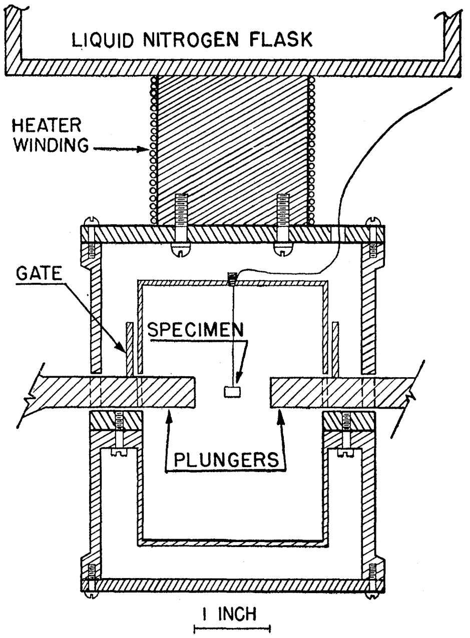

FIG. 2. Schematic diagram of the cylindrical copper calorimeter.

The specimens are machined from 0.99999 pure copper obtained from the American Smelting and Refining Company. They are in the form of short cylinders and each has a small (No. 74) hole drilled perpendicular to its axis. The specimens are polycrystalline with a grain size of about 0.1 mm. They are nominally $\frac{5}{32}$ in. long and $\frac{5}{32}$ in. in diameter, and thus weigh about 0.38 gram. Prior to use they are cleaned and then annealed in vacuum for 2 hours at 500°C. For a given experimental run one of the specimens is suspended in the calorimeter by a 10-mil copper wire which is inserted into the hole in the specimen. A similar dummy specimen is also suspended in the calorimeter at a symmetrical location and the two are connected by a 10-mil constantan wire which is also inserted into the holes. To insure good electrical and thermal contact, the dummy is then compressed at room temperature and annealed at 100°C. The wires form a differential thermocouple and the copper wires

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[9] A. W. Overhauser, Phys. Rev. 94, 1551 (1954).

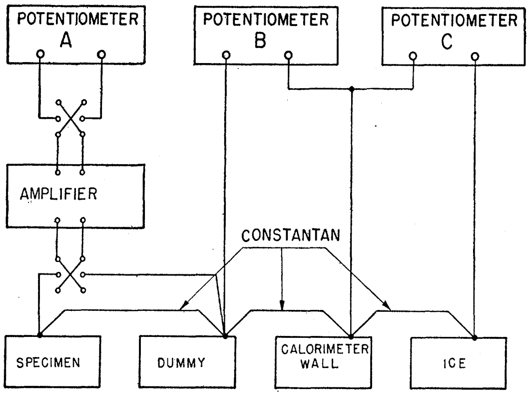

FIG. 3. Schematic of the measuring circuits and differential thermocouples.

are brought out of the vacuum system through wax seals. Another constantan wire connects the dummy to the calorimeter wall, and a copper-constantan thermocouple with an external ice-bath junction is used to measure the temperature of the calorimeter wall. The wiring schematic is shown in Fig. 3. Potentiometers (Leeds and Northrup, Type K) are used to measure the thermoelectric potentials developed by the wall temperature, T_W, and the wall-to-dummy temperature difference, T_W-T_D. The specimen-to-dummy temperature difference, T_S-T_D, which is no larger than one degree, develops a thermoelectric potential smaller than about 30 microvolts. This signal is amplified by a Leeds and Northrup breaker type dc amplifier and then measured using a potentiometer. The output of the amplifier was found to obey an equation of the form $E_{\text{out}}=A(E_{\text{in}}+x)$, where x is a fluctuating error of about 0.3 microvolt. Rubicon thermal-free reversing switches were therefore inserted in the input and output circuits of the amplifier and all measurements are taken with the error-voltage x alternately added to and subtracted from the desired signal.

