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UNITED STATES ATOMIC ENERGY COMMISSION

COO-104

RADIATION DAMAGE RESEARCH

Second Quarterly Report—October 1 to
December 31, 1952

March 31, 1953

Purdue University

Technical Information Service, Oak Ridge, Tennessee

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PROJECT PERSONNEL

Director	K. Lark-Horovitz
Consultants	W. P. Binnie
	I. G. Geib
Research Staff	J. F. Goff*
	T. C. Harman*
	E. E. Klontz*
	A. M. Liebschutz*
Technicians	L. Horvath*

*Paid in part or in full by PRF 612.

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PHYSICS

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I. THE THERMAL CONDUCTIVITY OF GERMANIUM SEMICONDUCTORS AT LOW TEMPERATURES

James Goff

C00-104

I. INTRODUCTION

This investigation of the thermal conductivities of semiconductors is part of the program of irradiation physics. It is known that the thermal conductivity of a solid is very sensitive to lattice imperfections; and therefore, it was expected that this might be a particularly important experiment to detect even those lattice imperfections which cannot be detected by electrical measurements. This expectation is supported by observations of the Oxford group on the thermal conductivity of crystalline quartz, which shows a large change in thermal conductivity after a moderate neutron bombardment. (1)

The thermal conductivity of germanium and silicon was determined around room temperature by Lark-Horovitz and Miller in 1943. (2) They used the so-called isotherm method to determine the ratio of the thermal conductivities of germanium and silicon to that of some known metal. The results of those experiments indicated that the thermal conductivity at room temperature and above was independent of the electrical conductivity and was, therefore, interpreted as a lattice conductivity. In highly degenerate samples, one should find a contribution to the thermal conductivity by the electrons; and it seems particularly important to investigate the thermal conductivities of single crystals of germanium over a wide range of temperatures before and after nucleon irradiation.

Therefore, K. Lark-Horovitz proposed that the influence of nucleon irradiation of the thermal and the electrical conductivities of semiconductors be investigated in the temperature range from 1° to 100° K. An apparatus has been constructed to do this, and measurements of the thermal conductivity of single crystals of germanium have been made in the range of 55° to 82° K to demonstrate the operation of the apparatus.

The method used to measure the thermal conductivity at low temperatures, was perfected in the Leiden laboratories. (3) A uniform rod-shaped sample is enclosed in a container which is immersed in a low temperature bath. This container is evacuated to a pressure of about $1 \cdot 10^{-5}$ mm of Hg to minimize gaseous heat conduction from the sides of the sample and so fulfill the condition of uniform heat flux. One end of the sample is connected to the bath, and the other end is connected to an electric heater. The heater current generates a heat flux W/a (W , the power input, a , the area of the cross section) which flows through the sample to the bath and sets up a temperature gradient in the sample. The temperature of the sample is measured at two points which are separated by a known distance L . If necessary the known power input W is corrected for any spurious inputs or losses. Then, the thermal conductivity k is determined by the equation $k (T \text{ average}) = - \frac{W}{\Delta T} \left(\frac{L}{a} \right)$.

The thermal conductivity is found at different temperatures by changing the temperature of the bath and measuring W and ΔT for each bath temperature.

Temperatures below 100°K are obtained by using liquified or solidified gases in the same manner as an oil bath at high temperatures. The liquids used and their temperature ranges are: helium, from 1° to 4.2°K ; hydrogen, from 14° to 20°K ; nitrogen, from 63° to 77°K ; and oxygen at temperatures from 54° to 90°K . By the use of solidified hydrogen, the hydrogen temperature range is extended to 10°K and the use of solidified nitrogen extends that range down to 45°K .

The temperatures of these liquids and solids is regulated by controlling their vapor pressure. This is done by means of a mechanical pump with a controlled pumping speed.

Temperatures which are not within the range of any liquified or solidified gas are obtained by using an auxiliary heater to raise the temperature of the sample above that of the surrounding bath. This heater is placed between the sample and a high resistance path to the bath in order to decrease the amount of power required to heat the sample.

II. Apparatus

The apparatus is shown in figure 1. This figure is accurate except for two details which have not been shown in their proper perspective for the sake of clarity. Although the sample (S) is centered axially in the inner container (Q), it has not been drawn in section in order to better show the attachment of the thermometer bulbs (U). The Kovar-glass seals (C), (D), and (F) have been shown rotated 45° about the container axis for sake of clarity.

Figure 1. The Apparatus

Legend of Figure 1

- (A) Thermometer capillaries (1.1 mm ID)
- (B) Monel pumping tube
- (C) Kovar-glass seal for electrical conductivity electrical connections
- (D) Kovar-glass seal for thermal conductivity electrical connections
- (E) Monel pumping tube for heat switch
- (F) Kovar-glass seal for auxiliary heater and thermistor connections
- (G) Lid of the outer container
- (H) Lid of the inner container
- (I) Bakelite insulator
- (J) Radiation shield
- (K) Unions
- (L) Capillaries (0.559 mm OD)
- (M) Kovar-glass volume in the dead space capillary
- (N) Kovar-glass electrical insulators in thermometer capillaries
- (O) Outer container
- (P) Heater
- (Q) Inner container
- (R) Wire contact-supports for thermometer bulb
- (S) Sample
- (T) Supports for the sample-heater-thermometer assembly
- (U) Thermometer bulbs
- (V) Clamp for the sample-heater-thermometer assembly
- (W) Sample extension
- (X) Auxiliary heater
- (Y) Thermistor holder
- (e) Electrical contact points for electrical conductivity measurements
- (t) Electrical contacts for thermal conductivity measurements

The apparatus was designed so that measurements could be made at temperatures not only in the temperature range of some liquified or solidified gas but at temperatures between these ranges as well.

The sample (S) is enclosed by concentric brass containers (Q) and (O) which are surrounded by the bath. The inner container may be evacuated to provide thermal insulation for the sample; the outer container makes possible a "heat switch". For measurements at temperatures in the ranges covered by liquified or solidified gases the jacket between the inner and outer container is to be filled with an exchange gas. Then, the path for the heat flux which is generated in heater (P) is through the sample, the copper extension (W), and the exchange gas to the bath. In order to measure at temperatures above the bath temperature, the exchange gas is to be pumped out and the heater (X) turned on. The thermistor in block (Y) will be used to control the temperature of the inner container when the auxiliary heater is used.

The temperature gradient in the sample, which is caused by the flow of heat from the heater to the bath, is measured by the gas or vapor pressure thermometers (U). These thermometers are electrically insulated from each other by the Kovar-glass insulators (N) so that electrical conductivities can be measured.

There are three capillaries in the group labeled (A). The third capillary is to be used to measure the dead-space temperature of the thermometer capillaries. The Kovar-glass volume (M) duplicates the dead-space volume of the Kovar-glass insulators (N).

Except for the supports (T), which are fastened with small machine screws, the apparatus is held together with two kinds of solder. As a rule joints which are taken apart only for major repairs are soldered with 50-50 Pb-Sn solder, while joints which are taken apart more often are soldered with cerroseal, a low melting 50-50 Sn-In solder. The one exception to this rule is the soldering of the clamp (V) to the extension (W) with Pb-Sn solder in order to prevent the melting of this joint when the sample is soldered to the extension with cerroseal.

The temperature is measured with gas thermometers. Gas thermometers were chosen because they are easily adapted to the whole low temperature range. Further, if the thermometer capillaries are insulated from the bath, they can be used as vapor pressure thermometers in the appropriate temperature ranges.

The thermometer bulbs have an annular shape. They are made of copper which is tinned with solder to prevent leaks. They are attached to the sample as shown in figure 1 by four small copper wires. These wires are wound around the sample and soldered to it so that a pair of ends extends from each corner of the sample as shown in figure 2. These free ends are soldered to the bulbs and serve as supports for them as well as contacts between the sample and the bulbs. The bulbs are light and, being arranged symmetrically about the sample, cause no dangerous strain or shear on it. These thermal contacts are good enough for a constant volume type barometer to come to equilibrium in about 30 minutes.

These bulbs are connected to the pressure measuring devices by monel capillary tubing as shown in figure 3. The large capillaries have

Figure 2. Thermometer Contacts

Figure 3. Thermometers and Vacuum System

an inside diameter of 1.1 mm which is large enough to eliminate any pressure difference due to the thermomolecular pressure effect. It was necessary to use small capillaries in the container in order to bend them. However, calibration at the boiling point of the bath shows that no corrections are needed: This result was expected because there is only a small temperature gradient over the small capillaries.

Each bulb is connected to one side of a butyl phthalate oil manometer, which indicates the difference of bulb pressure in mm of oil. This pressure is easily changed to mm of Hg. The higher temperature bulb is also connected to a mercury barometer and a butyl phthalate barometer which indicates the absolute pressure of the bulb. These measurements of pressure difference and absolute pressure are converted to temperature difference and temperature, respectively.

III. Results

The thermal conductivity of one P type and of one N type germanium single crystal have been measured. The N type sample has been measured in a range from 65° to 82° K. The P type sample has been measured in the range from 55° to 81° K. The results of these measurements are shown by figure 4 .

Sample Sb-7 is an N type, antimony doped germanium single crystal with an electrical resistivity at room temperature of 0.013 ohm-cm. It was cut transverse to the axis of crystal growth to insure the greatest possible homogeneity. The sample axis was cut parallel to a 110 direction.

Sample Al 8 4-1 is a P type aluminum doped germanium single

Figure 4

crystal with an electrical resistivity at room temperature of 0.2 ohm-cm. It was also cut transverse to the axis of crystal growth to insure the greatest possible homogeneity. However, the sample axis was not cut parallel to any particular crystal plane.

Both crystals were examined by x-rays to determine whether they were still single crystals after their thermal conductivities had been measured. It was found that they were still single crystals.

The thermal conductivity results are consistent with expectations based upon previous studies of the thermal conductivity of other materials. The more pure sample has the higher thermal conductivity. The decrease of the difference between the values of the thermal conductivities as the temperatures increases is consistent with the results of K. Lark-Horovitz and E. P. Miller, who showed that at room temperature the thermal conductivity of germanium is independent of the electrical conductivity. (2)

REFERENCES

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2. K. Lark-Horovitz and E. P. Miller, Purdue Research Foundation Final Report No. 184. N.D.R.C. No. 14-585 (November 1945) 61.
3. W. J. de Haas and W. H. Capel; Physica I, 725 (1934).

