

## Isothermal Annealing of Deuteron-Irradiated Al and Au below 60°K\*

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Foils, made out of 99.999% pure Al (4 mil) and 99.999% pure Au (2 mil), were bombarded with 21-MeV deuterons at a temperature not exceeding 8.5°K. With a total flux of  $2.5 \times 10^{16}$   $d/cm^2$ , the damage introduced was  $0.33 \times 10^{-7}$  ohm-cm and  $0.45 \times 10^{-7}$  ohm-cm, respectively, about five times smaller than the theoretical value. For Au the  $1/E$  law for the damage production holds. No radiation annealing was observed for either metal. Isothermal annealing was performed in steps of 1°K for one hour at each temperature. Up to 50°K 65% of the damage anneals out in Al, 17% in Au. The isochronal plot of the resistance decrease for Al shows a small peak (5%) centered at 17°K, a large one at 34°K, and two at 39 and 46°K. The annealing in Au, appreciable already at the lowest annealing temperature, 9.7°K, was rather constant over the whole temperature range examined except for a large peak at 33°K and a smaller one at 45°K. Changes in the temperature-dependent part of the resistivity can for both metals be explained as a deviation from Mathiessen's rule as resistance measurements at 6°K indicate. This is in agreement with measurements on Al and Au alloys. The activation energy spectrum for Al, obtained with a frequency factor of  $\ln B = 29$ , shows also 4 peaks, at 0.056 eV, 0.110 eV, 0.130 eV, and 0.146 eV. The spectrum for Au is rather complex, due to the large range of the interaction of defects and the anisotropy of this metal. A recalculation of data for the annealing of deuteron-irradiated Cu and Ag shows a fine structure in peak  $I_D$ . A way to choose the proper temperature increase for isothermal annealing measurements is given.

### I. INTRODUCTION

WHILE a large number of measurements have been done to study the production and the annealing of displacement damage in the noble metals, there are still problems which are not understood, for example, the geometry of the interstitial. Of the noble metals, Cu is the one which has been most thoroughly studied, while only a few radiation experiments with Au have been reported.<sup>1-3</sup> For deuteron-irradiated Au no large drop in the radiation introduced resistance has been found at low temperatures,<sup>1,2</sup> and, since the peaks in the activation energy spectrum shift to lower temperatures if one goes from Cu to Ag, it was thought that in Au, annealing may go on at very low temperatures.

The purpose of the experiment described here was to measure the annealing in Au after deuteron bombardment at the lowest temperature feasible to determine whether discrete annealing processes occur and to determine their activation energies. Deuteron flux vs damage production measurements should provide information about radiation annealing<sup>1</sup> and the use of deuterons with higher energy would serve as a check of the  $1/E$  law for damage production.

Al, being an elastically isotropic metal, was included in this project in order to see how much it would differ from the highly anisotropic Au.

### II. EXPERIMENT

The cryostat used in this project was of the same design as that used and described in detail by Magnuson,

Palmer, and Koehler,<sup>2</sup> except for a few changes made to achieve a lower specimen temperature. Since two specimens of each metal were mounted, 30 wires were required to make the necessary connections for the measurements. Because of the large number of wires, care had to be taken to avoid a large heat flow to the block and especially to the specimens themselves. The 4-mil copper wires, insulated with fiberglass sleeving, were passed through serum caps on the top plate of the cryostat, wound around the cylindrically shaped nitrogen Dewar, and then fed into two  $\frac{1}{8}$ -in. stainless steel tubes. These tubes were located in the space between the nitrogen Dewar and the helium Dewar with the upper ends soldered to the nitrogen Dewar. The wires were then wound around the stainless steel cylinder of the heat switch where they were supported by Teflon spacers and finally led into the radiation shield. There they were carefully glued down to the block with GE varnish 7031 in order to make good thermal contact. Furthermore, to get a true temperature reading and to minimize any heat exchange between the block and the specimen, both the copper and the constantan wires for the differential thermocouple spotwelded to the specimen were free floating for a length of 8 to 10 cm before they were allowed to touch the block. The minimum block temperature thus obtained with the measuring wires in position was 6°K.

The specimens were cut out of foil by hand under a microscope to the shape shown in Fig. 1. The large areas on the ends served to increase the heat conduction to the

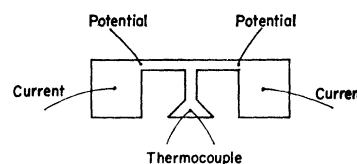


FIG. 1. Shape of the specimens.

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<sup>1</sup> H. G. Cooper, J. S. Koehler, and J. W. Marx, *Phys. Rev.* **97**, 599 (1955).

<sup>2</sup> G. D. Magnuson, W. Palmer, and J. S. Koehler, *Phys. Rev.* **109**, 1990 (1958).

<sup>3</sup> J. B. Ward and J. W. Kauffman, *Phys. Rev.* **123**, 90 (1961).

block. After cleaning, a short length of 4-mil copper wire and a 10-cm length of constantan wire for the thermocouple were spotwelded to the specimen. After spotwelding the specimens were cleaned with acetone and methanol.

The residual resistance of the specimens was measured after annealing and the specimens with the best ratios were selected for mounting. This procedure was especially necessary for the gold, because the specimens prepared from the same foil and treated in the same way varied in the ratio by as much as a factor of 2.

Specimens mounted in the manner described by Magnuson, Palmer, and Koehler<sup>1</sup> tend to lose thermal contact with the block because the polyvinyl alcohol cracks. Therefore, the following method was used: GE varnish 7031, thinned with toluene-ethylalcohol 50:50, was applied to the block and covered with  $\frac{1}{4}$ -mil Mylar foil. Then more varnish was applied and the specimen was carefully dropped onto the block. The end faces of the specimens were firmly pressed down so that the excess varnish was squeezed out. In this way the specimens were separated from the block practically only by the Mylar foil, which served as an electrical insulator. The small triangle, to which the thermocouple was attached, was glued down onto several layers of cardboard on the side of the block window, using Duco cement.

The temperature difference between the specimens and the block was kept down to 0.1°K for aluminum and to less than 0.5°K for gold. This was the difference after bombardment, when the heat conductivity had deteriorated due to the radiation damage introduced; before bombardment the temperature difference was practically negligible. Therefore, the thermocouple reading on the specimen was taken to be valid over the whole length of the specimen and no corrections were made for the drop in temperature along the specimen, which would have been necessary for larger temperature differences. These corrections are almost impossible to make unless the thermal resistance to the block or the temperatures of the ends of the specimen are known. A small difference in temperature between the block and the specimen also minimizes the effect of thermocouple calibration errors.

The aluminum specimens were prepared from 99.999% pure Al from the Aluminum Werke, Singen/Hohentwiel, Germany (courtesy of Professor Th. Heumann, Münster, Germany), which was rolled down to the thickness of 4 mil and then etched with a solution of 96% H<sub>3</sub>PO<sub>4</sub> and 4% HNO<sub>3</sub> at 100°C (suggested by G. de Pasquali).

The gold specimens were prepared from 2 mil 99.999% pure Au foil supplied by the Sigmund Cohn Company. Before spotwelding on the leads, the gold specimens were cleaned with methanol, acetone, boiling HNO<sub>3</sub> and HCl, and then soft annealed at 400°C for 3 min in air.

The Al specimens were annealed in vacuum (better than  $5 \times 10^{-5}$  mm Hg) for 3 h at 450°C, and the Au

specimens in a dried argon atmosphere for 10 min at a temperature between 600 and 650°C.

