

The Pressure Coefficient of Thermal Conductivity of Metals

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The pressure coefficients of thermal conductivity of copper, silver, and gold were determined by means of an improved longitudinal heat flow method. The results indicate that the ratio of the thermal to the electrical conductivity (the Wiedemann-Franz ratio) for these metals, over a pressure range of 12,000 kg/cm², has a small positive coefficient of approximately 1 percent in 10,000 kg/cm². These results are at variance with those of Bridgman who used a similar method but found that the pressure coefficient of the Wiedemann-Franz ratio may be either negative

or positive and is more often negative. Experiments are reported which prove that the negative coefficients found by Bridgman were due to a systematic convection error undiscovered in his longitudinal heat flow method. It is reasonable to suppose that the positive pressure coefficient of the Wiedemann-Franz ratio is due to the nonelectronic part of the thermal conductivity, and this assumption is further supported by the correlation between these positive coefficients and the volume compressibilities of the metals.

INTRODUCTION

THE theory of electrical and thermal conductivity of metals based on quantum mechanics has given a qualitative understanding of most experimental results. One of the most important results explained has been the Wiedemann-Franz law, which states that the ratio of the thermal to the electrical conductivity is equal to LT , where T is the absolute temperature and L is a constant known as the Lorenz number which is the same for all metals. The quantum theory and the previous electron theories of conduction have based their quantitative deduction of this law upon the assumption that the conduction of heat in metals is due to the motion of "free" electrons. The results of these deductions were in fair agreement with experiment for a large number of metals. The quantum-mechanical derivation of the Wiedemann-Franz law, based on the electron motion assumption, is theoretically valid for most metals. Because of the approximations made in the theory, the results do not hold exactly for the transition metals or bismuth, or for temperatures much less than the Debye characteristic temperature. The theory neglects the contribution to the thermal conductivity made by the lattice vibrations and therefore should give too low a value for poor conductors. Aside from these exceptions, the fact that the theoretical result agrees well

with experiment would indicate that the major phenomena involved in thermal conduction in metals had been accounted for.

The experimental investigation of the Wiedemann-Franz law as a function of pressure has been undertaken by Lussana¹ and Bridgman,² with widely divergent results. To the first order, the theory indicates that the ratio of thermal and electrical conduction should be independent of pressure. Since a pressure of 10,000 kg/cm² (1 atmosphere = 1.0332 kg/cm²) affects the electrical conductivity by only a few percent, the effect of pressure on the thermal conductivity should also be only a few percent—an amount difficult to determine precisely experimentally. Lussana, working up to 3000 kg/cm², had measured the effect of pressure on twelve metals. He found that the Wiedemann-Franz ratio remained nearly constant. However, the method he used was extremely unreliable in that the corrections for heat loss were more than ten times the effect investigated, and Lussana made the correction very inaccurately. A critical analysis of Lussana's results appears in Bridgman's paper. Bridgman used two methods for measuring the change of thermal conductivity with pressure. The first was a radial flow method and had the advantage of requiring very few corrections. The specimen was in the form of a cylinder that almost filled the bore of the pressure chamber. A heater wire was placed along the axis

* This work was done at the physics laboratory of Harvard University during the year 1936-37, while the author was a Charles A. Coffin Fellow and a Research Fellow in physics.

¹ S. Lussana, *Nuovo Cimento* **15**, 130 (1918) and **25**, 115 (1923).

² P. W. Bridgman, *Proc. Am. Acad. Sci.* **57**, 77 (1922).

of the specimen to produce radial heat flow and the temperature difference between two points at different radial distances from the axis was measured. The difficulties involved in preparing a homogeneous specimen with accurately placed thermocouple and heater wires limited the use of this method to poor conductors, Pb, Sn, and Cd. For good conductors, Bridgman used a longitudinal flow method. A source of heat was placed at one end of a rod, a sink at the other, and the temperature drop along the rod measured by a differential thermocouple. The heat loss from the specimen to the pressure cylinder was an important correction, of the order of magnitude of the effect being investigated. Using the longitudinal flow method Bridgman measured the pressure effect on Zn, Fe, Pt, Ag, Cu, Ni, Sb, and Bi.