Once the specimens are mounted in the calorimeter, the system is evacuated and then liquid nitrogen is added to the flask. When the calorimeter is cold, the plungers are cooled. After the observed temperature of the specimen, which is in contact with the plungers, reaches a steady value, the specimen is compressed slowly enough that its temperature does not rise more than a few degrees. It was observed that a rapid compression could raise the specimen temperature an undesirable amount in spite of the good thermal contact with the liquid nitrogen in the cooling tubes. Following the compression, the plungers are withdrawn and dry nitrogen gas is admitted to the system through a cold-trapped line. In order to insure reproducible starting temperatures and to allow the specimen to assume its final position, the liquid nitrogen is not removed from the flask until a half hour has elapsed. The glass wool was found necessary to prevent the calorimeter temperature from rising during this time. Power is supplied to the heater at the time that the liquid nitrogen is removed from the flask, and the calorimeter starts warming at a rate of 2°K per minute. At intervals of about two minutes, the three difference temperatures are simultaneously measured. At predetermined values of the calorimeter wall temperature, the power supplied to the heater is increased to maintain the warmup rate. Because the specimen and dummy have a moderately good thermal contact with the calorimeter, they remain about three degrees colder than the calorimeter during the entire warmup. The temperature difference between the specimen and dummy is less than one degree.

III. THEORY OF THE MEASUREMENT

In analyzing the data, it is assumed that Newton's Law of Cooling is valid for each specimen and that any interaction between the dummy and the specimen can be ignored. Under these assumptions, one can write:

$$\frac{dT_S}{dt}=A(T_W-T_S)+\frac{1}{mc}\frac{dU}{dt},$$

$$\frac{dT_D}{dt}=\frac{A}{1+B}(T_W-T_D).$$

Here T_S, T_D, and T_W are the temperatures of the specimen, the dummy, and the calorimeter wall, respectively. The term involving U accounts for the release of stored energy in the specimen whose specific heat is c and mass is m. If thermal contact A is eliminated between the equations and T_D replaces the time t as the independent variable, one obtains

$$\frac{1}{mc}\frac{dU}{dT_D}=\frac{T_S-T_D}{T_W-T_D}+\frac{d}{dT_D}(T_S-T_D)-B\frac{T_W-T_S}{T_W-T_D}.$$

Here $(1/mc)dU/dT_D$ is expressed in terms of the measured temperature differences and the quantity B. Under ideal conditions of similarity between dummy and specimen, B would be zero and a single warmup would be sufficient to determine $(1/mc)dUdT$. In practice, however, it is necessary to determine B as a function of temperature from an additional warmup in which dU/dT can be assumed zero as a result of the previous annealing warmup. Thus the first or primary warmup during which the stored energy is released results in a curve which contains a contribution from $(1/mc)dU/dT$ and an unknown contribution from the unbalance term B. The next or background warmup determines the contribution of B only, and the difference between these curves gives $(1/mc)dU/dT$ as a function of T_D. Since it is essential that B be reproduced accurately on the background warmup, precautions are taken to assure that all experimental conditions are reproduced as accurately as possible. In each experimental run, a third warmup was taken to verify the reproducibility of B. Unfortunately, because of its dependence on geometry, it is not possible to determine B before cold-working the specimen. It was found that the reproducibility of the background was good when the warmup rates were nearly identical and when the gas pressure in the calorimeter did not differ appreciably from atmospheric.

The thermocouple wire used was calibrated to fit an equation of the form $E = aT + bT^2 + cT^3$ which was then used to convert the measured voltages to actual temperature differences. Because of the need to solve this equation for T by numerical methods, and in the interest of accuracy and economy, the arithmetical treatment of the data was performed by the University of Illinois' digital computer, ILLIAC. The calculation is made in two parts.

The first of these gives $(T_S - T_D)/(T_W - T_D) + d(T_S - T_D)/dT$ as a function of T_D and is calculated directly from the data for each warmup. The second calculation gives $(1/mc)dU/dT$ as a function of T_D by interpolating all necessary factors to a fixed set of temperatures and then subtracting the average value of the two backgrounds from the primary. Since the data are taken at arbitrary values of T_D, the interpolation is necessary for making direct subtractions. This calculation also numerically evaluates the integral of this difference and thus gives the value of the energy released. The values of the specific heat of copper used in the integration are calculated from an empirical equation which fits published values[10] in the temperature range required.