The resistance of the specimens was measured by means of the usual potentiometric methods using a 6 dial Rubicon potentiometer for the potential (and for the thermocouple reading) and a Leeds and Northrup K3 to monitor the current. For faster results the current was kept constant at 120 mA rather than reading its value each time a potential was measured. Since the resistance of the lead wires inside the cryostat changes due to heating up, the current was supplied by eight 12-V batteries in series. Thus, the current could easily be regulated with a 1000 to 0.1  $\Omega$  resistor box to which a self-made 0.01- $\Omega$  decade box was added. The current regulation was better than 1 part in 10 000.

The error of a single reading during the annealing was 0.01% of the total damage for both Al and Au. This includes the error in the block temperature which affected the gold measurements more because gold has a much lower Debye temperature.

A calibrated Pt thermometer was soldered with Woods metal into a hole in the block near the specimens, where the common point of the differential thermocouples was also fixed. The connection wires for the thermocouples were matched so that the Thomson emf's were small and reproducible within 0.05  $\mu$ V.

Since one objective of this experiment was to determine whether there is any low-temperature annealing in Au, the temperature had to be kept as low as possible with a reasonable beam current. Therefore, painstaking efforts were made to align the system with respect to the beam. The window in front of the nitrogen radiation shield, which served as aperture for the beam, was adjusted with respect to the block windows so that the beam could pass through the specimens without hitting the block. The front face of the block was fixed in a vertical position so that a line through the middle of the portholes on the cryostat passed through the middle of the windows in the block. The portholes were then optically aligned to the outlet tubing of the cyclotron. With the system in position the beam was turned on and a radiograph taken to check the uniformity of the beam after it had passed through the system. The beam intensity was also measured with a motor-driven grid of probes,<sup>4</sup> placed just in front of the cryostat while the specimens were protected by a valve. These probes were used during the run as a relative check, when radiographs could no longer be taken. The deviation from beam uniformity, as measured by the probes, was about 5% of the average beam current.

When these checks were finished, a Faraday cage was mounted on the cryostat to collect the deuteron beam, the system cooled down, and the actual run started. The increase in the helium loss rate and in the block temperature were very small, the latter about 0.4°K

<sup>4</sup> T. G. Nilan, Ph.D. thesis, Urbana, Illinois, 1961 (unpublished).

with a beam intensity of  $0.1 \mu\text{A}/\text{cm}^2$ . This served as a final check for the alignment.

The beam current was adjusted so that the temperature of the specimen never rose above  $8.5^\circ\text{K}$ . The beam intensity initially was  $0.1 \mu\text{A}/\text{cm}^2$ . This later had to be cut down to  $0.04 \mu\text{A}/\text{cm}^2$ . The reason for this is that the resistance increase is accompanied by a thermal conductivity decrease. In a previous run with a constant beam current, the temperature difference between the block and the gold specimen did rise to  $6^\circ\text{K}$ .

Incidentally, the damage produced during the alignment, when the beam current could not be measured, is the reason that the damage vs flux curves do not go through the origin.

### III. RESULTS

#### 1. Total Damage

With a total flux of  $2.5 \times 10^{16} d/\text{cm}$  the resistivity increase for Al was  $\Delta\rho = 33 \times 10^{-9} \Omega \text{ cm}$ ; for Au,  $\Delta\rho = 45.5 \times 10^{-9} \Omega \text{ cm}$ . One may calculate the damage to be expected following the formalism given by Seitz and Koehler,<sup>5</sup> who assumed a step function for the displacement probability. The question then arises as to what displacement energy should be used and what contribution an individual defect makes to the resistance. Lucasson and Walker<sup>6,7</sup> have given displacement energies and  $\Delta\rho$  values for Frenkel pairs in a number of metals. They pointed out, however, that their  $\Delta\rho$  may be too small by a factor of about 2. Using the displacement energy  $E_d = 32 \text{ eV}$ <sup>6,7</sup> for Al and the minimum value  $E_d = 40 \text{ eV}$ <sup>6,7</sup> for Au given by Lucasson and Walker, the defect concentration calculated after Seitz and Koehler is  $c_{\text{eq}} = 2.3 \times 10^{-4}$  for Al and  $c_{\text{eq}} = 8.2 \times 10^{-4}$  for Au. Since the only information available on the resistance of a Frenkel pair in either metal is that provided by Lucasson and Walker,<sup>6,7</sup> one may for expedience make the simplified assumption that the resistivity increases twice as much for Frenkel pairs as for vacancies. Simmons and Balluffi<sup>8</sup> calculated from their length and lattice expansion experiments that  $\Delta\rho = 3 \mu\Omega \text{ cm}/\%$  monovacancies for Al; while for Au, Seitz and Koehler<sup>5</sup> give  $\Delta\rho = 1.5 \mu\Omega \text{ cm}/\%$  vacancies. Using these numbers the results for the theoretical resistivity increase are  $\Delta\rho = 0.136 \mu\Omega \text{ cm}$  and  $\Delta\rho = 0.245 \mu\Omega \text{ cm}$ , respectively. The theoretical values are higher by factors of 4.2 for Al and 5.4 for Au, in agreement with the factor 5.0 given for Cu by Seitz and Koehler,<sup>5</sup> which increases to 5.7 if the threshold energy  $E_d = 22 \text{ eV}$ <sup>6,7</sup> is used. If one uses the value of  $\Delta\rho$  given by Lucasson and Walker, the theoretical values are too high by a factor 2.4 for both Au and Al.

<sup>5</sup> F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), p. 307.

<sup>6</sup> P. G. Lucasson and R. M. Walker, *Discussions Faraday Soc.* **31**, 57 (1961).

<sup>7</sup> P. G. Lucasson and R. M. Walker, *Phys. Rev.* **127**, 1130 (1962).

<sup>8</sup> R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 62 (1960).

If a correction is made for the different deuteron energy used, one gets from Cooper's<sup>1</sup> flux vs damage curve for Au a resistivity increase of  $50 \times 10^{-9} \Omega \text{ cm}$  compared to  $45.5 \times 10^{-9} \Omega \text{ cm}$  obtained in this experiment. This shows that, within the limits of error, the damage is proportional to the reciprocal deuteron energy.

#### 2. Radiation Annealing

During the bombarding the beam was stopped several times to measure the accumulated damage  $\Delta\rho$ . As shown in Fig. 2,  $\Delta\rho$  is a linear function of the flux. No indication of the radiation annealing reported for Au by Cooper *et al.*<sup>1</sup> was found in either metal. These authors describe their damage production curve as  $\Delta\rho = A[1 - \exp(-\beta\phi)]$  with  $A$  and  $\beta$  constants and  $\phi$  the flux. Using their  $\beta$  value,  $\Delta\rho$  at the conclusion of the bombardment in this experiment should have been 3% less than was observed. This bending over would have been noticed, if real, since it is well outside the experimental error.

The most likely explanation for this discrepancy lies in the fact that Cooper *et al.*<sup>1</sup> could not actually measure the specimen temperature. Since, as mentioned above, with a constant deuteron flux the temperature of the specimen will go up as a result of the resistivity increase, an undetected temperature rise would have the same effect as a slow increase in the block temperature. In other words, while new defects are generated, part of the previously introduced damage anneals out in a complicated manner depending on flux, accumulated damage, and the activation energy spectrum. In the experiment reported here the specimen temperature was constantly monitored and did never exceed a preset maximum. Since, under carefully controlled conditions within the experimental error no radiation annealing was found, it is presumed, that the effect reported by Cooper *et al.* was due to their apparatus.