II. RESISTANCE CHANGES IN GERMANIUM SINGLE CRYSTALS DURING ELECTRON BOMBARDMENT.

E. E. Klontz

A P-type sample of Ge (referred to in our First Quarterly Report 1952-53), has been rebombarded for a total of 16.5 hours. Prior to this bombardment, the resistivity of the sample was .320 ohm-cm at liquid nitrogen and 2.18 ohm-cm at room temperature. Bombardment at liquid nitrogen temperature, for time intervals from 100 sec. to 2000 sec. were made with 4.2 Mev electrons from the linear accelerator. Beam currents up to .035 μ amp were incident on the specimen. A ballistic galvanometer was used for measuring total incident flux; the bombarding current was measured with an accuracy of about $\pm 3\%$. This was accomplished by using a large (32 μ f) condenser for storing the collected charge so that after bombardments of 2000 sec it would be charged to only about 1.5 volts which we found was low enough to be unaffected by ionization from radiation produced by the beam.

The initial slope of the conductivity vs. flux curve (figure 1) corresponds to a removal of only .03 carriers per-cm³ per unit incident flux. As in previous tests with this sample, when the beam was turned off in the course of the experiment, and the sample was allowed to stand for a period of several hours, the resistance continued to change. For a better picture of these changes a plot of $\ln \sigma$ against total flux is included in figure 2. Points lettered A-E indicate conductivity variations after bombardment has stopped. At A and B when bombardment starts again, the original curve is continued. For points C to E, the original curve is never again reached,

P-TYPE GERMANIUM ELECTRON BOMBARDMENT

TEMP = 77°K

ENERGY = 4.2 Mev

$R_0(77^\circ\text{K}) = 2500 \text{ cm}^3/\text{clmb}$

$\rho_0(77^\circ\text{K}) = .32 \text{ ohm-cm}$

$\left. \frac{d\sigma}{df} \right)_0 = 3.5 \times 10^{-17} \text{ cm ohm}^{-1}$

$\left. \frac{dn}{df} \right)_0 = .033 \frac{\text{carriers/cm}^3}{\text{unit flux}}$

Figure 1

Variation of conductivity with total incident flux of P-type germanium under electron bombardment.

Figure 2

Logarithmic plot of conductivity flux variation for P-type germanium under electron bombardment, showing healing which occurs during periods when bombardment is suspended.

This is due to the fact that our flux is really quite low and even with about two hours actual bombardment time we have not quite returned to the initial curve. For higher flux or longer bombardment time prior to an extended period of shut down, we should continue the flux curve.

The decay observed at points A to E should yield information as to rates and perhaps processes of healing in the sample. Qualitatively it appears there is a short lived (of the order of minutes) and a medium long lived (of the order of several hours) decay rate, the former associated with the initial stages of bombardment while the latter dominates the later stages. For obtaining data on these decay rates, we will utilize a Leeds and Northrup recording voltmeter which will automatically record resistance changes over a long period of time.

For further interpretation of the curves obtained during bombardment, a knowledge of the number of carriers present at each stage of bombardment is necessary. No information of this type has been obtained in any electron bombardments up to now. Since future experiments are to be carried out on the accelerator in its final form, some minor design changes in equipment are being made now. These changes have been extended to include a method for measuring Hall values during bombardment while still maintaining constant low temperatures of bombardment. A complete description of the bombardment chamber, Hall measuring and resistivity measuring methods will be described later.

III. HARDNESS OF DEUTERON IRRADIATED MOLYBDENUM

T. C. Harman, L. Horvath and I. G. Geib

In the October 1, 1952 report, factors which influence the hardness number obtained with the Bergsman tester were discussed. These include vibration insulation of the Vickers microscope, and load, rate of descent of sample and time of indentation. Fig. 1 shows the effect of building vibration on hardness number and the improvement in consistency of measurement obtained by insulation from vibration. Indentations were made in a single large grain of H-19 using a 50 gm load and a rate of descent of 1 mm/min. H-19 was cut from a sheet of 10 mil cold-rolled Mo, heated for 20 hr x 2400°F in dry hydrogen, polished and etched. As shown in the graphs, insulation from vibration gives larger hardness numbers for times of indentation up to 600 sec. Some of the points obtained with no insulation fall rather far from the smooth curve drawn through the points. With the microscope mounted on sponge rubber, the points obtained fall close to a smooth curve. Furthermore, the hardness numbers are reproducible quite accurately. The rubber was replaced with new rubber, the microscope re-leveled and the measurements repeated. The points obtained fall close to the curve drawn through the points obtained after rubber was under the microscope for 18 days. Another factor which affects the measurements is the quality of the surface of the sample. A large number of indentations were made in this grain. It is believed that the reason for the 40 sec and 600 sec points being high after the rubber was changed is that the indenter hit a slight scratch in the grain.

Figure 1. Effect of vibration on hardness number.

Fig. 2 shows the variation of hardness number with load and figs. 1 and 2 show the variation of hardness number with time of indentation. The rate of descent of sample was 1 mm/min for all values in fig. 2. The values plotted in fig. 2 were obtained from indentations made in another large grain of H-19. A smaller number of points was obtained for the 100 gm load, since the grain was becoming filled with indentations. As the curves in fig. 2 show, the hardness number increases with decreasing load. Since the 50 gm load gives consistent values and is small enough to give micro-hardness and permit quite a few indentations to be made in a single grain, a 50 gm load has been used for most measurements.

When smooth curves are drawn through the points in figs. 1 and 2, it is evident that the hardness number changes rapidly with time of indentation for small times. The number varies more slowly with time for times greater than 110 sec. Since times greater than 110 sec will reduce the effect of an error in measuring time, a time of indentation of 120 sec has been used for most measurements. The instructions for the Bergsman tester suggest a time of 15 sec. This is in the range where the number changes rapidly with time.

Fig. 3 shows the variation of hardness number with rate of descent of sample for a load of 50 gm and a time of indentation of 50 sec, indentations being made in another large grain of H-19. It is evident that the hardness number varies slowly with rate of descent over the range studied. A convenient rate of 1.0 mm/min has been used for all measurements.

All hardness numbers given in this report are V.P.N.* Unless stated
* Vickers - Pyramidal-Number

20

Figure 2. Variation of hardness number with load and time of indentation.

21

Figure 3. Variation of hardness numbers with rate of descent of sample.

otherwise, they were obtained with a load of 50 gm, a rate of descent of 1 mm/min and a time of indentation of 120 sec. Even with careful vibration insulation and the selection of the best conditions for measurements, it is found that hardness numbers for an annealed Mo sheet vary from grain to grain by approximately 20 V.P.N. It is to be noted in fig. 2 that rotation of the sample with respect to the indenter may be a reason for the fluctuation of the 100 gm values.

The effect of rotating the sample around the vertical axis of the sample holder and indenter was studied using another large grain in H-19. Fig. 4 shows the effect of rotating the sample holder through 90° , indentations being made after 15° rotations. In all measurements, the horizontal and vertical diagonals of the indentations are measured. In general, the two values are not exactly the same for each indentation and the average value is used in determining the hardness number. For fig. 4, hardness numbers were calculated from both horizontal and vertical diagonals to follow variations with rotation. On the curve drawn for the hardness numbers from the vertical diagonals, there is a maximum at 30° and a minimum at 75° . On the curve for the hardness numbers from the horizontal diagonals, there is a maximum between 20° and 25° and a minimum between 65° and 70° . The number of degrees between the maximum and minimum is approximately 45. Over part of the range of these curves, the vertical diagonal gives a higher hardness number than the horizontal diagonal. The curves cross at two points and over the remainder of the range the horizontal diagonal gives a higher hardness number. These curves indicate that the grain is harder in one direction than in the other. It is to be noted that one maximum is displaced between 5° and 10° from the other. This may be a result of the orientation of the

Figure 4. Effect of sample rotation on hardness number.

indenter with respect to the three crystal axes. Using average values, the hardness of this grain varies from a minimum of 185 to a maximum of 205. These results show that the hardness number depends on the orientation of the grain with respect to the indenter and indicate a reason for some of the variation from grain to grain.

The rotation experiment was repeated using a very large grain in H-14. H-14, a sample prepared for irradiation, is a Mo sheet cut from 10 mil stock, thickness 7 mil, which was heated 20 hr x 2400°F in dry hydrogen, polished and etched. The surface of the grain appeared to be very good. The average hardness numbers given in table 1 and plotted in Fig. 5 show the same increase to a maximum followed by a decrease to a minimum. It is evident that more points are needed, if the shape of the curve is to be determined precisely. To show the consistency of the measurements, the two measured values for each angle are given in table 2, with the average values and the deviations from the averages. The variation from maximum to minimum hardness is greater than any of the deviations.

These measurements were repeated after the sample had been given a total irradiation of $7.6 \mu \text{ amp} \cdot \text{hr/cm}^2$ with 8.4 to 10 Mev deuterons. The grain was stained as a result of the irradiation. The staining will be discussed in detail later. The average values are given in table 1 and plotted in Fig. 5. The measured values, the averages and the deviations are given in table 3. It was evident that the deviations were larger than before irradiation and three indentations were made at each angle setting. A possible explanation for the larger deviations is that the stain reduced the quality of the surface. The average values show the same increase to a maximum and decrease to a minimum. The sample was

Table 1

Hardness of One Grain, Annealed Mo Sheet, H-14

Rotation, degrees	Hardness before bomb.	After 7.6 μ amp-hr/cm ²	After cleaning	ΔH before cleaning	ΔH after cleaning
0	209	211	202	+2	-7
15	212	220	212	+8	0
30	201	216	213	+15	+12
45	199	216	205	+17	+7
60	188	197	193	+9	+5
75	186	200	197	+14	+11
90	194	208	201	+14	+8

Table 1 shows the effect of cleaning the sample with acetone and trichloroethylene on the hardness measurements made in the single large grain of H-14. Hardness changes given as ΔH , before cleaning, show an average of +11, in agreement with the statement made later in this report that the hardness of H-14 tends to be greater after irradiation but the change for this sample is small. The values given as ΔH , after cleaning, which removed the stain almost completely, show that the effect of the cleaning was to decrease the hardness number by approx. 6.

Figure 5. Effect of sample rotation on hardness number, H-14.