Bridgman's results showed that the pressure coefficient of the Wiedemann-Franz ratio could be either positive or negative, and in many cases was so large as to indicate that an appreciable part of the thermal conductivity was nonelectronic in nature. For example, in the case of Ni, a pressure of 12,000 kg/cm² decreased the measured thermal conductivity by 14.5 percent and increased the electrical conductivity by 1.8 percent. The pressure could, at most, wipe out completely the nonelectronic part of the thermal conduction. Thus, the above result would place a lower limit of 16 percent upon the magnitude of the nonelectronic part of the total thermal conductivity. (Bridgman erroneously interpreted this limit as an upper limit.) If the nonelectronic part is not completely wiped out, but has a pressure coefficient similar to that of insulators, the fraction of the total thermal conductivity due to the nonelectronic part may be very much larger. The theoretical value for the Lorenz number due to electronic conduction alone is 2.45×10^{-8} (volt/degree)², and the best values for Ni give an experimental Lorenz number of 2.28. Not only is this difference too small to agree with the above analysis, but it is also of the wrong sign. In addition, the pressure coefficients of thermal conductivity of insulators, as found by Bridgman,³ are all positive, as would be expected. It would therefore seem reasonable

that if the nonelectronic part of the thermal conductivity of metals is due to lattice vibrations, this part should have a positive pressure coefficient, rather than the negative coefficient observed in most of the metals Bridgman investigated. Apparently, if Bridgman's experimental results were all correct, some fundamental phenomenon must have been overlooked in the theories of conduction in metals. Alternately, if the theories were fundamentally sound, the experimental results must have been vitiated by some unknown systematic error. Credence was lent this latter possibility by the fact that the metals investigated by the radial flow method, Pb and Sn, showed positive pressure coefficients, whereas all those investigated by the longitudinal flow method showed the anomalous negative coefficients. In an attempt to settle this question, the research reported in this paper was undertaken. Measurements were made on Cu, Ag, and Au by means of an improved longitudinal flow method. The results found showed that the Wiedemann-Franz ratio for these three metals, over a pressure range of 12,000 kg/cm², has a very small positive coefficient, and that the anomalous negative coefficients found by Bridgman were due to a systematic convection error undiscovered in his work.

METHOD AND APPARATUS

The difficulties involved in all thermal conductivity measurements are greatly enhanced in high pressure measurements due to the necessity of making the specimen small enough to fit into the pressure chamber, and because of the increased heat losses caused by the liquid used to transmit the hydrostatic pressure. The change of electrical conductivity in 12,000 kg/cm² pressure change is about 5 percent or less for most good conductors, and the corresponding change in thermal conductivity of the liquid used, petroleum ether, is about 125 percent. It is therefore essential, for precise measurements, that the fraction of the total heat input to the specimen that is lost through the liquid be made as small as possible. Any small heat loss not a function of pressure does not contribute to the experimental error since only the relative change in thermal conductivity is of interest.

³ P. W. Bridgman, *The Physics of High Pressure* (Macmillan, 1931).

The known methods for measuring the thermal conductivity of metals fall into two general groups, dynamic and static. The dynamic methods have the valuable advantage of eliminating the necessity for determining heat losses, but unfortunately they cannot be used when the specimen is surrounded by a dense medium such as a liquid.⁴ In the static methods, the variable heat losses may be determined as a function of pressure or minimized to such an extent that they do not affect the precision of the measurement. The radial method used by Bridgman utilized this latter principle, but as has been mentioned, had a limited applicability. In the longitudinal method, Bridgman determined the variable heat losses by theoretical analysis of the geometry of the apparatus. These losses, except for the best conductors, were generally of the same order of magnitude as the effect sought. It is apparent that the best method would be one that was of general applicability and utilized the principle of minimizing the heat losses. For this purpose a guard cylinder method was developed for use in this research. The specimen in the form of a long rod was mounted in the center of the pressure cylinder, one end in a large copper block and the other containing a heating coil as in the longitudinal flow method. Midway between the specimen and the pressure cylinder was placed a copper guard cylinder. The specimen and guard cylinder had a common cold sink, and the hot end of the guard cylinder completely enveloped the hot end of the specimen. By suitable adjustment of the current in the guard cylinder heating coil, the hot end of the guard cylinder could be brought to the same temperature as that of the specimen. This resulted in an approximately similar temperature distribution along the guard cylinder and the specimen, and the heat loss from the specimen was therefore very small and calculable. With this apparatus a number of tests were made upon a copper specimen, but the method was finally discarded because of the mechanical difficulties involved in precisely aligning the small sized apparatus, the trouble encountered with the six electrical leads into the pressure cylinder, and the length of time required to reach the thermal