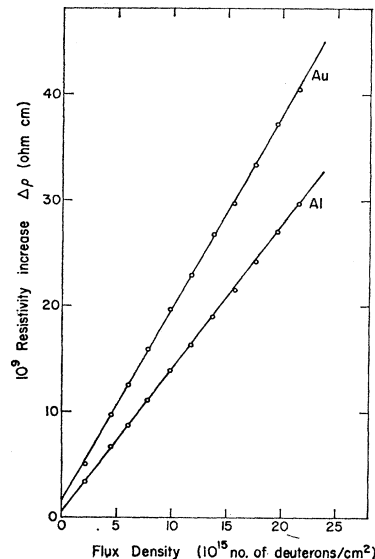


FIG. 2. The accumulated damage as a function of the total deuteron flux.

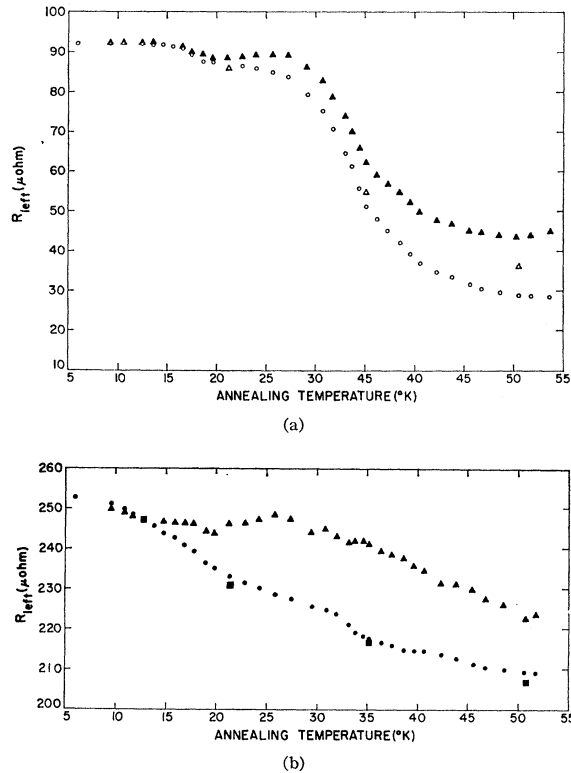


FIG. 3. Isochronal annealing curves for (a) Al and (b) Au. The upper curves represent the radiation introduced resistance left at the end of an annealing at temperature  $T$  measured at temperature  $T$ , while the lower curves are corrected for the deviation from Matthiessen's rule. The single points (open triangles and squares, respectively) are measurements at He temperature.

### 3. Deviations from Matthiessen's Rule

The isothermal annealing was carried out in steps of about  $1^\circ\text{K}$  for approximately 1 h at each temperature. The thermal part of the resistance of all specimens was measured in two runs before bombardment. The geometrical factor was calculated from the room-temperature measurements using the Metals Handbook data. The resistance at  $0^\circ\text{C}$  was  $6890$  and  $12\,380\ \mu\Omega$  for Al and Au and the resistance ratio  $R(0^\circ\text{C})/R(6^\circ\text{K})$  was  $840$  and  $820$ , respectively. These data were used to calculate  $\Delta\rho_{\text{dam}}$ , assuming that Matthiessen's rule holds.

The percentage of the damage annealed out up to  $50^\circ\text{K}$  was  $61\%$  for Al and  $17\%$  for Au. Magnuson, Palmer and Koehler<sup>2</sup> found  $60\%$  for Cu and  $40\%$  for Ag.

Both sets of isothermal annealing curves show discontinuities. The radiation-introduced resistance left at the end of one annealing seems to be smaller than the one at the beginning of the next annealing at higher temperature. This effect was first observed by Magnuson, Palmer, and Koehler<sup>2</sup> for deuteron-irradiated Cu and Ag. They tried to explain it as a decrease in the Debye temperature  $\Theta$  due to changes in the lattice vibrations and gave a way of calculating  $\Delta\Theta$  using the Bloch-Grüneisen formula.

To discuss this problem further, the isochronal annealing curves for both Al and Au are given in Figs. 3(a) and (b). In the upper curves the radiation-introduced resistance left at the end of an annealing at temperature  $T$  has been plotted vs  $T$ . Only the temperature-dependent resistance as measured before bombardment has been taken into account. As can be most clearly seen in the case of Au, the steps in the isothermal annealing curves overcompensate for the part of the resistance annealed out, so that an apparent increase in resistance results. Unless we assume that during the time the block is heated up (20 to 60 sec) to the next higher temperature more resistance is generated, the simplest explanation for the steps is an error in the correction for the temperature-dependent part of the resistance. Additional resistance could be generated, for example, by breaking up clusters of defects into simpler defects which have together a larger resistance than the cluster. But this process is unlikely since the steps can be seen after a few seconds. The breaking up of defect clusters would have to be very fast; this is not expected at these low temperatures. This point of view can be further supported. The lower curves take into account the steps and can be derived in two ways: At each point on the upper curve the sum of all previous steps is subtracted from the resistance measured at temperature, or for each temperature the sum of the resistance annealed out in all previous annealings is subtracted from the total damage. The latter method is somewhat more accurate and is therefore applied here. Furthermore, at four temperatures,  $21.0$ ,  $35.0$ ,  $50.5$ , and  $59.6^\circ\text{K}$ , the resistance was measured at He temperature after annealing. This directly measures the defect annealing and eliminates the effect of a change in the temperature-dependent part of the resistance.

For Au, these four points agree within the limits of error with the lower curve, providing a strong support for the interpretation given above. The points at  $35$ ,  $50.5$ , and  $59.6^\circ\text{K}$  for Al lie between the corrected and the uncorrected curve, but this is not in contradiction with the explanation given above. A simple displacement of the isothermal annealing curves parallel to the  $R$  axis only gives correct results if the change in the correction necessary for the temperature-dependent part of the resistance is constant with time, in other words, does not anneal out while the specimen is held at constant temperature. Otherwise, at the end of an annealing too large a correction is made, resulting in a curve which is too low, since the error accumulates. This is the case for Al. Therefore, the damage annealed out at  $50^\circ\text{K}$  should correctly be given as  $61\%$  instead of  $68\%$  as derived from the lower curve. Also, the difference between the corrected curve and the points taken at He temperature increases up to  $50^\circ\text{K}$ , thus indicating that at least some of this "change" anneals out simultaneously with the big drop in resistance centered at  $35^\circ\text{K}$ . A more quantitative statement requires a knowledge of the underlying mechanism.

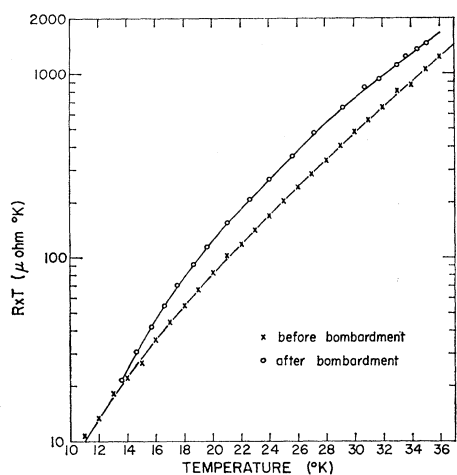


FIG. 4.  $\rho T$  vs  $T$  curves for Al, before and after annealing.