Table 2

Hardness, H-14, Before Bombardment

Rotation, degrees	Hardness	Ave. Hardness	Deviation
0	208.4	208.5	-0.1
	208.6		+0.1
15	211.7	211.5	+0.2
	211.3		-0.2
30	200.1	200.8	-0.7
	201.6		+0.8
45	199.4	199.4	0.0
	199.4		0.0
60	187.6	188.2	-0.6
	188.8		+0.6
75	185.6	185.8	-0.2
	186.1		+0.3
90	192.2	193.6	-1.4
	195.1		+1.5

Table 3

Hardness, H-14, After Bombardment

Rotation, degrees	Hardness	Ave. Hardness	Deviation
0	206.4	211.2	-4.8
	214.8		+3.6
	212.3		+1.1
15	215.8	219.6	-3.8
	220.8		+1.2
	222.3		+2.7
30	213.1	215.8	-2.7
	215.7		+0.1
	218.4		+2.6
45	213.4	215.5	-2.1
	217.3		+1.8
	215.7		+0.2
60	202.2	197.4	+4.8
	196.9		-0.5
	193.3		-4.1
75	202.7	199.8	+2.9
	197.5		-2.3
	199.4		-0.4
90	212.1	207.7	+4.4
	204.1		-3.6
	207.0		-0.7

cleaned and the measurements were repeated. The average values are given in table 1 and plotted in Fig. 5. The measured values, the averages and the deviations are given in table 4. Five of the averages fall between the curves drawn for the sample before and after bombardment. The deviations are such that the 15° point falls between the curves within the experimental error but the 0° value is too low. The results check those for H-19 and show that the measured hardness number depends on the orientation of the grain with respect to the indenter.

Hardness measurements made on single crystals are suggested as a means of studying the variation of hardness number with orientation. Single crystals of tellurium (hexagonal lattice) and germanium (diamond lattice) are available to us. Both these materials are brittle. A single crystal of Te was supplied by R. S. Caldwell and preliminary measurements were made on this crystal. According to information supplied which was obtained by macroscopic etch, cleavage and X-ray diffraction, the directions of the crystal axes are known. The surface of the crystal was not very good and work should be done on the etching to improve the surface. The crystal was set with the vertical axis of the indenter parallel to the a-axis and the horizontal diagonal parallel to the c-axis of the crystal. The brittleness of the Te is shown by cracking around the impression. A 5 gm load and a time of indentation of 15 sec were used to reduce the cracking to a minimum. The vertical diagonal of the indentation is much longer than the horizontal diagonal. Calculations made from the vertical diagonal gave a hardness of 35 and those from the horizontal diagonal a hardness of 83. These measurements are being continued to study variations produced by rotating the sample with respect to the indenter axis.

Table 4

Hardness, H-14, After Cleaning

Rotation, degrees	Hardness	Ave. Hardness	Deviation
0	201.9	201.8	+0.1
	201.6		-0.2
15	214.2	212.2	+2.0
	210.2		-2.0
30	214.0	213.4	+0.6
	208.8		-4.6
	217.4		+4.0
45	202.2	205.1	-2.9
	207.4		+2.3
	205.8		+0.7
60	192.1	193.2	-1.1
	194.2		+1.0
75	196.2	197.4	-1.2
	198.6		+1.2
90	200.0	201.2	-1.2
	202.4		+1.2

In the October 1, 1952 report, results of measurements on annealed Mo sheets, H-6 and H-7, were given/^{which} showed that the hardness of an irradiated region is greater than the hardness of a shielded region after deuteron bombardment. It was pointed out that the effects of surface conditions must be considered. The samples were allowed to stand to determine if the magnitude of the difference between bombarded and shielded regions changed with time. The samples were heated in dry hydrogen to determine if the increased hardness could be returned to the value before bombardment by heat treatment. All hardness measurements for a given sample are made with the sample in the same position with respect to the indenter.

Using the averages of the values previously reported, H-6 after 13.5μ ampehr/ cm^2 deuteron irradiation had a bombarded region 50 V.P.N. harder than the same region before irradiation, and 38 V.P.N. harder than the shielded region. Standing 6 days did not change the hardness numbers, and an additional irradiation of approximately the same amount did not change the hardness. The sample was stored in a cardboard box in the laboratory lead box at room temperature, and measured 117 days after the last bombardment. The sample appeared as clean and bright as when it was stored. The grains measured are not the ones measured previously, for these did not have space for more indentations. Hardness numbers are given in table 5. On the average, the bombarded grains had a hardness of 253. This is 52 greater than the hardness, 201, of the shielded region. The difference between bombarded and unbombarded regions was still present after 117 days.

Table 5

Hardness of Annealed Mo Sheet, H-6

	Grain	Hardness, 117 days after bombardment
Center region (Bombarded)	1	237
	2	259
	3	263
	4	252
Front region (Shielded)	1	195
	2	199
	3	201
Back region (Shielded)	1	205
	2	206
	3	202

H-7 after 13.4μ amp-hr/cm² deuteron bombardment had a bombarded region 83 V.P.N. harder than the same region before irradiation and 67 V.P.N. harder than the shielded region. (See previous report). Standing 7 days did not change the hardness numbers and an additional bombardment of approximately the same amount gave a badly stained sample which could not be cleaned. This sample was heated in dry hydrogen for 1 hr x 1600°F, a temperature slightly below the recrystallization temperature of Mo. (J.H. Kittel, Journal of Metals, p. 196, February 1952 gives data which indicates recrystallization begins near 900°C, 1652°F. This is confirmed by observations made in this laboratory which indicate that recrystallization does take place at 1700°F, for diffraction patterns of cold-rolled Mo sheets heated 24 hr x 1700°F show the appearance of some spots from large crystals which have grown during the heating.) The heat treatment cleaned the sample enough so that grain boundaries were defined clearly and grains which appeared clean could be selected for measurements. The sample was measured 147 days after the last bombardment

with the results given in Table 6. On the average, the bombarded grains had a hardness, 250, 54 greater than the hardness, 196, of the shielded region. A difference between bombarded and unbombarded regions was still present after 147 days. It is to be noted that H-7 was heated 1 hr. x 1600°F after bombardment while H-6 was measured without heat treatment after removal from storage. The close agreement of the hardness numbers for H-6 and H-7 may be fortuitous.

X-ray diffraction patterns were recorded by back reflection from the bombarded and shielded regions of H-6. There is no difference between the patterns which would explain the bombarded region being harder than the shielded region. H-6 was run on the Philips spectrometer. The trace shows a strong Mo line at 1.283 Å, a very strong Mo line at 1.572 Å and an extra weak line. Calculations show that the weak line may be the β line of the very strong Mo line. No impurity pattern was detected.

Table 6

Hardness of Annealed Mo Sheet, H-7

Grain		Hardness 147 days after bombardment and after 1 hr x 1600°F
Center region (Bombarded)	1	250
	2	248
	3	245
	4	255
Front region (Shielded)	1	193
	2	194
Back region (Shielded)	1	194
	2	203

Although the heating of the Mo samples was carried out in supposedly dry hydrogen, difficulty has been encountered in maintaining a clean surface. Samples consistently

came from the furnace with the surface rather dull and gray. This did not affect the hardness measurements of the annealed samples, for the samples were polished and etched after annealing. It may affect the actual hardness, if impurities are added to the grain boundaries. It did prevent the carrying out of the experiments on the heat treatment of the bombarded samples until a clean surface could be obtained. Studies of the nature of the surface layer are being made using X-ray diffraction analysis.

In the October 1, 1952 report, it was stated that a series of bombardments on H-8, H-14 and H-15 had been begun to determine if the staining could be reduced by using short bombardment times, and to study the variation of hardness with irradiation up to $13.5 \mu \text{ amp-hr/cm}^2$. The samples were bombarded with 8.4 to 10 Mev deuterons and were cooled with dry ice and alcohol during bombardment.

H-15 is a cold-rolled Mo sheet cut from 10 mil stock. It was polished and etched and the surface preparation reduced the thickness to 8.5 mil. It was given $3.8 \mu \text{ amp-hr/cm}^2$ irradiation. The sample appeared clean. It was radioactive and was allowed to decay as usual before testing. The hardness numbers are given in table 7 and show that in this cold rolled sample there is no difference between bombarded and shielded regions.

H-8, a Mo sheet, cut from 10 mil stock*, annealed for 20 hr x 2400°F , polished and etched, thickness 7 mil, was given $1.9 \mu \text{ amp-hr/cm}^2$ irradiation. There was no stain evident. The sample was radioactive and was allowed to decay as usual before testing. Hardness numbers are given in table 8. It is evident that the irradiation had little, if any, effect on the hardness.

*H-6, H-7 were cut from 5 mil stock

Table 7

Hardness of Cold rolled Mo Sheet, H-15

	Center Region (Bombarded)	Front Region (Shielded)	Back Region (Shielded)
Before Bombardment	273	275	273
After 3.8 μ amp-hr/cm ²	285	290	289
41 days later	278	280	273

Table 8

Hardness of Annealed Mo Sheet, H-8

	Grain	Hardness before bombardment	Hardness after 1.9 μ amp-hr/cm ²
Center region (bombarded)	1	192	193
	2	187	191
	3	199	210
	4	198	199
Front region (shielded)	1	192	193
	2	199	200
Back region (shielded)	1	190	191
	2	189	191

H-14, discussed previously, a Mo sheet, annealed for 20 hr x 2400°F, polished and etched, thickness 7 mil, was given successive irradiations of 1.9, 1.9 and 3.8 μ amp-hr/cm². After the first 1.9 μ amp-hr/cm² irradiation, the bombarded region was stained somewhat with a very light, non-uniform stain. The sample was not cleaned. The hardness numbers obtained are given in table 9. The non-uniform staining may indicate that the irradiation was not uniform over the surface of the bombarded region. Of the grains originally measured, only grain 3 was stained. This grain did show an increase in hardness of 15, while the other center grains showed increases from 2 to 5, too small to be considered definite changes. With added bombardments, the stain appeared more pronounced and uneven. The sample

Table 9

Hardness of Annealed Mo Sheet, H-14

	Grain	Hardness before bombardment	Hardness after 1.9μ amp-hr/cm ²	Hardness after 3.8μ amp-hr/cm ²	Hardness after 7.6μ amp-hr/cm ²
Center region (bombarded)	1	196	201	202	203
	2	197	200	207	205
	3	189	204	206	211
	4	197	199	205	196
	5			209	212
	6			208	212
Front region (Shielded)	1	183	183	187	187
	2	182	185	189	186
Back region (Shielded)	1	192	193	192	194
	2	191	195	202	202

outside the bombarded region appeared to be stained very lightly and unevenly after the third bombardment. Two stained grains in the center region were added to those measured before and after the last bombardment. The increases in hardness of the center region, and of the shielded regions are very small compared to the changes produced in H-6 and H-7 by 13.5 and 13.4 μ amp-hr/cm², respectively.

The bombardment experiments were terminated by the shutting down of the cyclotron for rebuilding. Samples should be irradiated by other methods to check on surface stains and hardness changes produced by irradiating Mo.