As a means of checking the foregoing analysis (and the apparatus in general), a measurement of the heat of fusion of mercury was taken. For this purpose, a pair of steel containers weighing about 3.4 grams was prepared and 0.0217 gram of mercury was placed in one of them. They were then suspended in the calorimeter in the usual manner. While warming through the melting temperature of mercury, the temperature difference between the dummy and specimen was observed to increase suddenly and then recover its initial value slowly. A routine analysis of the data resulted in the solid curve shown in Fig. 4. Also shown in the figure as a dotted curve is the difference temperature $T_S - T_D$. In this particular case it is not possible to obtain a background warmup since the mercury will change state each time it passes through the melting temperature. Since the signal was of short duration, however, the background could easily be extrapolated through this region. The finite width of the peak is due to the use of the dummy temperature T_D rather than the specimen temperature as abscissa. It is interesting to note that, whereas the sudden rise of the curve is a result of the sudden increase in the difference $T_S - T_D$, the rapid decrease to the original value is not so obviously related to the data, but instead is due to the change in the derivative $d(T_S - T_D)/dT_D$. The entire experiment was repeated using the same mercury and containers and resulted in a similar curve. However, in this case the warmup rate was increased and resulted, as expected, in a lower and broader peak which was somewhat displaced toward higher temperatures. An integration of the area enclosed by these peaks and the extrapolated backgrounds, i.e., the shaded area in the figure, gave values of the energy absorbed which agreed to better than five percent. The average value was about 0.016 cal/g. The heat of fusion of mercury, calculated from this average value and the measured mass of the mercury, was about ten percent lower than the published value of 2.82 cal/g. This discrepancy is a measure of the error introduced by neglecting the interaction between the dummy and the specimen. Actually, part of the heat, which is either released in annealing processes or absorbed in the change of state of the mercury, is transferred between the dummy and the specimen and thus not accounted for in the analysis. This heat transfer takes place through the connecting constantan wire and through the nitrogen gas in the system. A calculation of the heat transferred by the constantan wire accounts for an error of about five percent while an estimate of the heat transfer in the gas accounts for an additional error of about the same magnitude. Thus the observed error seems to be well understood. An attempt was made to reduce this error by using 2-mil constantan (cupron) wire, but the results were erratic, presumably due to inhomogeneities in this wire. It is evident that this error, while reducing all measured values of released energy, will not significantly alter the characteristics of the observed annealing spectra.

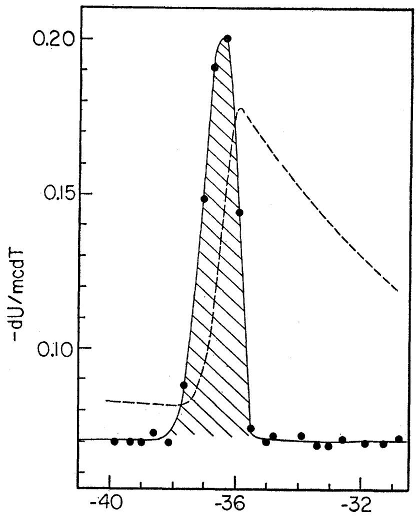

FIG. 4. Energy absorption curves for a specimen containing a small quantity of mercury. The dotted curve illustrates the behavior of the measured difference temperature.

For the cold-worked specimens, three other sources

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[10] F. W. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

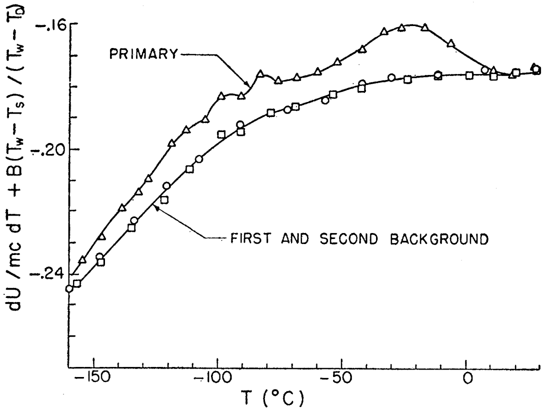

Fig. 5. Energy release spectrum for a copper specimen before subtracting the background contribution which is also shown.

of systematic error must be considered. The first of these is due to the altered thermoelectric power of the cold-worked thermocouple junction. Blatt[11] has estimated this effect to be about 1 microvolt per degree for a defect concentration of 1 atomic percent in copper. The fact that the junction in question, which is the first point of contact of the copper and constantan wires, is not as severely cold-worked as the specimen, together with an estimate of the defect concentration, result in an estimate of about one percent for the error due to this effect. The second source of error results from the possibility that the presence of defects may significantly alter the specific heat of the specimen. If this is true, the thermal behavior of the specimen containing defects, whether mobile or not, would be different from that of the annealed specimen. Such a difference would be misinterpreted by the present analysis as a release of stored energy. Overhauser has discussed this possibility and estimated the magnitude of the error to be expected.[9] He concludes that the error is probably small enough to be ignored. Furthermore, the integrated energy release is not influenced by this effect. The annealing spectra, as calculated here, would require some reinterpretation if this effect is not negligible, but peaks in the annealing spectra would still correspond to annealing processes.