If we assume, as Magnuson, Palmer, and Koehler<sup>2</sup> did, that this change is due to a decrease in the Debye temperature, a calculation can be made using the Bloch-Grüneisen formula. By multiplying both sides of the equation by  $T$ , one gets for a given metal:

$$\rho T = \text{const} \frac{T^6}{\Theta^6} \int_0^{\Theta/T} \frac{Z^5}{(e^Z - 1)(1 - e^{-Z})} dZ = F\left(\frac{\Theta}{T}\right).$$

If we plot  $(\rho T)$  vs  $T$ , we get for  $(\rho T)_{\text{bef}} = (\rho' T')_{\text{after}}$ , with  $\Theta' = \Theta + \Delta\Theta$  that  $\Delta\Theta/\Theta = (T' - T)/T$ . The values so calculated are given in Table I together with the numbers obtained by Magnuson, Palmer, and Koehler for Cu and Ag.

$\rho T$  values up to 30°K were used for Al and up to 20°K for Au. At 30°K,  $\Delta\Theta$ , calculated thus, decreases quite rapidly for Al, as can be seen from the  $\rho T$  vs  $T$  curve in Fig. 4, indicating an annealing of " $\Delta\Theta$ ."

The decrease in  $\Theta$  is large even with the relatively small damage achieved in this experiment. Therefore, this explanation has been challenged<sup>9</sup> with the argument that a decrease in  $\Theta$  means a decrease in the zero point energy. This would tend to cancel the energy stored in defects. Hence, the actual stored energy would be larger than the value observed in stored energy experiments. Another argument derives from calculations of Mitra and Joshi<sup>10</sup> for the Debye temperature of fcc metals.

TABLE I. Apparent change in the Debye temperature.

Metal	$\Theta$ (°K)	Decrease in $\Theta$ (%)	$\Delta\Theta$ (°K)
Cu	333	4.5%	-15
Ag	223	4.5%	-10
Au	175	3.5%	-5
Al	395	9.5%	-23

<sup>9</sup> A. V. Granato (private communication).

<sup>10</sup> S. S. Mitra and S. K. Joshi, *Physica* **27**, 376 (1961).

These authors found that  $\Theta$  is proportional to the inverse square root of the compressibility and got good agreement with experimental values for a number of metals. A decrease in  $\Theta$  would correspond to an increase in compressibility, in the case of Al of about 20%, which would be a rather large effect for a defect concentration of  $10^{-4}$ .

Another cause for the steps in the annealing curves could be the fact that Matthiessen's rule is no longer strictly valid. Kohler<sup>11</sup> has shown that a correction term has to be added to the formula expressing Matthiessen's rule,

$$R(T) = R_{\text{id}}(T) + R_{\text{res}} + \Delta R(T) \quad \text{with} \quad \Delta R(T) \geq 0,$$

where  $R_{\text{id}}(T)$  is the ideal resistance due to the vibrations if the lattice is otherwise perfect and  $R_{\text{res}}$  is the residual resistance caused by imperfections in the lattice.

Such deviations have been investigated among others by Klemens and Lowenthal<sup>12</sup> in Pt; by Alley and Serin<sup>13</sup> in Al, Sn, and Cu alloys; and by Krautz and Schultz<sup>14</sup> in Ag and Au alloys and cold-worked tungsten. Bross<sup>15</sup> has calculated the deviation from Matthiessen's rule for Cu assuming anisotropic scattering of the electrons by the phonons. In that case, the total resistance produced by the scattering of the conduction electrons by the phonons as well as by the static lattice defects is larger than the sum of the single effects. The author claims good agreement between the values calculated by the use of this theory and the data for  $\Delta R(T)$  reported by Magnuson, Palmer, and Koehler.<sup>2</sup> His calculated curve for  $\Delta R(T)$ , however, fails to show a maximum as found experimentally by Krautz and Schultz<sup>14</sup> for alloys of the other noble metals. Sondheimer and Wilson have treated<sup>16</sup> the case of two-band conduction, where the two bands are differently affected by lattice defects. The influence of such a mechanism would probably be quite different for mono- and multivalent metals. Krautz and Schultz<sup>14</sup> used the theory of Sondheimer and Wilson in discussing their measurements of the deviation from Matthiessen's rule and the temperature dependence of the Hall coefficient in Ag and Au alloys. In order to get agreement between the two sets of data they calculate an apparent defect electron concentration of 5-10% of the electron concentration. This seems to be an excessive number for noble metals. They also try to explain the maximum found in a Au+1% Ag alloy [9% of  $R_{\text{res}}(T)$ ] for  $\Delta R_{\text{id}}(T) \propto \Delta R_{\text{res}}$  as an overlapping of two effects: the deviation described by the Sondheimer and Wilson theory cited above, which should be valid for two-band conduction only, and a small deviation from Matthiessen's rule, calculated after Sondheimer for monovalent

<sup>11</sup> M. Kohler, *Z. Physik* **126**, 495 (1949).

<sup>12</sup> P. G. Klemens and G. C. Lowenthal, *Australian J. Phys.* **14**, 352 (1961).

<sup>13</sup> P. Alley and B. Serin, *Phys. Rev.* **116**, 334 (1959).

<sup>14</sup> E. Krautz and H. Schultz, *Z. Naturforsch.* **12A**, 710 (1957).

<sup>15</sup> H. Bross, *Z. Naturforsch.* **14A**, 560 (1959).

<sup>16</sup> E. H. Sondheimer and A. H. Wilson, *Proc. Roy. Soc. (London)* **A190**, 435 (1947).

metals, which should have a maximum for  $R_{id} \propto R_{res}$  of the order of 1%  $R_{res}$ . The maximum obtained experimentally was 2%  $R_{res}$ . Using the theory derived by Sondheimer and Wilson,<sup>16</sup> Klemens and Lowenthal approximate the deviation  $\Delta R(T)$  by

$$\Delta R(T) = \frac{R_{id}(T)R_{res}}{aR_{id}(T) + bR_{res}},$$

where  $a$  and  $b$  are supposed to be positive constants of the order of unity. It follows that  $\Delta R(T)$  is positive and  $\Delta R \rightarrow 0$  as  $T \rightarrow 0$ ; furthermore, at higher temperatures  $\Delta R(T)$  approaches a constant value  $R_{res}/a$  and Matthiessen's rule seems to be satisfied. Therefore, this deviation is significant only in the temperature range where  $R_{id}(T)$  and  $R_{res}$  are of the same order of magnitude.

In Figs. 5(a) and 5(b) the additional resistance per unit of damage  $\Delta R(T)/[R_{left}(T)/R_{dam}(6^\circ\text{K})]$  has been plotted vs temperature for both Al and Au. The curve for Al resembles very much the curve given by Klemens and Lowenthal in their Fig. 1 as predicted by the Sondheimer theory.