Table 10 summarizes the observation on the stains or surface layers which have been encountered on Mo and such information as has been obtained on their removal and their influence on hardness number. Work is being continued on the effects of surface layers on hardness measurements.

Table 10

Summary of Observations on Stains and Surface Layers

Stain	Produced by:	Color	Microscopic view	Removed by:	Effect on hardness of removal
A	Cyclotron bombardment (when stained) (except H-7)	Brown	Not uniform, grain boundaries visible	Acetone and trichloroethylene	Decrease in hardness, ~6 V.P.N.,
B	Cyclotron bombardment, H-7	Grayish black	Not uniform, grain boundaries visible	Heating 1 hr x 1600°F in dry hydrogen (partially)	Unknown
C	Heating at 1200°F and/or 1600°F (except H-6 and part of H-21)*	Gray	Fairly uniform, grain boundaries visible	Etching	---
D	Heating at 1200°F and 1600°F, center of H-6	Gray	Quite uniform, grain boundaries not visible	Trichloroethylene	---
E	Heating at 1600°F, H-21*	Black	Not uniform, grain boundaries not visible	Methyl alcohol and trichloroethylene	Unknown

*H-21 is a Mo sheet, cut from 10 mil stock, which was heated 20 hr x 2400°F in dry hydrogen, polished and etched. Thickness 8 mil. All heatings were carried out in supposedly dry hydrogen.

Summary

The effects of vibration insulation and variations in load, rate of descent of sample and time of indentation on the hardness number obtained with the Bergsman tester were investigated. As a result of this work, a load of 50 gm, a rate of descent of 1mm/min and a time of indentation of 120 sec were selected for hardness tests of Mo sheets. Using these conditions a variation in hardness number of an annealed Mo sheet of approximately 20 V.P.N. from grain to grain was observed.

To study the variation in hardness number, a series of indentations were made in a single large grain of an annealed Mo sheet, as the sample was rotated around the vertical axis of the indenter. The variation of hardness number with angle of rotation is shown graphically, the hardness varying between a minimum of 185 and a maximum of 205. This experiment was repeated with a large grain in another Mo sheet and a similar variation was observed, showing that the hardness number depends on the orientation of the grain with respect to the axis of the indenter.

The hardness of an irradiated, annealed Mo sheet was measured 117 days after the last irradiation to determine if the hardness difference, 38 V.P.N., observed after irradiation between irradiated and shielded grains was still present. On the average, the bombarded grains had a hardness of 253, 52 greater than the hardness of 201 of the shielded region. Measurements on another Mo sheet, 147 days after the last irradiation, gave a similar difference but these measurements may be influenced by the fact that this sample was stained.

A cold-rolled Mo sheet, thickness 8.5 mil, was given $3.8 \mu \text{ amp-hr/cm}^2$.

irradiation with 8.4 - 10 Mev deuterons. The hardness of the bombarded region was the same within experimental error as the hardness of the shielded region. An annealed Mo sheet, thickness 7 mil, was given 1.9μ amp-hr/cm² deuteron irradiation. This irradiation had little, if any, effect on the hardness. Another annealed Mo sheet, thickness 7 mil, was given successive deuteron irradiations of 1.9, 1.9 and 3.8μ amp-hr/cm². Only one grain showed a definite change in hardness, an increase of 15 V.P.N. after the first 1.9μ amp-hr/cm². The grain whose hardness increased by 15 was stained with a light brown stain. This stain was removed by cleaning with acetone and trichloroethylene. The effect of the cleaning was to decrease the hardness number by approximately 6.

A table is given summarizing the stains or surface layers which have been observed on Mo.

IV. AN X-RAY STUDY OF RADIATION DAMAGE IN SINGLE CRYSTALS

W. P. Binnie and A. M. Liebschutz

Part I. - Introduction

The theory of diffraction of X-rays by a crystal lattice shows that, for a crystal of measurable size, the diffraction conditions must be strictly fulfilled if there is to be any appreciable scattered intensity. In a real crystal, however, a measurable amount of scattering does occur when the interference conditions are not satisfied. Even allowing for Compton scattering, this general scattering of radiation of unchanged wave length is greater than that permitted by the simple theory. This is due to the fact that in an actual crystal the lattice is not as regular as is assumed in the simple theory, and any departure from strict regularity in the arrangement of the scattering particles will tend to weaken the interference maxima, and to increase the radiation scattered in other directions.

The type of irregularity with which we are concerned here is not that due to mosaic structure, in which a single crystal may in effect consist of misorientated blocks, but that due to certain random type irregularities introduced into a lattice which affects the exact positions of the scattering points.

The most obvious cause of such irregular displacements of atoms in a real crystal from their ideal lattice positions is thermal vibration. This effect was treated theoretically as early as 1913 by Debye⁽¹⁾. In the following pages we shall modify the expression for the intensity of x-radiation scattered by an ideal lattice, at rest, to take into account the random displacement of the lattice points, and we shall introduce the connection between this extra general scattering and the elastic

properties of the crystal.

Assume the points to be fixed, when in their ideal positions, by the vectors

$\vec{r}_1, \vec{r}_2, \dots, \vec{r}_m, \vec{r}_n, \dots$. The incident x-ray wave train will be scattered by the

whole lattice, the resultant disturbance being

$$Y = \frac{\Phi_0}{R} e^{i\omega t} \sum_{\text{all lattice points}} e^{-ik\vec{r}_n \cdot \vec{S}} \quad (1)$$

where Φ_0 is the amplitude of the scattered wave at a unit distance from

a single scattering point in the direction of the "reflected" beam, k is the

magnitude of the wave vector $\left(\frac{2\pi}{\lambda}\right)$, $\vec{S}$ is the vector normal to the reflecting

plane of magnitude $2 \sin \theta$. The displacement caused by a wave which is scattered

from a point at the origin of the lattice and reaches a point Q at a time t is

$\Phi_0 e^{i\omega t/R}$, where Q is at a distance R from the crystal large in comparison

with the linear dimensions of the crystal, so that all lattice points are at a constant

distance R from Q. The scattered intensity due to the undisturbed lattice is therefore

$$J_0 = Y^* Y = \frac{|\Phi_0|^2}{R^2} \sum_{n=1}^N \sum_{m=1}^N e^{-ik(\vec{r}_n - \vec{r}_m) \cdot \vec{S}} \quad (2)$$

where N is the total number of lattice points. For a parallelepiped this

expression reduces to the usual Laue expression

$$J = \frac{|\Phi_0|^2}{R^2} \prod_{i=1}^3 \frac{\sin^2 N_i \psi_i}{\sin^2 \psi_i}, \quad (\psi_i = \frac{1}{2} k \vec{S} \cdot \vec{a}_i) \quad (3)$$

($\vec{a}_i$ being the direct lattice vectors). J has appreciable values only for

$$\vec{S} \cdot \vec{a}_i = h_i \lambda \quad i = 1, 2, 3 \quad (4)$$

which are the three Laue equations.

Considering small vector displacements $\vec{u}_1, \dots, \vec{u}_m, \vec{u}_n, \dots$ of the lattice points

from their ideal positions, we obtain the scattered intensity of the disturbed lattice as

$$J = \frac{|\Phi_0|^2}{R^2} \sum_{n=1}^N \sum_{m=1}^N e^{-ik(\vec{r}_n - \vec{r}_m) \cdot \vec{S}} e^{-ik(\vec{u}_n - \vec{u}_m) \cdot \vec{S}} \quad (5)*$$

* In equation (5) we consider the oscillation frequency of the lattice points to be small compared with that of the incident radiation, so that any configuration will exist for a time long compared with the period of the wave, an assumption which is fully justified in the case of thermal vibration.

Since the lattice points are oscillating due to the thermal waves in the lattice, we must take the mean of (5), which represents the intensity of an instantaneous configuration of points, over a period which is long compared with the vibration period of an individual point.

Only the second factor under the double sum varies with time; therefore, we must compute the mean of this factor which involves the displacements of atoms n and m . Define

$$p_{nm} = k(\vec{u}_n - \vec{u}_m) \cdot \vec{S} \quad (6) \text{ Ott (2)}$$

has shown
$$\overline{e^{-i p_{nm}}} = e^{-\frac{1}{2} \overline{p_{nm}^2}} \quad (7) \text{ to a good approximation.}$$

Therefore

$$\overline{J} = \frac{|\phi_0|^2}{R^2} \sum_{n=1}^N \sum_{m=1}^N e^{-i k(\vec{r}_n - \vec{r}_m) \cdot \vec{S}} e^{-\frac{1}{2} \overline{p_{nm}^2}} \quad (8)$$

Now (6) can be written

$$p_{nm} = \frac{2\pi}{\lambda} (2 \sin \theta) (u_{ns} - u_{ms}) \quad (9)$$

where u_{ns} and u_{ms} are the components of the displacement of two lattice points n and m parallel to the direction of the vector $\vec{S}$.

Debye made the assumption, in his first paper that all oscillations of the different lattice points were independent, and that all had the same mean energy.

If this were true

$$\overline{u_{ns} u_{ms}} = 0; \quad \overline{u_{ns}^2} = \overline{u_{ms}^2} = \overline{u_s^2} \quad (10)$$

where $\overline{u_s^2}$ is the mean-square displacement of any lattice point from its mean position in a direction which is parallel to the vector $\vec{S}$. In equation (8) the double

sum contains N^2 terms; in N of these terms $n = m$ and for each of these the exponential factor is unity. For all terms involving a pair of lattice points

$\frac{1}{2} \overline{P_{nm}^2}$ is the same, is equal to $2M$ if

$$M = 8\pi^2 u_s^2 \left(\frac{\sin \theta}{\lambda} \right)^2 \quad (11)$$

Consequently (8) may be written

$$\overline{J} = \frac{|\phi_0|^2}{R^2} N(1 - e^{-2M}) + J_0 e^{-2M} \quad (12)$$

where J_0 is defined in equation (2).

The second term of (12) represents the Bragg spectra and since J_0 is proportional to $|\phi_0|^2$, the effect of temperature vibration on the interference maxima may be taken into account by considering the lattice at rest with a new scattering power $\phi = \phi_0 e^{-2M}$. Therefore these spectra are undiminished in sharpness with respect to the spectra obtained when the lattice is at rest, because the second term has appreciable values only when the three Laue equations (4) are satisfied, but their intensities are all reduced by the Debye factor e^{-2M} .