Another source of error results from ignoring the energy release in the constantan wire which actually formed a part of each specimen. Since the ratio of volumes was greater than 200, the energy release per gram in the constantan would have to be an order of magnitude larger than that of the copper to contribute five percent of the observed energy release. Also, any processes attributable to constantan should be observed in other specimens containing constantan wire. A comparison of the annealing spectrum of a brass specimen with that of the copper specimens shows no such correlation.

In addition to the errors discussed, many other possible sources of systematic errors have been considered. Among these are the following: stray thermal potentials in the lead wires to the difference thermocouples, variations in the mean gain of the dc amplifier, potential gradients in the calorimeter walls and in the specimens, variations in the ice bath temperature, and deviations of the thermoelectric powers of the thermocouples from that assumed in the calculation. All such errors are believed, on the basis of measurements and estimations, to be quite small. The net contribution to the total error is estimated to be a few percent at most.

Random errors due to many sources, such as the fluctuating gain of the amplifier, all contribute to the point scatter in the annealing curves. An examination of this point scatter indicates that the sensitivity of the measurement is about 10^{-4} cal g^{-1} deg^{-1}. The measured rate of energy release was about an order of magnitude larger than this and could thus be in error by as much as ten percent. On the basis of a random walk approximation, the integrated total energy release, as calculated, is expected to contain an error of about two percent due to these random errors.

Note added in proof.—Mr. J. H. Bredt points out that error may result from heat conducted in from room temperature along the copper thermocouple leads. This error may amount to 25%.

IV. RESULTS

Measurements were made on three high purity copper specimens and one specimen in which the 0.99999 copper was alloyed with 4.53 atomic percent of zinc to make an alpha brass. The three copper specimens were deformed to different strains and the brass was deformed to a strain comparable to one of these. The data were processed numerically as described in the preceding section. The points computed in the first calculation are plotted in Fig. 5 for the copper specimen having the least deformation. This figure shows only those alternate points which were taken with the same input polarity to the amplifier. The other set of alternate points, taken with the opposite polarity, result in similar

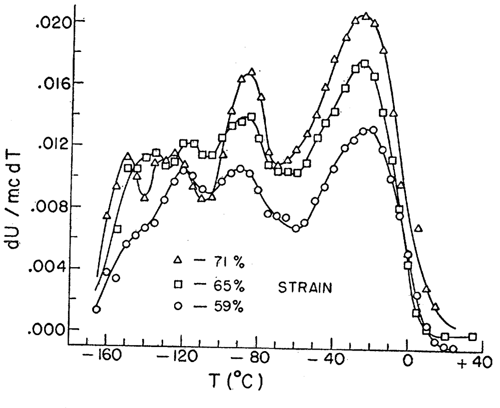

Fig. 6. Energy release spectra for three high-purity copper specimens.

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[11] F. J. Blatt, Phys. Rev. **100**, 666 (1955).

curves which are displaced vertically. Figure 5 shows clearly the extent to which the background is reproducible. This is typical of the other similar graphs which are not shown.

The quantity of physical interest is $(1/mc)dU/dT$ which is essentially the difference between the primary curve and the background curve. This quantity is obtained from the second part of the calculation. The average of the two background curves is used for each set of alternate points, and then the average of the two sets of alternate points is plotted. The use of these averages may reduce the point scatter by a factor of two. The results of this calculation for the three copper specimens are shown in Fig. 6. It is seen that the annealing processes in the temperature range investigated result in at least three resolvable peaks. The most prominent of these centers at -25°C and is separated from another peak at -90°C by a minimum occurring at a temperature $T_{\min}$. Bredt's correction may modify the annealing structure observed, particularly below $T_{\min}$. However, energy is definitely released over the broad region from -150°C to $T_{\min}$. The calculated values of the released energy, corrected for the 10% error discussed in the foregoing, are given in Table I.