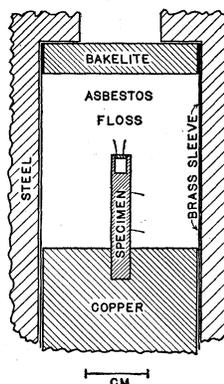


FIG. 1. Specimen mounted in pressure cylinder.

balance. However, if the experimental results warrant the work involved in an extremely high precision investigation, this method could be used. Finally an improved longitudinal flow apparatus, similar to the original apparatus of Bridgman, was developed. The results reported in this paper were found with this apparatus.

The specimen used in this longitudinal flow method was about 2 cm long and about 3 mm in diameter. The specimen was mounted concentric in the pressure cylinder, as shown in Fig. 1, and one end was soldered into a massive copper block which formed the cold sink. The heat source at the other end of the specimen consisted of a diminutive coil made of No. 36 D.C.C. Nichrome V wire embedded in a square bottomed hole 3 mm deep and made with a No. 44 drill. The coil contained enough wire to have a resistance greater than 10 ohms. A silicate (dental) cement was used to hold the coil in place since it was found that any movement of the coil, when the pressure was changed, altered the distribution of the heat flow and gave unreproducible results. A snug fitting copper disk was used to close the hole. The heating coil was thus completely surrounded by metal and therefore most of the heat developed entered the specimen. The Nichrome wire was soldered to No. 36 copper leads at a small distance from the specimen.

The thermocouples used for the three metals investigated, Cu, Ag, Au, were all made of No. 36 Advance wire. Since the difference in temperature of two points along the specimen was desired, the two couples were connected differentially with the specimen itself as the common

⁴ C. Starr, *Rev. Sci. Inst.* 8, 61 (1937).

lead. This permitted the soldering of the Advance wire to the specimen. Bridgman used copper-constantan couples differentially connected and loosely held in holes in the specimen. This resulted in a movement of the thermocouples when pressure was changed and caused scattered readings. The method of direct soldering completely obviates this difficulty. The thermocouples were placed far enough from the ends of the specimen to be in a region of uniform heat flow and far enough apart to produce a satisfactory e.m.f.

The massive copper block fitted snugly into a thin brass sleeve (14 mil wall) which, in turn, fitted snugly into the pressure cylinder. The top of this sleeve was closed off by a Bakelite plug as shown in Fig. 1. The space between the specimen and this sleeve was completely filled with tightly packed asbestos floss. This asbestos floss served the very essential purpose of preventing convection currents in the surrounding liquid.

The dimensions of the apparatus and specimen were the result of a compromise between the ideal conditions and experimental convenience. The longer the specimen the smaller is the heat input required to produce a precisely measurable temperature difference and the less critical is the thermocouple placement. However, in order to reduce the fraction of the heat input lost laterally by the specimen to the pressure cylinder walls, it is desirable that the specimen be as short as possible and have a large cross section area. A simple calculation shows that the optimum diameter for the specimen is approximately one-half that of the pressure cylinder, but this would cause complications due to nonuniform heat flow. The maximum size of the pressure chamber was determined by the limitations of the hydrostatic pressure apparatus. A larger volume than that used would not have permitted reaching such high pressures. While a large inner bore is desirable in order to reduce lateral heat loss, an inner diameter greater than that used, about 1 inch, would require too heavy a cylinder for easy handling. The heating coil and the thermocouple leads were large enough in diameter (5 mils) for handling, but a simple calculation showed that they were not large enough to cause an appreciable heat loss along the leads. As only the change in this heat loss with pressure

affects the final result, and this is very small, it can be neglected.