The first term, however, has no sharp maxima; it contains two factors which depend on the angle of scattering; namely $|\phi_0|^2$, which decreases with increasing θ , and $1 - e^{-2M}$ which rises steadily from zero for zero scattering angle as e^{-2M} decreases with increasing θ . The product of these two factors corresponds to a very broad maximum of general scattering at moderate angles. The intensity distribution in the reciprocal lattice representing the scattering is spherically symmetrical, about the origin.

The theoretical work of Faxen⁽³⁾ in 1918 and in 1923 and the later work in 1923 through 1925 of Wallen⁽⁴⁾, and the experimental work of Laval⁽⁵⁾, Lonsdale and co-workers⁽⁶⁾ and Zacharissen and co-workers⁽⁷⁾ showed that the treatment

of Debye was too simple, and was not in agreement with the experimental facts. The more accurate treatment, which we shall deal with now, treats the lattice points as coupled oscillators. This treatment gives the same result as given above for the interference maxima, but the term giving the general scattering is modified and shows weak maxima coinciding in position with the interference maxima, but far more diffuse.

According to the more accurate treatment (8) becomes

$$\overline{I\left(\frac{\vec{s}}{\lambda}\right)} = |f_0|^2 e^{-2M} \overline{I_0\left(\frac{\vec{s}}{\lambda}\right)} + \frac{1}{2} |f_0|^2 e^{-2M} \sum_{\phi_j} G_{\phi_j} \left\{ \overline{I_0\left(\frac{\vec{s}}{\lambda} - \vec{q}\right)} + \overline{I_0\left(\frac{\vec{s}}{\lambda} + \vec{q}\right)} \right\} \quad (13)$$

where

$$G_{\phi_j} = \frac{kT}{mN} \cdot \frac{1}{\omega_{\phi_j}^2} (k\vec{s} \cdot \ell_{\phi_j})^2 \quad (14)$$

m being the mass of a single lattice point, ℓ_{ϕ_j} is a unit vector in one of the three independent directions of vibration of the lattice associated with the lattice wave ϕ , ω_{ϕ_j} is the circular frequency using normal coordinates⁽⁹⁾ of the lattice vibrations, k the Boltzman constant, $\vec{q}$ is a vector in the direction of the wave normal of the lattice wave whose magnitude is $\frac{1}{\lambda}$, and $\overline{I} = \frac{\overline{J_v} |f_0|^2}{R^2}$

Equation (13) can be most easily understood if we use the reciprocal lattice.

To each point of the reciprocal lattice we can ascribe a scattering function

$I\left(\frac{\vec{s}}{\lambda}\right)$, the value of which corresponding to a point at the end of the vector $\frac{\vec{s}}{\lambda}$ (drawn from the reciprocal lattice origin), gives the intensity scattered by the crystal when the incident and reflected directions are related $\vec{s} - \vec{s}_0 = \vec{S}$; where $\vec{s}_0$ and $\vec{s}$ are the unit vectors defining the directions of the reflected incident beams, respectively. Taking $|f_0|^2 = 1$ we can express the intensity in terms of that scattered by a free electron under the same conditions. The

interference function has maxima at the reciprocal lattice points themselves, i.e. when the vector $\frac{\vec{s}}{\lambda}$ is a vector of the reciprocal lattice. Since a real crystal contains a large number of cells, the intensity of the distribution is negligible except in the neighborhood of these points. This distribution is modified when the lattice is subject to thermal vibrations.

To the first term of equation (13), there corresponds a distribution which is that of the interference function I_0 multiplied by e^{-2M} , which is a function of $\frac{\vec{s}}{\lambda}$. The farther the reciprocal lattice point is from the origin (the higher the order of the spectrum), the more the intensity associated with it is diminished; but there is no change in sharpness of the maxima due to the first term. This is the ordinary Debye effect mentioned above.

There also is a distribution in reciprocal lattice space corresponding to the second term of (13). This term gives the diffuse scattering, and is everywhere zero when the lattice is at rest. We see that the second term is made up of independent contributions from each state of polarization j of each lattice wave $\vec{\phi}_j$. If we consider only a single wave $\vec{\phi}$ with wave vector $\vec{q}$, and reciprocal wave length $|\vec{q}|$, in a state of polarization j , we see that the second term gives two interference functions $I_0(\frac{\vec{s}}{\lambda} \pm \vec{q})$ which are of the same form as $I(\frac{\vec{s}}{\lambda})$. Therefore these functions will also give rise to two maxima in the distribution associated with this wave. These maxima are not at the reciprocal lattice points, but on either side of them at a distance $\pm \vec{q}$ i.e. corresponding to the condition that $I_0(\frac{\vec{s}}{\lambda} \pm \vec{q})$ has a maximum only when $\frac{\vec{s}}{\lambda} \pm \vec{q}$ is a vector from the origin to a reciprocal lattice point.

Each of the three independent states of polarization, j , of the wave gives an independent pair of maxima at the same positions, and the total value of the scattering function corresponding to them is the sum of the values corresponding to the individual distribution.

Therefore the thermal motion is equivalent to $3N$ lattice waves to each of which corresponds a pair of maxima in the scattering function. The total effect then of all these waves is a continuous distribution of intensity about each reciprocal lattice point. The shorter the lattice wave, the greater is the distance of the corresponding maxima from any given reciprocal lattice point, and since the shortest acoustical waves in a crystal lattice have wave lengths of the order of twice the lattice spacing it can be seen that this intensity distribution will be much more diffuse than that corresponding to the ordinary lattice spectra.

Consequently, around each lattice point is a sharp maximum corresponding to the Bragg scattering. These intensity maxima are reduced by thermal motion, but are not made less sharp. These Bragg maxima are the nuclei of much weaker and more diffuse distributions: the diffuse scattering. These diffuse regions also have their maximum at the reciprocal lattice points, but the distribution (shape of the diffuse cloud) is not the same about each reciprocal lattice point, and depends both on the order of the spectrum and especially on the elastic behavior of the crystal.

The second term of Equation (13) can be conveniently written in the form

$$I_z\left(\frac{\vec{s}}{\lambda}\right) = |f_0|^2 e^{-2M} \sigma \quad (15)$$

$$\sigma = \frac{1}{2} \sum_{\phi_j} G_{\phi_j} \left\{ I_0\left(\frac{\vec{s}}{\lambda} + \vec{q}\right) + I_0\left(\frac{\vec{s}}{\lambda} - \vec{q}\right) \right\} \quad (16)$$

James⁽⁸⁾ shows that

$$\sigma = \frac{RTN}{m} \frac{R^2}{r^2} \sum_j \frac{\cos^2 \alpha_{sj}}{v_{\phi_j}^2} \quad (17)$$

where R is the distance

of the point (in reciprocal lattice space) considered from the reciprocal lattice origin, r its distance from the relevant reciprocal lattice point, α_{sj} is the angle between the vector $\vec{S}$ and the direction of vibration of the component j, and v_{ϕ_j} is the velocity of the lattice wave $\vec{\phi}_j$.

Jahn⁽¹⁰⁾ has shown how to calculate the appropriate form of the surfaces surrounding each reciprocal lattice point over which σ has a constant value. These are the surfaces of "equal diffusion" i.e. "isodiffusion" surfaces.

Following Jahn's method let L, M, N be the direction cosines of the vector $\vec{r}_m^*$ from the origin to the reciprocal lattice point m(h,k,l), l, m, n those of the wave vector g, and A_j, B_j, C_j those of the direction of vibration j of the lattice wave all referred to the axes of the reciprocal lattice. Since $\frac{\vec{S}}{\lambda} = \vec{r}_m^* + \vec{g}$, and using the approximation that $|\vec{r}_m^*| \gg |\vec{g}|$ we get for a cubic crystal for the reciprocal lattice point m(h,k,l)

$$\sigma = \frac{RTN}{m} \frac{(a^*)^2}{|\vec{g}|^2} \sum_j \frac{(LA_j + MB_j + NC_j)^2}{v_{\phi_j}^2} \quad (18)$$

If r is the distance from the reciprocal lattice point m(h,k,l) of a point on the surface of equal diffusion, we may write since $r = |\vec{g}|$

$$r^2 \sim \sum_j \frac{(LA_j + MB_j + NC_j)^2}{v_{\phi_j}^2} \quad (19)$$

The three velocities of v_{ϕ_j} , corresponding to the three independent components of the elastic wave $\vec{g}$ (lmn) in a cubic crystal of density ρ are given in terms of the three elastic constants c_{11}, c_{12}, c_{44} by the three solutions of the simultaneous equations

$$\begin{aligned}
\{c_{11}l^2 + c_{44}(m^2 + n^2) - \rho v_j^2\} A_j + (c_{12} + c_{44})(lm B_j + ln C_j) &= 0 \\
\{c_{11}m^2 + c_{44}(n^2 + l^2) - \rho v_j^2\} B_j + (c_{12} + c_{44})(mn C_j + ml A_j) &= 0 \\
\{c_{11}n^2 + c_{44}(l^2 + m^2) - \rho v_j^2\} C_j + (c_{12} + c_{44})(nl A_j + mn B_j) &= 0 \quad (20)*
\end{aligned}$$

Equation (19) then becomes

$$\begin{aligned}
\kappa^2 \sim L^2(A^{-1})_{11} + M^2(A^{-1})_{22} + N^2(A^{-1})_{33} \\
+ 2LM(A^{-1})_{12} + 2LN(A^{-1})_{13} + 2MN(A^{-1})_{23}
\end{aligned} \quad (21)$$

where $(A^{-1})_{ij}$ is an element of the inverse matrix to (A), the matrix (A) being given by

$$(A) = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{12} & A_{22} & A_{23} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \quad (22)$$

$$\begin{aligned}
A_{11} &= C_{11} l^2 + C_{44} (m^2 + n^2) \\
A_{22} &= C_{11} m^2 + C_{44} (l^2 + n^2) \\
A_{33} &= C_{11} n^2 + C_{44} (l^2 + m^2) \\
A_{12} &= (C_{12} + C_{44}) lm \\
A_{13} &= (C_{12} + C_{44}) ln \\
A_{23} &= (C_{12} + C_{44}) mn
\end{aligned} \quad (23)$$

*These equations are derived using the equations of motion for small displacements of an elastic body by Love⁽¹¹⁾, p. 85, and considering the elastic wave motion described by the equations:

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} A_j \\ B_j \\ C_j \end{pmatrix} e^{i[lx + my + nz - v_j t]}$$

We shall now change to the notation of Ramachandran and Wooster⁽¹²⁾

which will be used in the rest of this report and in subsequent reports.