The annealing process observed near -25°C is seen to contain about half of the released energy. The overlap of this process and the one in the vicinity of -90°C makes it difficult to measure the individual contribution of either process. This probably accounts for the apparent anomaly in the values of energy released below $T_{\min}$.

Figure 7 shows the energy release spectrum for the brass specimen which was deformed to a strain of 0.58, and reproduces the curve for the pure copper specimen having a strain of 0.59. The total energy released in the brass specimen in the temperature range shown in 0.33 cal/g. The addition of zinc to the pure copper clearly modifies the annealing spectrum. The prominent peak is now observed at -10°C and the details of the low-temperature processes have been lost. Furthermore, the spectrum extends to at least $+80$°C which was the maximum temperature at which observations were made. Evidently the presence of chemical impurities results in significant changes in the annealing processes. This would indicate a need for caution when comparing results obtained from specimens of varying purity.

After one month at room temperature, one of the copper specimens was examined by x-rays for evidence of recrystallization. No such evidence was observed.

Table I.

Strain $\Delta L/L_0$	Total energy released cal/g	Energy released below $T_{\min}$ cal/g	Energy released above $T_{\min}$ cal/g	$T_{\min}$ °C
0.59	0.13	0.07	0.06	-60
0.65	0.17	0.09	0.08	-65
0.71	0.19	0.08	0.11	-70

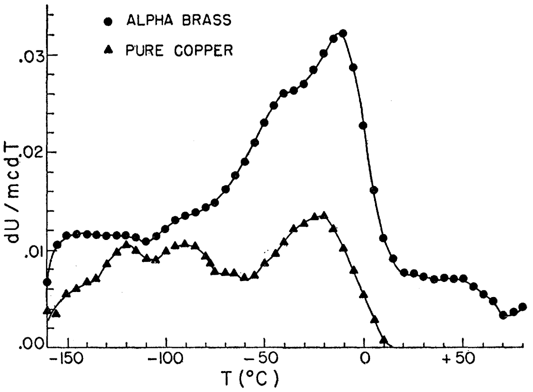

Fig. 7. Energy release spectrum for an alpha brass specimen compared with that of a copper specimen having a comparable strain.

An estimate of the fraction of the total work done which is released from -160°C to $+20$°C was made. The calculation assumed a linear stress strain curve and negligible volume change on compression. For 59% compression, the energy released amounts to about 2% of the total work done.

The vacancy concentration produced by deformation can be estimated if it is assumed that the -25°C process involves vacancies and if it is supposed that the entire vacancy energy of 1.4 ev is given up in the process.[12] For 65% compression, $C=1.6\times10^{-4}$.

V. DISCUSSION

The most interesting feature of the annealing spectrum in pure copper is the multiplicity of low-temperature processes. Observations of the resistivity recovery spectrum of cold-worked copper have disclosed only two distinct processes, one of which is certainly the process centered at -25°C in the present investigation. The other process according to Manintveld[13] occurs at -100°C in copper and is associated with an activation energy of about 0.25 ev.

Bartlett and Dienes[14] estimate that the activation energy required to move a divacancy is a half or a third of the energy to move a single vacancy. If we suppose that the annealing at -25°C represents vacancies and use Overhauser's[12] measurements of the activation energy for the process, the activation energy for divacancy motion ranges from 0.34 to 0.23 ev. Hence, present theoretical estimates suggest that divacancies

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[12] The activation energy for self diffusion in copper is 2.07 ev. M. S. Maier and H. R. Nelson, Trans. Am. Inst. Mining Met. Engrs. **147**, 39 (1942). The energy to move a vacancy is probably measured by investigations of the annealing at -25°C and is 0.68 ev. A. W. Overhauser, Phys. Rev. **90**, 393 (1953). Hence the formation energy E_F should be 1.39 ev.

[13] M. J. Druyvestyn and J. A. Manintveld, Nature **168**, 868 (1951); J. A. Manintveld, Nature **169**, 623 (1952); see also J. A. Manintveld, thesis, Delft, 1954 (unpublished).

[14] J. H. Bartlett and G. J. Dienes, Phys. Rev. **89**, 848 (1953).