As already mentioned,  $R_{dam}(T)$  has been measured at four points both at the annealing temperature and after

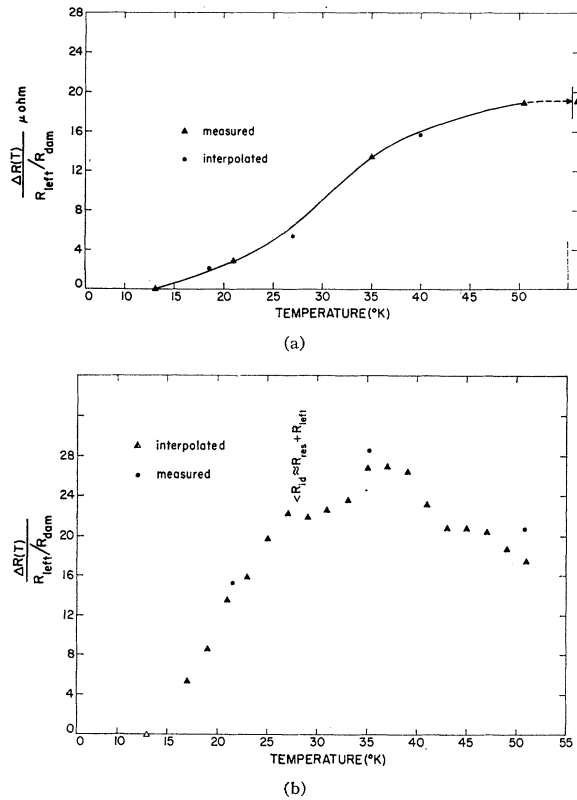


FIG. 5. The additional resistance per unit of damage plotted as a function of temperature for (a) Al and (b) Au. The dashed line in (a) indicates how the curve approaches the point at the highest temperature measured (out of scale).

TABLE II. Measured and calculated correction terms (in  $\mu\Omega$ ) for Matthiessen's rule in Al.

Temperature ( $^\circ\text{K}$ )	21.06	35.06	50.54	59.55
$R_{bef}(T)$	12.6	38.3	149.0	272.7
$R_{dam}(6^\circ\text{K}, T)$	85.9	55.2	36.3	35.3
$\Delta^+R(T)$	2.7	8.0	7.3	7.4
$\Delta_{bef}R(T)$	1.3	1.6	1.7	1.7
$\Delta_{exp}R(T)$	4.0	9.6	9.0	9.1
$\Delta_{cal}R(T)$	3.6	10.0	9.1	9.1

cooling down to  $6^\circ\text{K}$ , where the temperature-dependent part of the resistance is small. For Al the experimental results can be fit using the following constants in the Sondheimer formula:  $a=4.65$  and  $b=0.75$  ( $R_{res\ bef}=8\ \mu\Omega$ ). The extent to which experiment and theory agree is shown in Table II for Al.  $\Delta^+R(T)$  is the additional resistance,  $\Delta_{bef}R(T)$  the correction for the unbombarded specimen.

As can be seen, there is good agreement between the experimental and calculated values over the whole temperature range examined. However, our value for  $a$  is smaller by about a factor 2 than  $a=8.35$  which one can obtain from Alley and Serin's<sup>13</sup> data for Al alloys. It seems that the results can at least be taken as qualitative support for Sondheimer's theory. The curve for Au, being less accurate than the curve for Al, shows nevertheless a distinct maximum near  $R_{id} \approx R_{dam}$ , being somewhat on the higher temperature side. The maximum value of  $\Delta R(T)$  is approximately 10% of  $R_{res}(T)$ . This is in good agreement with the measurements reported by Krautz and Schultz<sup>14</sup> for both Ag and Au alloys. So far, it seems that the deviations from Matthiessen's rule outlined above give the best explanation for the steps in the annealing curves. In fact, we would suggest the use of radiation-damage methods to look further into this problem since the same specimen can be measured with a wide variety of impurity content, thus eliminating the difficult problem of comparing results obtained with specimens of different geometry. As Alley and Serin<sup>13</sup> have pointed out, a small error in the geometrical factor can lead to serious errors in the determination of  $\Delta R(T)$ .

#### 4. Isochronal Annealing

The isochronal annealing curve for Al shows that several distinct annealing processes occur in the temperature range studied. The annealing in Au, starting as low as  $9.5^\circ\text{K}$ , is rather constant up to  $50^\circ\text{K}$  and even higher. For both curves the derivatives were evaluated. These are not strictly isochronal since the annealing time was not exactly constant at each temperature; hence accuracy is not claimed, but the general features should be preserved. (Incidentally, above  $25^\circ\text{K}$  the annealing times were much more nearly constant than those below  $25^\circ\text{K}$ .) With these precautions in mind, we can see that the annealing spectrum for Al shows at least four peaks, one isolated at  $17^\circ\text{K}$ , a large one at

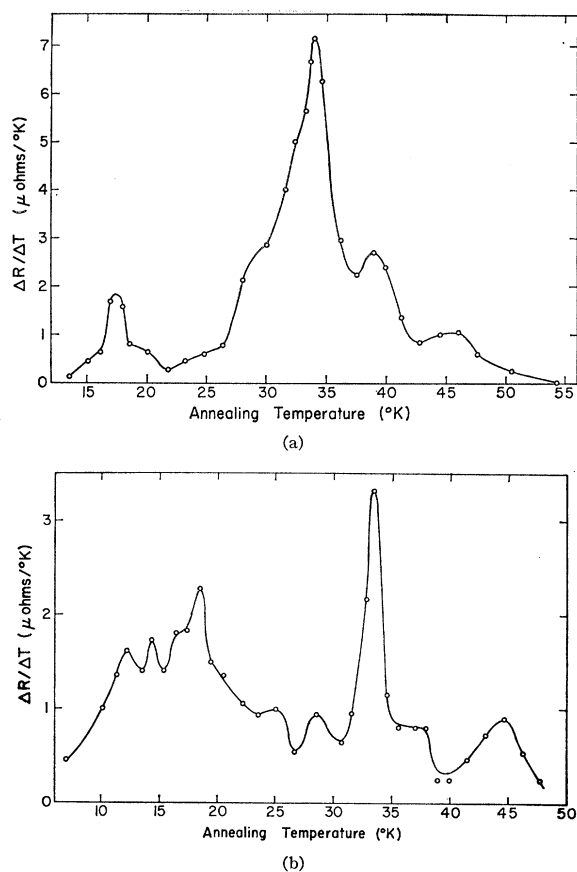


FIG. 6. Isochronal annealing ( $\Delta R/\Delta T$ ) curves for Al (a) and Au (b).

34°K, and two at 39 and 45°K [Fig. 6(a)]. Unfortunately, the experimental error is much larger for Au, but these two peaks are well established [Fig. 6(b)], a small one at 45°K and a large one at 33.5°K. There is no clear indication of a peak between 20 and 30°K, while in the range from 10 to 20°K there are probably two peaks, one at 12 to 13°K and another at about 18.5°K.

If we compare our results for Au with the measurements by Ward and Kauffman<sup>3</sup> on electron-bombarded Au, the first significant difference is in the amount of recovery. Only half as much damage is annealed out at 50°K in the case of deuteron-bombarded Au. Furthermore, annealing was observed even at 9.6°K in the present experiment. (In the case of neutron-bombarded Au, recovery has been observed at temperatures as low as 4°K.<sup>17</sup>) Ward and Kauffman claim five peaks in the temperature range up to 50°K. The first and second peaks (at 14.5 and 18.3°K) have been found with deuterons, the first one probably slightly displaced toward lower temperatures. Within our accuracy we did not find the third and fourth peaks, and the fifth peak is centered at 45°K instead of 42°K. The largest peak in the case of deuteron-irradiated Au at 33.5°K cannot be

<sup>17</sup> M. L. Swanson (private communication).

TABLE III. Recovery in stage I and Au.