The necessary electrical measurements were the current through and the resistance of the heating coil, and the thermal e.m.f. produced by the temperature drop. The heating coil resistance was measured on a resistance bridge. The heating current, about 0.2 ampere, was supplied by a large capacity storage battery source and was measured by means of a standard 1 ohm resistance in series with the heating coil. The voltage drop across this standard resistance was determined with a potentiometer. The thermal e.m.f. was measured by an auxiliary potentiometer system. A variable dry-cell voltage source was connected in series with a 10,000 ohm and a 10 ohm manganin resistance. The voltage across the 10 ohm resistance was used to balance the thermal e.m.f. with a galvanometer as a null instrument. The voltage across the 10,000 ohm resistance was measured by the potentiometer. This system had a maximum voltage sensitivity better than 10^{-8} volt.

A reversing switch in the heating current circuit permitted the elimination of the effect of leakage currents. Although the heating circuit was well insulated from the thermocouple circuit, the latter was so sensitive that only a slight leakage was sufficient to affect the readings. The pressure transmitting liquid, petroleum ether, was an excellent insulator, but some leakage occurred in the four-terminal plug that carried the leads into the pressure cylinder, probably due to moisture in the insulation. A reversing switch was also used to eliminate parasitic e.m.f.'s in the galvanometer circuit. This switch was enclosed in a thermally insulated copper chamber so as not to become a source of thermal e.m.f.'s. Parasitic e.m.f.'s in the remainder of the thermocouple circuit could not be thus eliminated, so they were determined by measuring the residual e.m.f.'s before and after each set of readings with no heat input to the specimen. The parasitic e.m.f.'s were made as small as possible by placing the electrical connections and pressure cylinder in a constant temperature bath.

The production of the high pressures and the technique of high pressure measurements has been completely described by Bridgman.³

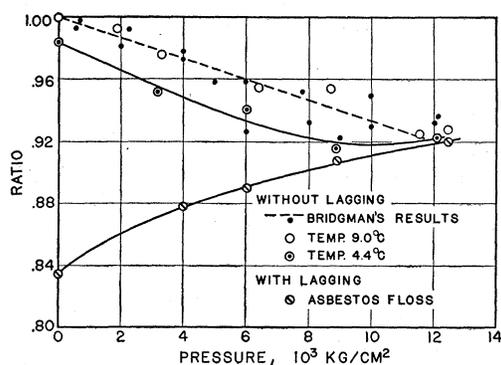


FIG. 2. Ratio of heat input to temperature drop (W/θ), in relative units, as a function of pressure for a copper specimen. The effect of temperature and lagging upon convection losses is illustrated. Bridgman's results are plotted for comparison.

EXPERIMENTAL PROCEDURE

The procedure for making the measurements was the same for all the specimens and for each value of the pressure. The apparatus was completely surrounded by a well-stirred ice bath and allowed to come to temperature equilibrium. With no input to the heating coil, the residual parasitic e.m.f. was recorded. The resistance of the heating coil was measured on a bridge, and the heating current switched on. In about fifteen minutes thermal equilibrium was reached and measurement of the thermal e.m.f. was made as previously described, for both positions of the galvanometer reversing switch, and for both positions of the heating current reversing switch. This gave four readings of the thermal e.m.f. Heating current was determined before and after each set of measurements. The input to the heating coil was then switched off, and after temperature equilibrium had been reached the residual parasitic e.m.f.'s were again determined. The pressure was then changed to the next desired value and after temperature equilibrium had been reached the parasitic e.m.f.'s were determined for the next set of measurements.

The true thermal e.m.f. for any given set of measurements was determined by subtracting the average parasitic e.m.f. from the average thermal e.m.f. The ratio of the heating coil watts to the true thermal e.m.f. was thus determined for each value of the pressure. Before and after each set of pressure measurements on a speci-

men, this ratio was determined at atmospheric pressure and with air in the pressure cylinder instead of petroleum ether. The apparatus was not disturbed for this purpose, the pressure cylinder being filled and emptied by means of a vacuum pump.