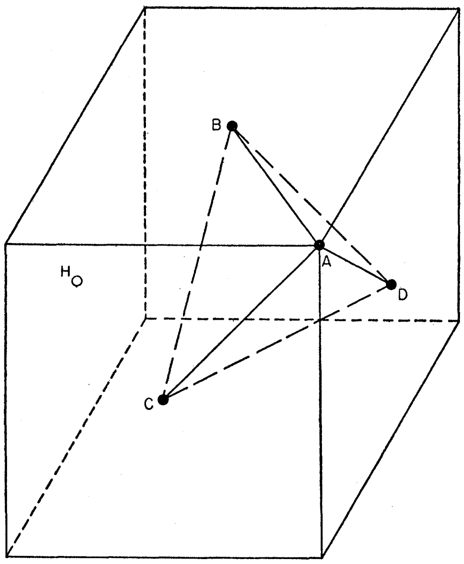

FIG. 8. Showing the influence of internal stresses on divacancies. In polycrystals most grains are compressed along the cube diagonal through *A*. Note that the divacancies are either perpendicular or make a 35° angle with the stress axis.

should anneal with an activation energy of about a quarter of an electron volt.

Let us therefore tentatively assume that the multiple peaks bound in the release of stored energy below $-70°C$ are associated with divacancy motion. It is still necessary to explain why three peaks occur in the release of stored energy whereas only one appears in the recovery of resistivity. It will be assumed here that this difference arises from the presence of residual internal stress which is present in the massive energy specimens but not in the thin resistivity samples.

Consider things in more detail. According to Barrett,[15] the preferred orientation produced during wire-drawing in copper is that in which most grains have a [111]-type direction parallel to the wire axis. Some grains have a [100] direction along the wire axis. Let us suppose that a compressive stress exists parallel to the [111] direction; the divacancies are then divisible into two classes, one class which is perpendicular to the stress axis and another which makes an angle of $35\frac{1}{4}°$ (see Fig. 8). Of the six possible divacancy axes, three are perpendicular and three are "slant." Consider next divacancy motion. Three possibilities exist: ⊥→⊥, /→/, and /→⊥. One might suppose that the migration energy for ⊥→/ could differ from that of /→⊥, in which case there would be four possibilities. Such a difference can only exist if the energy of a ⊥ divacancy differs appreciably from that of a /. An order of magnitude calculation indicates that the energies do not differ appreciably. For example, if the internal stress is of order 2×10^{9} dyne/cm^{2} and if the divacancy volume changes by about a tenth of an atomic volume in going from / to ⊥, then the work done is very roughly $p\Delta V=1.4\times10^{-3}$ ev. Suppose that the activation energy is linearly related[16] to the absolute temperature at which the annealing occurs most rapidly during a warmup at uniform rate. If the one constant in this relationship is evaluated by using Manintveld's data (which shows that the 0.25 ev process occurs at about 173°K), then the difference in the activation energies giving peaks in energy release at $-150°C$ and at $-120°C$ is of the order of 4×10^{-2} ev. (A somewhat different method of chosing the linear relation gives 2×10^{-2} ev.) Hence the ⊥ and the / energies do not differ appreciably and there are thus three types of migration energy.

Experimentally the three peaks become more distinct as the amount of deformation increases. This is just what should occur since the internal stress increases. The fact that considerable background exists, so that nowhere is the rate of release equal to zero, is not surprising since some [100]-type grains exist and also since the internal stresses are certainly not uniform over the specimen.

Two other points should be examined. First, in what order should the migration energies be arranged? Second, what are the relative intensities of the peaks? Consider the ⊥→⊥ migration. This will have a large migration energy because two atoms (i.e., *A* and *H* of the figure) are pushed by compression closer to the saddle point position of the migrating atom (which in the figure is roughly the midpoint of the line *BC* for the case in which divacancy *BD*→*CD*).

In the case /→/, such as *AB*→*AC*, the atom *A* is missing so that the migration should be easy. The atom *H* is, of course, still pushed into the migration path.

In the case ⊥→/, such as *BC*→*AC*, the atom *A* moves roughly along the line *AB*. The two atoms in the vertical front face centers above the top of the cube will be pushed down into the path of the moving atom. It is therefore difficult without detailed calculation to decide whether ⊥→⊥ or ⊥→/ has the higher activation energy.

There is still the intensity question to be examined. If we assume that all orientations of divacancies are equally likely, then the intensities of the various types of jump are as follows:

⊥→⊥ : 12,
/→/ : 12,
⊥→/ or /→⊥ : 24.