Ramachandran and Wooster define the ratio of the "reflected" diffuse intensity per unit solid angle per unit cell in a given direction to that scattered by a free electron as the diffuse structure intensity, D_1 ,

$$\text{where } D_1 = \frac{A T}{\tau} \cdot \frac{|F_T|^2 R^2}{r^2} K[ABC] h k l \quad (24)$$

$$K[ABC] h k l = \sum_{j=1}^3 \frac{\omega_j^2 \alpha_j}{\rho v_{\phi j}^2} \quad (25)$$

F_T is the structure amplitude at temperature T , τ is the volume of the unit cell,

A, B, C are the direction cosines of $\vec{g}$ with respect to the reciprocal axes, h, k, l are the Miller indices of the associated relp (reciprocal lattice point).

Equation (24) is of the same form as equation (15), the latter now being defined as the diffuse structure intensity for N unit cells, each containing one lattice point.

Therefore $|f_0|^2 e^{-2M}$, the square of the temperature corrected atomic form factor, is replaced by $|F_T|^2$, the square of the unit cell form factor.

If Q is a relp then along any rekha (direction through a reciprocal lattice point) the intensity varies as $1/r^2$. On the other hand, the intensities at points on a circle at a given distance from Q will vary as the values of the constants $K[A, B, C]_{h, k, l}$ for these rekhas. Consequently if we consider two points at the same distance along two rekhas $[A_1, B_1, C_1]$ and $[A_2, B_2, C_2]$ associated with the same relp h, k, l then

$$\frac{D_1[A, B, C]_{h k l}}{D_1[A_2, B_2, C_2]_{h k l}} = \frac{K[A, B, C]_{h k l}}{K[A_2, B_2, C_2]_{h k l}} \equiv K \left[\frac{A, B, C}{A_2, B_2, C_2} \right]_{h k l} \quad (26)$$

Evidently, the quantity $K \left[\frac{A, B, C}{A_2, B_2, C_2} \right]_{h k l}$ is a function only of the indices

h k l, of the direction cosines A_1, B_1, C_1 ; A_2, B_2, C_2 ; of the two rekhas, and of the elastic constants, all other quantities in (24) dropping out completely. We may describe this function as the "K ratio". Experimentally this quantity may be determined by measuring the slopes of the D_1 vs $1/r^2$ graphs along two rekhas for a given relp and finding their ratio.

For cubic crystals there are two independent ratios of elastic constants, which we may define

$$\psi_1 = \frac{C_{12}}{C_{11}}, \quad \psi_2 = \frac{C_{44}}{C_{11}} \quad (27)$$

In principle a measurement of a K ratio for two different relps is sufficient to determine ψ_1 and ψ_2 ; but in practice it is advisable to check the observations by additional measurements.

Part II.

As was mentioned in the previous report, the Supper Weissenberg with a Geiger counter attachment is being used to determine the elastic constants of silicon by measurement of the diffuse scattering intensity. To check the sensitivity and response of the Geiger counter Weissenberg, the diffuse scattering intensity of an oxalic acid dihydrate crystal was examined and compared with Lonsdale's published data (Acta Cryst. 1, 126 (1948).)

For this purpose the crystal was oriented about the b-axis and a Weissenberg moving film of the (hol) zone was taken and indexed. Using filtered radiation the diffuse scattering from the (202) reflection was analyzed. The diffuse intensity at a given angular increment from the Bragg reflection was of the same order as that measured by Lonsdale, and this scattering was detected over a greater angular range than that measured by Lonsdale.

In order to accurately measure diffuse intensities it is necessary to use a strictly monochromatic X-ray beam. The available monochromating crystals were NaCl and CaF_2 , the former giving a theoretical ratio of first to second order of 20:1 while the latter gives a ratio of 600:1. Thus CaF_2 should furnish a beam of higher purity than NaCl and permit operation at optimum voltages. To check the theoretical values a series of experiments were carried out to measure the ratio of first to second order and of first to third order of these two crystals for various X-ray tube voltages using a copper target X-ray tube; in the case of the CaF_2 crystal experiments were also run using molybdenum $\text{K}\alpha$ radiation.

If the logarithm of the counting rate is plotted against the thickness of the absorber, the percentage of second and third order wave lengths to first order are determined by extrapolating back to the intensity axis. Below are listed the experimentally determined values.

Monochromating Crystal	% 2nd order 30 KVP, $\text{CuK}\alpha$	% 2nd order 35 KVP $\text{CuK}\alpha$	% 2nd order 30 KVP Mo $\text{K}\alpha$	% 2nd order 35 KVP Mo $\text{K}\alpha$
NaCl	0.4% ⁽¹³⁾	4.35	---	---
CaF_2	Not detectable	Not detectable	Not detectable	Not detectable
Monochromating Crystal	% 3rd order 30 KVP $\text{CuK}\alpha$	% 3rd order 35 KVP $\text{CuK}\alpha$	% 3rd order 30 KVP Mo $\text{K}\alpha$	% 3rd order 40 KVP Mo $\text{K}\alpha$
NaCl	---	---	---	---
CaF_2	0.17%	0.48%	Not produced	Not produced

To establish that the change in slope of the CaF_2 curve was really due to third order rather than to second order, the mass absorption coefficient of the aluminum

foils used as absorbers was calculated. The value $\mu_m = 2.03 \text{ cm}^2/\text{gm}$ obtained from the above curves is in agreement with that calculated from the value given in the "Handbook of Chemistry and Physics": $\mu_m = 1.90 \text{ cm}^2/\text{gm}$ for $\lambda = 0.497\text{\AA}$; therefore $\mu_m = \left(\frac{0.514}{0.497}\right)^3 \times 1.90 = 2.11 \text{ cm}^2/\text{gm}$ for $\lambda = 0.514\text{\AA}$, which is the λ of third order of copper K_α . (Since μ_m varies as λ^3 on either side of an absorption discontinuity.)

Thus the experimental data shows that CaF_2 is the better crystal to use in order to eliminate harmonics and still work at a reasonable tube voltage above the excitation voltage.

Consequently, a monochromator of the Fankuchen type was designed to be used with a CaF_2 crystal and built in the instrument shop.

Plateau curves were run using a Co^{60} source to determine the value of the operating voltage of the counter; the dead time was measured with a Tektronic oscilloscope having a triggered, continuously variable, calibrated sweep. The values obtained were $145\mu\text{s}$ and $165\mu\text{s}$, respectively, for two different counters and scaling units. When precise intensity measurements with a Geiger counter are made it is necessary to know the range in which the Geiger counter is linear. An intensity calibration curve was run using the above CaF_2 monochromator and operating the copper target X-ray tube at 35 KV. According to Figure 1, the response of the Philips Argon filled counter is linear in the range from zero to 650 c/sec. A calculation of the linear absorption coefficient from the data gives $\mu_1 = 435 \text{ cm}^{-1}$ for the nickel absorbers used, while the value given in "X-Rays in Theory and Practice" by Compton and Allison is $\mu_1 = 427 \text{ cm}^{-1}$. Taking into account a stated one percent error in the measurements of Allison and a possible

Figure 1

error in the density used, the error of 1.8% is well within the expected accuracy.

A silicon single crystal, Dupont Hyperpure, completely bathed in the X-ray beam was oriented so the the $[111]$ axis (needle axis) was perpendicular to the X-ray beam. Moving film photographs were taken for the zero and first layer lines using filtered copper K_{α} radiation. A fiducial mark was obtained by stopping the translation at some suitable spindle dial reading. As seen in Figure 2 this gives a layer line corresponding to the zero layer line of an ordinary rotation photograph. By the measurement of the distance from the line to a reflection, the spindle dial reading for this spot can be determined. From measurement of rotation and moving film photographs a_0 was determined equal to $5.430\text{\AA}$ and the diameter of the camera was calculated to be 56.658 millimeters which makes 1mm equivalent to 2.023° . From these data the Bragg angle was calculated; knowing 2θ Bragg and the spindle angle, the Geiger counter can be set so that the Bragg reflection will be recorded by the counter.

The CaF_2 monochromator was placed on the spot focus of the X-ray tube window and the monochromator and Weissenberg apparatus were aligned to give a uniform beam of maximum intensity passing through the collimator.

An important factor in accurate intensity measurement is that the beam should be of uniform cross section. As shown in Figure 3a the best possible alignment using a fluorescent screen gave a beam with a hollow center. Thus it is impossible to see how a really uniform beam profile can be obtained by the standard methods of adjustment.

Figure 2 Weissenberg photograph of single crystal silicon.

Figure 3. BEAM PROFILES

Using the method outlined by H. T. Evans, Jr. ⁽¹⁴⁾ a uniform profile was obtained. This was accomplished by placing a fine pinhole in front of the Geiger counter tube; a low intensity beam (from the monochromator) is scanned vertically and horizontally in turn, stepwise, by manual adjustment of the Geiger counter tube arm screw and the Weissenberg equi-inclination adjustment. By repeated adjustment of the leveling screws and repeated scanning a uniform beam profile as shown in Figures 3b and 3c is obtained. From these profiles the zero positions on the vertical and horizontal scales of the Geiger counter can be determined.

To remove all eccentricity from the sample, further scanning runs were made with adjustments of the translation screws on the crystal goniometer until equivalent beam profiles were obtained at the 0° , 90° , 180° , 270° positions as shown in Figure 4.

Determination of the elastic constants necessitates the measurement of X-rays diffusely reflected along two rekhas for at least two relps. Thus the settings on the spindle dial and for the Geiger counter corresponding to these movements must be determined. Calculations show that suitable rekhas for the $(2\bar{2}0)$ reflection are the rel-vector (vector from the origin of the reciprocal lattice through the relp), $[\bar{1}\bar{1}0]$, and the rekha $[10\bar{1}]$.

Figure (5) shows the crystal geometry for the $[\bar{1}\bar{1}0]$ direction while figure (6) illustrates the crystal geometry for the $[10\bar{1}]$.

In Figure (5) O is the origin of the reciprocal lattice, C the center of a circle of radius one reciprocal lattice unit. OA is the direction of the rel-vector while CX is the direction of the diffracted beam.

To measure the diffuse intensity along the rel-vector at point A we rotate the

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Figure 4. ECCENTRICITY BEAM PROFILES

$$\alpha_A = 1/2 \beta_A$$

$$\alpha_B = 1/2 \beta_B$$

$$XB = d_{2\bar{2}0}^* - 2 \sin(\Theta_{2\bar{2}0} - \alpha_B)$$

where $d^* = \frac{\bar{\Lambda}}{d_{2\bar{2}0}}$

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reciprocal lattice about $[111]$ to bring A to A^1 on the sphere of reflection. This corresponds to a rotation of the spindle axis by α . Then rotate the Geiger counter by β from CX where $\beta = 2\alpha$ since the diffracted beam is now in the direction CA^1 . To record at point B on the other side of the relp ($2\bar{2}0$) rotate both the crystal and the Geiger counter in the opposite direction by α , and 2α respectively. The distances XA and XB from the relp are given in Figure (5) in terms of $\theta, \alpha, \lambda, d$.