Stage	Temperature (°K)	Rec. here (%)	Rec. W and K (%)	Ratio
I <sub>a</sub>	10.0–16.5	3.8	6.9	0.55
I <sub>b</sub>	16.5–20.5	2.8	9.0	0.31
I <sub>c</sub>	20.5–25.0	2.0	5.0	0.40
I <sub>d</sub>	25.0–38.0	5.5	8.0	(0.69)
I <sub>e</sub>	38.0–50.0	2.4	4.4	0.55
Total	10.0–50.0	16.5	33.3	0.50

related to any peak in the Ward and Kauffman spectrum. The small peak width indicates the annealing process to be of first order.

A comparison of the recovery in the substages I<sub>a</sub> · · · I<sub>e</sub> with the data given by Ward and Kauffman<sup>3</sup> in their Table II reveals the differences more clearly. The compiled data are given in Table III. The last row gives the ratio of the recovery measured in this experiment to that measured by Ward and Kauffman. Because of the large shift in temperature by about 5°K for peak I<sub>d</sub>, we do not feel justified to refer to our large peak four as the I<sub>d</sub> in Ward and Kauffman's paper. However, it could correspond to the large peak found for Cu and Ag by Magnuson, Palmer, and Koehler.<sup>2</sup>

### 5. The Derivation of the Spectrum of Activation Energies for Annealing

A property  $p$ , for example, the resistance, may be proportional to the number of defects in a system which can decay in a thermally activated process. Then one can write the differential equation for the decay of this property. If the change in the property per time unit is proportional to the number of defects left (first-order process), then

$$-dp/dt = Bp \exp(-\epsilon/kT),$$

with  $t$  the time,  $\epsilon$  the activation energy,  $k$  the Boltzmann constant, and  $T$  the annealing temperature.  $B$  is a constant called the frequency factor with the unit  $\text{sec}^{-1}$ . The differential equation can easily be solved, giving

$$p = p_0 \exp[-Bt \exp(-\epsilon/kT)] = p_0 \theta(t, T),$$

where  $p_0$  is the value of  $p$  for  $t=0$ . If several defects are involved, having slightly different activation energies, only the total value,  $P(t)$ , of the property can be measured. This is given by

$$P(t) = \int_0^\infty p_0(\epsilon) \theta(\epsilon, t, T) d\epsilon.$$

These equations and their applications have been studied quite thoroughly by Primak<sup>18,19</sup> and for more details one should refer to these papers. It can be seen that annealing at a constant temperature does not reveal the

<sup>18</sup> W. Primak, Phys. Rev. **100**, 1677 (1955).

<sup>19</sup> W. Primak, J. Appl. Phys. **31**, 1524 (1960).

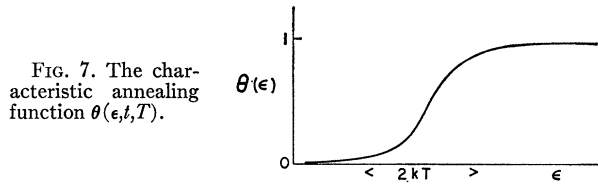


FIG. 7. The characteristic annealing function  $\theta(\epsilon, t, T)$ .

original distribution (called the annealing spectrum in Magnuson, Palmer, and Koehler's paper) unless the frequency factor is known. Since this is normally not the case, annealing at at least two different temperatures must be carried out (step annealing).

In order to understand the resulting equations, a few details about the characteristic annealing function  $\theta(\epsilon, t, T)$  may be given.  $\theta$  as a function of the energy  $\epsilon$  is plotted in Fig. 7.

$\theta(\epsilon)$  varies from zero to one over only a small energy range of the order of  $2kT$  and is translated along  $\epsilon$  with unaltered shape as time proceeds. A product of different  $\theta$  functions, for convenience called the  $F$  function, will have a shape similar to the characteristic annealing function.

After annealing for a time  $t_1$  at a temperature  $T_1$ , the original distribution has been changed to

$$p_1(\epsilon) = p_0(\epsilon)\theta(\epsilon, t_1, T_1),$$

and after the  $n$ th annealing to

$$p_n(\epsilon) = p_0(\epsilon)\theta(\epsilon, t_1, T_1)\theta(\epsilon, t_2, T_2) \cdots \theta(\epsilon, t_n, T_n) = p_0(\epsilon)F_n(\epsilon),$$

$F_n(\epsilon)$  depends on the energy only and describes the annealing history as given by the annealing temperature and the total annealing time for each step in the step annealing. The total value  $P(t)$  of the property during the  $(n+1)$ th annealing at a temperature  $T_{n+1}$  is then

$$P(t) = \int_0^{\infty} p_0(\epsilon)F_n(\epsilon)\theta(\epsilon, t, T_{n+1})d\epsilon.$$

Since  $p_0(\epsilon)$  is the function to be determined, this integration cannot be carried out. However, the rate of property change  $dP/dt$  can be measured.

$$\frac{dP}{dt} = \int_0^{\infty} p_0(\epsilon)F_n(\epsilon) \frac{d\theta(\epsilon, T_{n+1}, t)}{dt} d\epsilon.$$

Because of the shape of the  $\theta$  function as given in Fig. 7, the integrand is essentially different from zero only over a small energy range. For this small range  $p_0(\epsilon)$  may be replaced by a constant average value  $\langle p_0(\epsilon) \rangle_{av}$  and taken out of the integral. Furthermore, because of the limited accuracy of the measurements, we may replace the differential quotient by the difference quotient, as first suggested by Bredt,<sup>20</sup> and get by multiplying both

<sup>20</sup> J. H. Bredt, Ph.D. thesis, Urbana, Illinois, 1960 (unpublished).

sides of the equation by  $\Delta t$ :

$$\Delta P = \langle p_0(\epsilon_0) \rangle_{av} \int_0^{\infty} F_n(\epsilon) \Delta\theta d\epsilon = \langle p_0(\epsilon_0) \rangle_{av} I,$$

$$\langle p_0(\epsilon_0) \rangle_{av} = \Delta P / I.$$

The related  $\epsilon_0$  can be calculated as the center of gravity for this integral by means of a weighted average:

$$\epsilon_0 = \frac{\int_0^{\infty} \epsilon F_n(\epsilon) \Delta\theta d\epsilon}{\int_0^{\infty} F_n(\epsilon) \Delta\theta d\epsilon}.$$

A closer look at the integral  $I$  reveals some useful information on how much to increase the temperature for step annealing, once the total annealing time has been selected. In Fig. 8 both factors under the integral have been plotted. For a fixed time interval

$$\Delta \ln t = \text{const}, \quad \Delta\theta_{n+1} = \theta_{n+1}' - \theta_{n+1}''$$

moves with increasing time to the right at a speed proportional to  $\ln t$ . For practical reasons (heating time comparable to the measuring time, instabilities in the temperature at the beginning of an annealing) the first measurements of the change in the property  $P(t)$  with time can be done only after some time has elapsed. Therefore, a proper temperature increase has to be picked in order to minimize the effects of experimental errors. In Fig. 8, the  $\Delta\theta_{n+1}$  curve *A* corresponds to too small a temperature step. Since  $\Delta\theta_{n+1}$  is to be multiplied by  $F_n$  and the  $F_n$  function is small and increasing with a rapidly increasing slope, a small shift in the  $\Delta\theta_{n+1}$  curve due to a small error in time will result in a large error in the integral. On the other hand, for curve *C*  $F_n$  is practically one; therefore, the exact position of  $\Delta\theta_{n+1}$  is not important. However, in this case the center of gravity  $\epsilon_0$  for the integral  $I$  has been moved out far to the right and information has been lost. A proper choice of  $\Delta T$  would result in a  $\Delta\theta_{n+1}$  curve like curve *B*. A good guess for  $\Delta T$  can be made by replacing  $F_n$  by  $\theta_n(\epsilon, t_n, T_n)$  and having the same point of inflection for both  $\theta_n(\epsilon, t_n, T_n)$  and  $\theta'(\epsilon, t_{n+1}, T_{n+1})$ . For a total annealing time of one hour and the first measurements made one minute after heating, this results, using a frequency factor of  $\ln B = 27$ , in

$$\epsilon' = kT_n \ln B t_n = kT_{n+1} \ln B t_{n+1},$$

$$T_{n+1}/T_n = 35.2/31.$$

The temperature increase has to be approximately 15%, which is in agreement with our practical experience.