In the case of grains oriented with their [100] direction parallel to the specimen axis, there exist ⊥ and / type divacancies. In this case, only /→/ and /→⊥ transitions are possible. In the same notation as before, the intensities associated with the two possible transi-

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[15] C. S. Barrett, *Structure of Metals* (1952), second edition, p. 443.

[16] C. Wert and J. Marx, Acta Metallurgica **1**, 113 (1953).

tions are

$$/\rightarrow/: 16,$$

$$/\rightarrow\perp \quad \text{or} \quad \perp\rightarrow/: 16.$$

Thus, it is quite possible that one of the transitions is associated with the [100]-type grains.

It is fortunate that so many possibilities are available since the following difficulty arises otherwise. Suppose that only [111]-type grains were available and that the migration energies were in the order $E_{/\rightarrow/} < E_{\perp\rightarrow\perp} < E_{/\rightarrow\perp}$. One would suppose that the first two transitions would get rid of all divacancies in [111]-type grains and hence no $/\rightarrow\perp$ transition would be seen. In the [100] case, both transitions appear to have the same migration energy. If so, this could be the large peak appearing at the highest temperature. These proposals could be checked by making energy release measurements on polycrystals having different fractions of [111]- and [100]-type grains.

There are several ways in which the suggestion made above can be checked. Some of the things which are at present being done to determine the validity of the proposal are:

1. The energy release from compressed copper single crystals is being measured. Since the final orientation in compression is near the [110] direction, it is to be expected that the energy release spectrum will differ from that of a polycrystal.

2. Attempts are being made to find a complex low-temperature annealing structure by electrical resistance measurements. On rolling polycrystalline copper, the [110] direction is found preferentially normal to the sheet with the [112] direction along the rolling direction.

For a compressive stress in the [110] direction, there are three types of divacancies: $\perp$, $/$, and parallel $/\!\!/$. A preliminary estimate indicates that the scattering cross sections of these three types of divacancy for electrical resistance are nearly equal, the smallest value being about 80% of the largest. The relative size of the various drops of resistivity which occur on annealing will therefore be mainly determined by the relative numbers of divacancies annealing out in each step.

An examination of how the nearby atoms are pushed into the divacancy by a stress indicates that there will be three different migration energies for a rolled sheet. The relative size of the drops in resistivity, supposing that all orientations are equally likely, would be 1, 1, and 3 where the two small drops should occur at temperatures below that of the large drop.

3. Small-angle x-ray scattering from the divacancies would appear to be a way of obtaining very direct evidence about the imperfection responsible for these effects. The concentration of the defects appears to be so small that it is doubtful that observable effects would be produced. The concentration can be estimated from the measurements of the total energy released below $-70°\text{C}$ if it is assumed that about 2.3 ev are required to make a single divacancy. The total energy released in the low-temperature region is 0.09 cal/g or 2.1×10^{19} ev per cc. Thus since there are 0.85×10^{23} atoms per cc, the concentration of divacancies is about 10^{-4}. This is rather small for x-ray measurements. The predicted resistivity change if one assumes that a divacancy produces twice the resistivity of a single vacancy is about 3×10^{-8} ohm cm. Blewitt, Coltman, and Redman[17] found changes of the order of 1×10^{-8} ohm cm or less on annealing single copper crystals pulled in tension at 4°K. Since fewer slip systems are active in single crystals than in polycrystals, the results seem reasonable qualitatively.

Manintveld[18] found somewhat larger changes in electrical resistance on annealing polycrystalline wires rolled at 78°K. For 65% reduction in cross-sectional area, the amount annealing out in the divacancy region is about 6×10^{-8} ohm cm. Manintveld's specimens were about 99.95% pure. It is not known whether these differences in resistivity result from a difference in the type of deformation or from some difference in the nature of the specimens.

4. Theoretical calculations are under way to determine whether internal stresses can change the divacancy migration energy by about the observed amount.

In conclusion, it is suggested here that the presence of internal stresses in cold-worked specimens can alter the migration energy of a divacancy. If this is so, it is important because it may enable one to decide beyond all doubt the nature of the annealing process which occurs at about $-100°\text{C}$ in cold-worked copper.

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[17] Blewitt, Coltman, and Redman, *Bristol Conference on Defects in Crystalline Solids* (Physical Society London, 1954), p. 369.

[18] J. A. Manintveld, thesis, Delft, 1954 (unpublished).