The geometry for the $[10\bar{1}]$ direction is slightly more complicated. The angle between the $[1\bar{1}0]$ and $[10\bar{1}]$ is 60° . To bring the diffuse spot A into the sphere of reflection rotate the crystal by α about O. This moves point X (the relp) to point X^1 . From Figure (6) it is seen that this requires a movement of the Geiger counter by 2β where 2β is given by eqn. (1) and A^1X^1 is given by eqn. (2), Figure 6.

The basic expression for finding the elastic constants is known as the "K" ratio which is a function of the elastic constants, the direction cosines of the rekha, and the Miller indices of the relp, as developed on Page 50, Part I. An example of a theoretical K ratio is given for ($2\bar{2}0$).

$$K \left[\frac{1\bar{1}0}{10\bar{1}} \right]_{2\bar{2}0} = \frac{4X_2(1-X_1)}{1-X_1^2 + 2X_2^2 + 4X_2 - 2X_1X_2}$$

$$\text{where } X_1 = \frac{C_{12}}{C_{11}}$$

$$X_2 = \frac{C_{44}}{C_{11}}$$

The first series of measurements made for the ($2\bar{2}0$) relp along the rel-vector showed that the accuracy of resetting the spindle angle and the counter angle was not sufficient to give reproducible readings. (This high degree of accuracy was not

necessary in the case of filtered radiation, since due to the higher intensity in the former case points along a rekha could be taken farther apart.) Therefore a graduated dial was affixed to the top of the worm which moved the spindle giving a resetting accuracy of $0.5'$ of arc, and a dial gauge was affixed to the Geiger counter adjustment so that an adjustment of $0.25'$ of arc could be obtained.

It was also found necessary to use a monitor to continuously record the intensity of the main beam reflected from the (531) plane of a silicon powder sample since the Philips stabilizer did keep the beam intensity constant to only within 3%.

With these necessary improvements intensity measurements were made along the rel-vector of the ($\bar{2}20$) reflection and a linear relationship between the diffuse intensity and $1/\lambda^2$ was obtained, as should be the case according to Jahn's formula.

According to Ramachandran and Wooster⁽¹²⁾ corrections must be applied for divergence of the incident and reflected beams, for Compton Scattering, for second order diffuse scattering, for white radiation, for the mosaic character of the crystal, for absorption, and for polarization. These corrections are being investigated theoretically, and future experimental data will indicate which of these corrections are important in our case. Therefore a discussion of these corrections will be left to further reports.

Part III.

The preliminary photographic survey of diffuse scattering from germanium and silicon single crystals before and after bombardment is now complete. The data from this study was examined in order to check the observed diffuse domains (as defined on page 47, Part I) with those calculated from the elastic constants and secondly to detect any changes in the diffuse domains recorded before and after

bombardment.

The shapes of the observed diffuse domains about relps were deduced from the shapes and intensities of the diffuse reflections for various crystal orientations. The shapes of the calculated diffuse domains were obtained from Jahn's formula⁽¹⁰⁾ which gives the relative value of the diffuse intensity at a point close to a relp and in a selected direction. This intensity is proportional to the mean square amplitude of vibration, $\overline{\xi}^2$, in the same direction.⁽¹⁷⁾

Therefore Jahn's expression gives not only the intensity of diffuse reflecting power surrounding a relp but also the spatial distribution of mean square amplitudes, $\overline{\xi}^2$. In order to give these values significance from one crystal to another, the individual wave amplitudes have been expressed in terms of the mean square amplitude of vibration, $\overline{u_s}^2$ (as defined on page 43, Part I) by means of the equation $\sum_n \overline{\xi}^2 = n \cdot \overline{u_s}^2$,⁽¹⁷⁾ where n is the number of wave directions along which the diffuse intensity or the mean square amplitude of vibration, $\overline{\xi}^2$, has been calculated. The number of directions considered about each relp for germanium and silicon is 26 and consists of all types of $[100]$, $[110]$, $[111]$ directions. Therefore isodiffusion curves (that is, curves of equal scattering power) have been drawn in a number of planes containing several of these directions and passing through the relps. These planes are called diffuse sections and the sums of the diffuse sections are the diffuse domains around the relps. A section passing through a relp and normal to a direction may be called the equatorial section of that direction.

Germanium: 3x3x0.2 mm. with (110) approximately parallel to the largest cross-section; cut from ingot grown by Miss Reth, Physics Department, Purdue University.

A) To compare calculated and observed diffuse domains.

For this purpose a thorough study of two reciprocal lattice points, $(2\bar{2}0)$ and (400) , was made by recording the diffuse scattering when these planes were removed from the Bragg position by small angular increments. This displacement was necessarily limited to a rotation about the $[001]$ axis, as already noted in August Report 1952, Page 2.⁽¹⁶⁾

$(2\bar{2}0)$ Reciprocal Lattice Point. Calculation using the elastic constants of Bond et al,⁽¹⁸⁾ shows that the diffuse domain is an oblate solid of revolution, extended in the $[110]$ direction and compressed in the $[\bar{1}\bar{1}0]$ direction, giving axial ratios of $[110] : [001] : [\bar{1}\bar{1}0] = 0.188 : 0.146 : 0.095$, expressed in terms of the root mean square amplitude of atomic vibration, $\sqrt{\langle u^2 \rangle} = 0.145\text{\AA}$,⁽¹⁷⁾ Figures 7 and 8.

Sections of the calculated diffuse domain were drawn on a scale that allowed ready comparison with the experimental ones. Also these sections, Figure 9, were made at positions corresponding to the different orientations of the $(2\bar{2}0)$ plane with respect to the X-ray beam. This was done by assuming an arbitrary angular range beyond which no diffuse intensity is recorded within a reasonable exposure (45 kilovolts peak; 30 milliamperes; 48 hours) and the limits of these film records were also made the limits of the weakest iso-diffusion curve drawn. This has no absolute significance, but permits the scale of the vibration amplitudes to be related to that of the angular rotation, and allows comparisons to be made between different reciprocal lattice points of the same lattice. The total angular range was $2\frac{1}{2}^\circ$; $1\frac{1}{4}^\circ$ on either side of the Bragg position.

The sections calculated in this manner can be conveniently described by the ratio of their axes in the $[001]$ and $[\bar{1}\bar{1}0]$ directions; by making an allowance for flat

DIFFUSE DOMAIN OF $(2\bar{2}0)$ OF GERMANIUM

a) $[00]$ Equatorial Section.

Films taken at $1/2^\circ$ intervals on rotating crystal about $[001]$.
Same as moving X-ray beam by $1/2^\circ$ intervals in $a^* b^*$ plane.
Scale $1/2^\circ \equiv 10^\circ$ in order to cover diffuse domain completely.

Figure 7

DIFFUSE DOMAIN OF (220) OF GERMANIUM

b) $[\bar{1}\bar{1}0]$ Equatorial Section

c) $[110]$ Equatorial Section

Figure 8

DIFFUSE DOMAIN OF $(2\bar{2}0)$ OF GERMANIUM

Figure 9

film distortion the calculated and observed sections show qualitative agreement.

Displacement From Bragg Position	Ratio $\frac{[001]}{[1\bar{1}0]}$ of Calculated Section Corrected For Flat Film	Shape and Ratio of Observed Section on Film
$\theta_B + 1\frac{1}{4}^\circ$	1.2	~ Circular
$\theta_B + 3/4^\circ$	1.3	Elliptical: > 1
$\theta_B + 1/4^\circ$	1.3	Elliptical: > 1
$\theta_B - 1/4^\circ$	1.3	Elliptical: > 1
$\theta_B - 3/4^\circ$	1.2	~ Circular
$\theta_B - 1\frac{1}{4}^\circ$	0.9	Elliptical: < 1

(400) Reciprocal Lattice Point. Calculation shows that the diffuse domain is an oblate sphere, compressed in the $[100]$ direction to give axial ratios of $[100] : [010] : [001] = 0.105 : 0.146 : 0.146$, again expressed in terms of the root mean square amplitude of atomic vibration. The domain therefore has a circular section parallel to (100) plane, Figures 10 and 11.

The sections, Figure 12, were drawn to the very same scale as used in the $(2\bar{2}0)$ study. The total angular range in this case was 2° ; 1° on either side of the Bragg position. The films at the limits of the angular range did not record any diffuse intensity for the maximum exposure because at this displacement from the Bragg position the sphere of reflection no longer cuts the diffuse domain, as clearly shown in the drawn sections, Figure 10. This confirms that the root mean square amplitude in direction $[110]$ of $(2\bar{2}0)$ is at least 25% greater than that in direction $[010]$ of (400). Calculated values are 0.188 Å and 0.146 Å, respectively.

DIFFUSE DOMAIN OF (400) OF GERMANIUM

a) $[001]$ Equatorial Section.

Films taken at $1/2^\circ$ intervals, crystal rotating about $[001]$.
 This is same as moving X-ray beam by $1/2^\circ$ intervals in $a^* b^*$ plane. $1/2^\circ \cong 10^\circ$.

Figure 10.

DIFFUSE DOMAIN OF (400) OF GERMANIUM

b) $[0\bar{1}0]$ Equatorial Section

c) $[100]$ Equatorial Section

Figure 11

DIFFUSE DOMAIN OF (400) OF GERMANIUM

d) Sections of (400) Diffuse Domains

Figure 12

Describing the sections in terms of the axial ratio $[001]/[100]$, comparison between the calculated and observed sections can be made.

Displacement From Bragg Position	Calculated Ratio $\frac{[001]}{[100]}$ Corrected for Flat Film	Observed Section on Film
$\theta_B + 1^\circ$	No Section	Nothing
$\theta_B + 1/2^\circ$	1	Circular
θ_B	1.1	~ Circular
$\theta_B - 1/2^\circ$	1	Circular
$\theta_B - 1^\circ$	No Section	Nothing

Hence qualitative agreement exists between the diffuse sections calculated from the elastic constants and those recorded on film.

B) To compare observed diffuse sections before and after bombardment.
(9 Mev. deuterons for 5 micro-ampere hours at -25°C).

Only a qualitative comparison can be made with regard to the shapes of the diffuse sections, but a somewhat more quantitative one can be made with respect to the Bragg position before and after bombardment. Films were taken at identical angular readings before and after bombardment, the tube voltages and exposure times also being maintained.