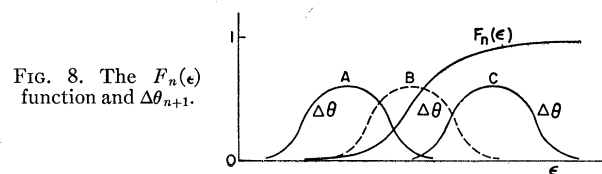


FIG. 8. The  $F_n(\epsilon)$  function and  $\Delta\theta_{n+1}$ .



The frequency factor can be obtained in the following way: For each temperature a section of the annealing spectrum can be calculated from the experimental data. The calculation is carried out for different values of  $B$ , until the sections obtained from data at different temperatures fit together smoothly. As Primak<sup>19</sup> has pointed out, under favorable conditions  $B$  can be determined to within an error of about 50%.

The integrals were calculated on the ILLIAC computer. With the restriction  $\Delta \ln t \leq 1$ , 25 values of  $F_n$  and  $\Delta \theta_{n+1}$  were computed in the range  $0.0001 \leq \theta_{n+1}'' \leq 0.9999$ . The integration was carried out using Simpson's rule which results in an error of about 0.01% for the integral.

The above equations are strictly valid only under the condition that the processes involved are independent of each other and obey first order kinetics with a constant frequency factor  $\ln B$ . Since a large error in  $\ln B$  should be noticed, as mentioned above, by the discontinuities in the resulting curve, a smaller error in  $\ln B$  merely shifts the peak position ( $\Delta \ln B = 2$  corresponds to an error in the peak position of about 10%). If some or all of the processes in question are of an order different from one, care has to be taken in the interpretation of the data. Primak<sup>18</sup> showed, however, that by replacing the  $\theta$  function by a step function, a first approximation can be calculated from the data independent of the order of the process. As long as  $kT$  is several times smaller than the spectrum, this should also be true for using an inappropriate function. Therefore, the spectrum calculated thus will at least give a qualitative picture of the activation energy spectrum.

It is generally agreed that in Cu the low-temperature processes are the annihilation of close Frenkel pairs. Therefore, it seems justified to assume the same kind of processes going on in Au and Al in order to carry out the calculations. But it must be kept in mind that some of the processes with higher activation energy may perhaps not obey first-order kinetics.

A big advantage of isothermal annealing measurements is the fact that they reveal many more details than isochronal measurements. The number of points on the spectrum curve is in practice limited only by the accuracy with which the decrease of the introduced resistance can be measured during the annealing. For isochronal annealing measurements each temperature step contributes only one point to the curve. For this reason the annealing spectra given below shows many more details than one would expect from the isochronal annealing data. It has, furthermore, to be pointed out that the curves are actually given by parametric equations for  $p(t)$  and  $\epsilon(t)$ , with  $t$  the annealing time. Therefore, the points have to be connected consecutively rather than in the way normally used for interpolating experimental data. (Because of the experimental errors this may result in some ambiguity.)

The computation of the activation energy spectrum outlined above reveals many more details than the

method used by Magnuson, Palmer, and Koehler.<sup>2</sup> Therefore, their data for the annealing in Cu and Ag have been re-evaluated in addition to the data for Al and Au obtained in this experiment. The resulting activation energy spectra are given in Fig. 9.

While there is general agreement between the curves for Cu and Ag obtained by the two different methods, using a frequency factor of  $\ln B = 27$ , the curves calculated with the computer definitely show more structure. The first significant difference is the substructure in the large peak for both metals. For Cu this has also been found with stored energy measurements by Granato and Nilan.<sup>21</sup> Furthermore, a small additional peak between peaks  $I_B$  and  $I_C$  with an activation energy of 0.089 eV and 0.053 eV, respectively, shows up clearly. For Cu there is strong evidence of two more peaks on the high-energy side of the large peak, one at about 0.13 eV, the other at approximately 0.14 eV. From the shape of the low-energy side of the high peak for both metals, one may be tempted to assume that there is more structure hidden, but this cannot be decided with the present data.

The curve for Al, obtained with a frequency factor of  $\ln B = 29$ , confirms the four peaks derived from the isochronal annealing data, but there is indication of an additional peak on the slope of the large peak with an activation energy of about 0.095 eV, which would correspond to a peak in the annealing spectrum at about 30°K. But this and the fact that the frequency factor for the first peak at 0.057 eV may be a little bit smaller cannot firmly be established within the error of our measurements. The error in the activation energy for Al is estimated to be less than 10%.

The situation for Au is more complex than anticipated from our isochronal curve. Recently the activation energy spectrum has been obtained for electron-irradiated Au<sup>22</sup> with a more appropriate choice in the temperature step  $\Delta T$  (corresponding to the case  $B$  discussed above), and with a better correction for temperature fluctuations during the annealing. The authors found, with  $\ln B = 27$ , a spectrum consisting of at least 10 peaks up to an energy of 0.15 eV. Because of the complexity of the gold spectrum, we could not establish a frequency factor; also, due to the error in the measurements, there may be some doubt about smaller details in the spectrum, as given in Fig. 9(d) with a frequency factor of  $\ln B = 27$ .<sup>22</sup> The high background, with only two really outstanding peaks, explains why so far with heavy particles only "nonspecific annealing" has been observed.

#### IV. DISCUSSION AND CONCLUSIONS

A comparison of the recalculated activation energy spectrum for Cu and Ag with the annealing data re-

<sup>21</sup> A. V. Granato and T. G. Nilan, Phys. Rev. Letters **6**, 171 (1961).

<sup>22</sup> W. Bauer, J. W. Deford, J. W. Kauffman, and J. S. Koehler, Phys. Rev. **128**, 1947 (1962).

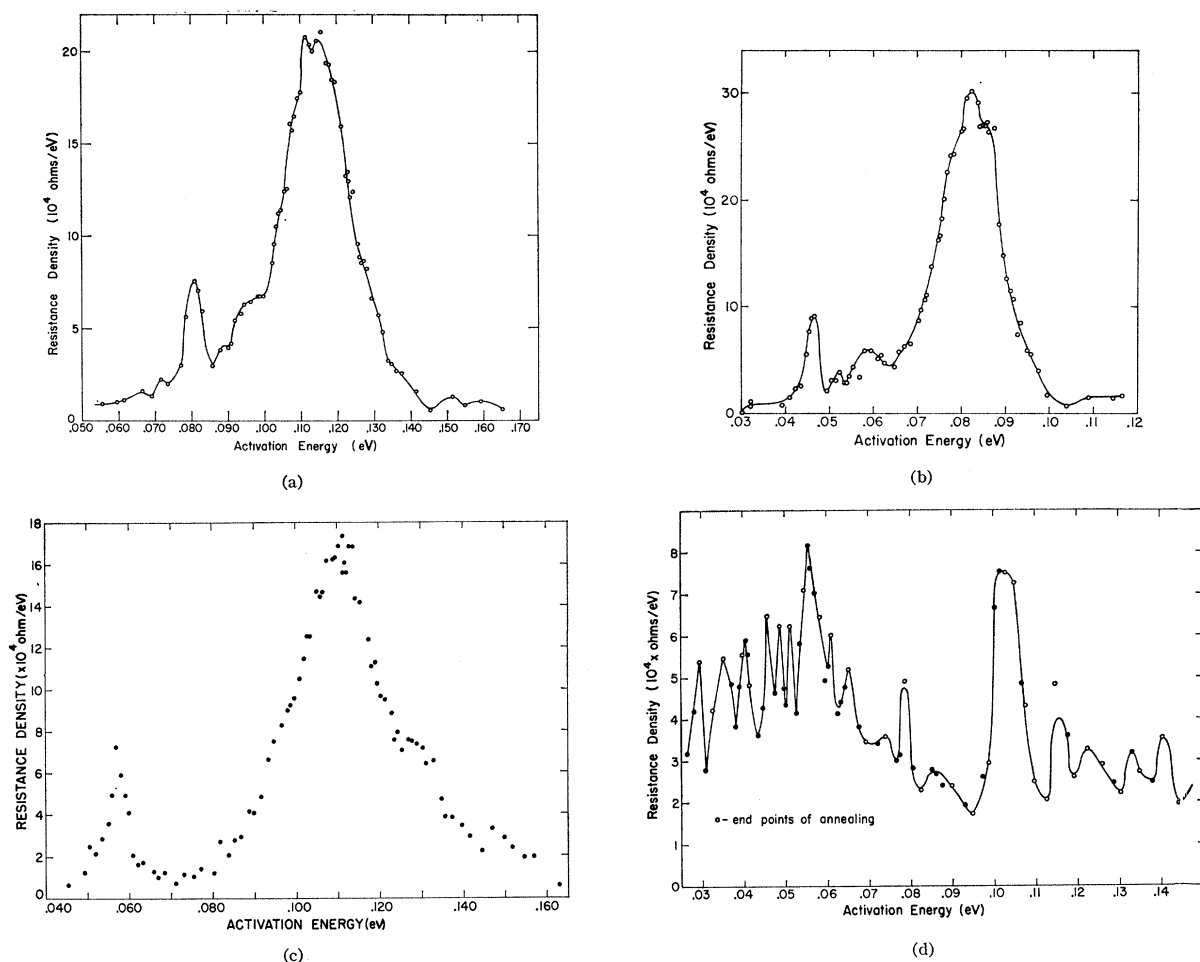


FIG. 9. Activation energy spectra for (a) Cu, (b) Ag, (c) Al, and (d) Au.

ported so far clearly leads one to the conclusion that the explanations given for the low-temperature annealing at least need some reconsideration. It is generally agreed that the peaks  $I_A$ ,  $I_B$ , and  $I_C$  correspond to close pair annealing, but nothing is really known theoretically about the configuration and migration energy of these close pairs nor has it ever been satisfactorily established why there should be just three peaks. In view of this situation, the simplest way to explain the additional small peak between peaks  $I_B$  and  $I_C$  for both Cu and Ag is, therefore, close pair annealing. The superstructure in peak  $I_D$  for both metals poses a more serious problem if one accepts peak  $I_D$  to be correlated interstitial-vacancy annihilation<sup>23</sup> with the interstitial moving. Granato and Nilan,<sup>21</sup> who first reported a fine structure in peak  $I_D$  for Cu, suggested that the peak  $I_D$  might be a superposition of several first-order processes with only small differences in their activation energies; this would easily account for the somewhat broader peak width.

On the other hand, it would leave no explanation for the peak or peaks suspected on the high-energy side of the large peak in Cu, unless one assumes that this is just peak  $I_E$ , corresponding to the freely migrating interstitial. Another explanation would be shallow trapping or clustering (di-interstitial?), but because of the lack of detailed information available no further comments can be made.

The activation energy spectrum for Al and Au can at least be qualitatively understood by discussing the range of interaction in both metals and the isotropy of Al.<sup>24</sup> Because of the relatively large space available for each ion in Al [ $R_{\text{atom}} - R_{\text{ion}}/R_{\text{ion}} = 2.16(25)$ ] and the high density of conduction electrons we expect a very short-range interaction between point defects, particularly between vacancies and interstitials. Therefore, only a few different configurations are possible for close Frenkel pairs. Since, furthermore, Al is a metal of high isotropy<sup>25</sup> we expect only small differences, if any, in the

<sup>23</sup> J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. 114, 1452, 1460 (1959).

<sup>24</sup> Some of these ideas have been suggested to the author by K. H. Bennemann, whose help is gratefully acknowledged.

<sup>25</sup> H. Jones, Physica 15, 13 (1949).

migration energies for Frenkel pairs of different orientation in the lattice. Therefore, only very few, if more than one, peaks due to the recombination of close Frenkel pairs should exist, with the total number of the population small compared to the population of the peak due to the free migrating interstitial. This line of reason leads one to conclude that the first peak in the activation energy spectrum for Al should correspond then to close Frenkel pair annihilation, while one is tempted to assign the large peak to free interstitial migration. The large amount of damage which anneals out in the large peak is easily understood by the fact that, because of the low threshold energy of Al and the short-range interaction, essentially only free interstitials are produced by deuterons. This is further supported by the observation that in electron-irradiated Al<sup>6</sup> the same fraction of introduced defects anneal out. Further experiments are necessary to clear up the situation.

Au is more densely packed [ $R_{\text{atom}} - R_{\text{ion}}/R_{\text{ion}} = 0.16$  (25)] than the other metals discussed here. The density of free electrons and the high compressibility<sup>25</sup> also suggest that the point defects interactions are relatively long ranged. Therefore, the lattice region defining close Frenkel pairs is large and we expect a great number of different close Frenkel pair configurations. In addition, Au is highly anisotropic, so it is reasonable that the annealing peaks due to close pairs will be split up into a number of peaks, resulting in the rather complex structure observed. This is also supported by the fact that the spectrum obtained with electron bombardment<sup>22</sup> is essentially the same as the one with deuteron bombardment. From the energy dependence of the peak

height (electron vs deuteron bombardment) there is some evidence that the large number of peaks may be subdivided into (four?) groups, each group corresponding to a peak in the Cu spectrum. This is suggested by the way the peaks are affected by a change in the energy of the bombarding particle.<sup>26</sup> In Cu, with decreasing energy of the bombarding particle (it has been investigated with electrons), the population of peak *A* decreases, while the population of peak *B* and *C* goes up, for peak *C* much more than for peak *B*. If that is true for Au too, then there would be essentially no difference in the activation energy spectra for the noble metals. But the question as to why the Au spectrum is more detailed than the Cu spectrum and why little recovery occurs in Au compared to Cu and even Ag then remains. Certainly this problem needs further investigation.

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The computer program was written by G. Thomas.

<sup>26</sup> A. Sosin, Phys. Rev. **126**, 1698 (1962).