($2\bar{2}0$) Reciprocal Lattice Point. After bombardment the Bragg position was found to have moved by $1/4 - 1/2^\circ$, this change corresponding to an increase in the parameter of at least 1 part in 100. This increase is so large that it was immediately suspected that the orientation of the crystal was not the same as before bombardment. Only this way one can understand the fact that the horizontal plane of

symmetry which should persist throughout the film record was not recorded.

(400) Reciprocal Lattice Point. A similar change in the Bragg position was found with removal of the horizontal plane of symmetry.

To check for a change in the parameter after bombardment a single-crystal back-reflection powder film was made using aluminum as a standard. The measured unit cell edge was $5.657 \pm .003$ Å, as compared with an unbombarded crystal's value of $5.656 \pm .001$ Å. No broadening of the α_1 and α_2 rings in the bombarded crystal's pattern could be observed.

Since the orientation of the crystal had changed on replacing it on the arcs after bombardment, no comparison can be made of the shapes of the diffuse sections.

Silicon: $5 \times 4 \times 0.3$ mm.* with (110) approximately parallel to the largest cross-section. Silicon and germanium are elastically anisotropic in the same sense, that is, $C_{11} - C_{12} < 2C_{44}$. The diffuse domains of silicon, calculated from the elastic constants⁽¹⁹⁾ have been brought to the same relative scale as the germanium ones by means of the mean square amplitude of atomic vibration in the silicon lattice. Their shapes are the same although the extent of the silicon domains is approximately one half of those of germanium. In spite of this the silicon diffuse sections are more readily recorded because of its low absorption for MoK α radiation. The use of CuK α radiation would probably give a truer record of the relative diffuse intensity of silicon and germanium.

A) To compare calculated and observed diffuse domains. The planes ($\bar{2}20$) and (400) were again examined in detail in the usual manner.

($\bar{2}20$) Reciprocal Lattice Point. Calculation shows that the diffuse domain is an oblate solid of revolution, extended in the $[110]$ direction and compressed in the $[\bar{1}\bar{1}0]$, giving axial ratios of

*Single crystal cut from a polycrystalline ingot obtained from M.I.T.

$[110] : [001] : [\bar{1}\bar{1}0] = 0.140 : 0.112 : 0.071$ expressed in terms of the root mean square amplitude of atomic vibration of silicon, $\sqrt{\langle u_s^2 \rangle} = 0.114 \text{ \AA}$, which was calculated from the Debye⁽²⁰⁾ characteristic temperature.

The scales and method of comparison employed in the case of germanium were used for silicon to give the following table and Figures 13, 14, and 15.

Displacement From Bragg Position	Calculated Ratio $\frac{[001]}{[\bar{1}\bar{1}0]}$ Corrected for Flat Film	Axial Ratio of Observed Section on Film
$\theta_B - 1\frac{1}{4}^\circ$	1.25	~ 1
$\theta_B - 3/4^\circ$	1.25	$> 1 : 001 \text{ longer}$
$\theta_B - 1/4^\circ$	1.35	$> 1 : "$
$\theta_B + 1/4^\circ$	1.35	$> 1 : "$
$\theta_B + 3/4^\circ$	1.25	~ 1

While the axial ratios of observed diffuse spots are qualitatively correct, the profiles of these diffuse spots are strikingly different in contrast to the reasonable agreement obtained with germanium. The profiles calculated are ellipses, yet at $\theta_B \pm 1/4^\circ$ a cross of intensity is observed, that is, spikes in approximately the $[001]$ and $[\bar{1}\bar{1}0]$ directions. At $\theta_B - 1\frac{1}{4}^\circ$ and $\theta_B - 3/4^\circ$, $(\bar{3}51)$ and $(\bar{3}5\bar{1})$ are also recorded across the horizontal plane of symmetry, and these also show a cross profile, whereas their calculated diffuse domains show no spikes of intensity, Figure 16.

(400) Reciprocal Lattice Point. Calculation shows that the diffuse domain is an oblate sphere, compressed in the $[100]$ direction, giving axial ratios of

$$[100] : [010] : [001] = 0.077 : 0.112 : 0.112, \text{ Figures 17, 18, and 19}$$

again expressed in terms of the root mean square amplitude of atomic vibration.

Figure 13

DIFFUSE DOMAIN OF $(\bar{2}20)$ OF SILICON

MoK α = 0.71 Å.U.

$a^* = b^* = c^* = 0.1308$ R.L.U.

Scale: 1 R.L.U. $\equiv$ 10 cms.

a) $[001]$ Equatorial Section.

Scale: $1/2^\circ \equiv 6^\circ$

DIFFUSE DOMAIN OF ($\bar{2}20$) OF SILICON

b) $[\bar{1}\bar{1}0]$ Equatorial Section.

c) $[1\bar{1}0]$ Equatorial Section.

Figure 14

d) Sections of ($\bar{2}20$)
diffuse domain of
Silicon.

Figure 15. DIFFUSE DOMAIN OF ($\bar{2}20$) OF SILICON

Equatorial Sections of $(\bar{3}51)$

Equatorial Sections of $(\bar{5}51)$

Figure 16. DIFFUSE DOMAINS OF SILICON

DIFFUSE DOMAIN OF (400) OF SILICON

a) [001] Equatorial Section.

Films taken at $1/2^\circ$ intervals,
 Scale: $1/2^\circ \equiv 4^\circ$

Figure 17

DIFFUSE DOMAIN OF (400) OF SILICON

b) $[0\bar{1}0]$ Equatorial Section.

c) $[100]$ Equatorial Section.

Figure 18

Figure 19. DIFFUSE DOMAIN OF (400) OF SILICON

This domain is the same in shape as the (400) of germanium with a circular section, parallel to the (100) plane.

By the usual method the following comparison can be made

Displacement From Bragg Position	Calculated Ratio $\frac{[001]}{[100]}$ Corrected for Flat Film	Axial Ratio of Observed Section on Film
$\theta_B + 1\frac{1}{4}^\circ$	.9	~ 1
$\theta_B + 3/4^\circ$	1	~ 1
$\theta_B + 1/4^\circ$	1.2	> 1 : $[001]$ longer
$\theta_B - 1/4^\circ$	1.1	~ 1
$\theta_B - 3/4^\circ$	1	~ 1

The cross-shaped profile of (400) is not distinct, but it may possibly be observed at $\theta_B + 1/4^\circ$. The diffuse region of (400) may be a more compact, less extended one compared with $(\bar{2}20)$ and hence spikes are more difficult to record. However, at $\theta_B + 1\frac{1}{4}^\circ$, $(\bar{5}51)$ and $(\bar{5}\bar{5}\bar{1})$ are also recorded across the horizontal plane of symmetry and these show a cross of intensity, whereas their calculated diffuse domains show no spikes of intensity, Figure 16.

It must also be remembered that the crystal size, the focal spot size, and the collimation of the X-ray beam also determine the shape of a Laue spot. In the present case, a large single crystal and a very slightly divergent beam, no greater than a few minutes, was used. This arrangement gives elliptical Laue spots with the minor axis radial and although the cross profiles of $(\bar{2}20)$ and (400) may be interpreted on this basis, it does not seem possible to use the same criterion to explain those of $(\bar{3}51)$ and $(\bar{5}51)$.

B) To compare observed diffuse sections before and after bombardment.
(9 Mev. deuterons for 5 micro-ampere hours at $-25^{\circ}\text{C}.$)

($\bar{2}20$) Reciprocal Lattice Point. No change in the Bragg position is observed and the diffuse shapes for corresponding angular displacements are similar. The horizontal plane of symmetry is maintained and ($\bar{3}51$) and ($\bar{3}5\bar{1}$) are still recorded with a cross-shaped profile.

(400) Reciprocal Lattice Point. Again no change in the Bragg positions is observed. The diffuse shapes for corresponding angular displacements are similar and there is no or little change in the extent of the diffuse shapes. The cross profile is still apparent and is also repeated for ($\bar{5}51$) and ($\bar{5}5\bar{1}$) across the horizontal plane of symmetry.

The above is entirely qualitative and any work of a quantitative nature pertaining to the recording of changes of diffuse scattering with irradiation or to checking the profiles of silicon diffuse sections must now be carried out with a more sensitive instrument, the Geiger counter Weissenberg which is treated in Part II.

Part IV.

The selection of silicon and germanium needle single crystals and germanium single crystal plates previously irradiated by neutrons (10^{17} neutrons/cm²) has now been examined for changes in spacings using a single crystal back-reflection powder technique. (15), (16)

A quadrant camera was used in the case of the needles and an unbombarded single crystal was used as a standard. Also lead lines were recorded in order to check that the film to crystal distance had not been altered. A pattern of GeN_9

after bombardment and another Ge single crystal Nl_a both grown by sublimation and taken from the same boat, were recorded on the same film, as shown in

Figure 20 An analysis of this photograph is given as follows:

* Line	Identification	hkl
1	Pb	$620 a_2$
2	Pb	$620 a_1$
3	Ge	$711 a_2$
4	Ge	$711 a_1$
5	Ge	$444 a_2$
6	Ge	$444 a_1$
7	Pb	$600 a_2$
8	Pb	$600 a_1$
9	Pb	$531 a_2$
10	Pb	$531 a_1$
11	Ge	$533 a_2$
12	Ge	$533 a_1$

* Numbering from the center out.

Similar films obtained for unbombarded and bombarded Si needle crystals showed the (620), (600), (531) lead lines and the (620) Silicon line.

To measure a change of lattice parameter slightly greater than the experimental error (1 part in 5000) requires a change in the diameter of the innermost rings of 0.3 millimeters. This change could easily be detected by visual inspection. Neither in the films of silicon nor in the films of the germanium needles were changes in ring diameters found greater than 0.1 millimeters. Therefore, the

Figure 20 Powder photograph of a single crystal of germanium, sample N9 before and after bombardment.

lattice parameters have not been altered by the neutron bombardment.

With the germanium plates; aluminum leaf was used as an internal standard. The following lines were recorded on films taken of the plates: (620), (600), (531) of lead; (422) of aluminum; (711), (444), (533), of germanium.

In the case of the germanium plates, the eccentricity error cannot be completely removed and the error of measurement is greater (3 parts in 5000); however, this method is still more accurate than the ordinary rotation method (1-2 parts in 1000). Nevertheless a change in lattice parameter outside experimental error was not detected. Since the rings recorded with these single crystals are spotty, and resolution of a_1 and a_2 is clear and sharp with both irradiated and non-irradiated crystals, there appears to be no change in texture due to bombardment.

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