The thermal conductivity of the specimen is determined by the equation

$$K_s = (W/\theta)(d/a)/(1-m)(1-n)(1+p),$$

where W is the heat input to the specimen; θ is the temperature drop between the two thermo-junctions, calculated from the thermoelectric power at atmospheric pressure; d is the distance between thermo-junctions at atmospheric pressure; a is the cross section area of specimen at atmospheric pressure; m is the temperature correction due to the pressure variation of thermoelectric power; n is the dimensional correction due to linear compressibility; p is the heat loss correction due to the pressure variation of the thermal conductivity of the pressure transmitting liquid (petroleum ether). The data necessary for these corrections have all been determined by Bridgman.³

The solution of the heat flow equations for the conditions of the specimen indicates that the magnitude of the heat loss correction may be determined by the first-order approximation $p = CK_e/K_s$, where K_e is the thermal conductivity of the liquid, and K_s is that of the specimen. Bridgman² estimated the magnitude of the heat loss constant C from the geometry of the apparatus, but unfortunately the unavoidable approximations required caused a large probable error in the result. In this research C was determined from experimental data at atmospheric pressure by means of the equation

$$C/K_s = (r-1)/(K_e - rK_s),$$

TABLE I. Measurements on copper specimen, at 1 kg/cm² and 0°C.

SURROUNDING MEDIUM	LAGGING	TEMP. OF HOT END, °C	RATIO W/θ
Petroleum ether	None	9.0	1.000
		4.4	0.982
Glycerin	None	9.0	0.872
		9.0	0.849
Petroleum ether	Asbestos floss	9.0	0.834
		9.0	0.800
Air	None	9.0	0.800

where r is the value of the ratio of $(W/\theta)_{\text{liquid}}$ to $(W/\theta)_{\text{air}}$; K_e is the thermal conductivity of the petroleum ether; K_a is the thermal conductivity of air. The (W/θ) ratio was determined with petroleum ether in the apparatus, and also with air, as described above. This experimental method appreciably reduced the probable error of the heat loss correction.

CONVECTION ERROR

Preliminary experiments to determine the value of the heat loss constant C , as described above, indicated an extremely large correction was necessary. Since the required correction was an order of magnitude greater than that calculated from the geometrical considerations, loss of heat by convection was suspected.

The quantity determined directly from the experimental measurements is the ratio of the watts input to the specimen to the thermal e.m.f. produced by the temperature drop along the specimen. This ratio is given by the equation (discussed above)

$$(W/\theta) = K_s(a/d)(1-m)(1-n)(1 + CK_e/K_s).$$

Since convection currents increase the heat loss from the specimen, their effect is similar to that of increased thermal conductivity of the surrounding liquid, i.e., they decrease the temperature drop for the same heat input and thus increase the ratio W/θ . In order to verify the presence of convection effects the ratio W/θ was determined at atmospheric pressure and 0°C with the space between specimen and cylinder filled with air, petroleum ether, and glycerine, and with this space also packed tightly with heat insulating material in order to hinder the motion of the liquid. The results of these measurements are tabulated in Table I. Fig. 2 shows the pressure measurements on a copper specimen with petroleum ether, with and without asbestos floss lagging. As the pressure increases, any convection effects tend to decrease due to the increased viscosity of the liquid. For this reason, all the experimental points at the high pressures tend to coincide. All the above data is consistent throughout with the behavior of convection effects. Bridgman's experimental points for copper are also plotted in Fig. 2. These would

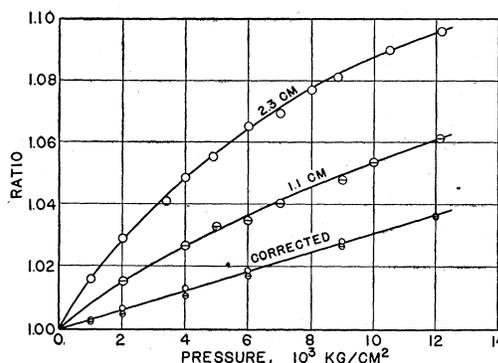


FIG. 3. Ratio of heat input to temperature drop (W/θ), in relative units, as a function of pressure for copper specimens of different lengths.

indicate that the error due to convection in Bridgman's measurements is about the same as that found with the present apparatus.

The theory of natural convection⁵ gives the relation $h/\theta = \text{constant} \cdot \theta^b$, where h is the heat loss per second from cylinder specimen; θ is the temperature excess; b is a constant ranging from about $1/10$ to $1/6$. Bridgman tested his apparatus for presence of convection effects by changing his heat input and thus the temperature differences by a factor of 2. He assumed that h/θ was proportional to θ , so that any loss due to convection should also change by a factor of 2. His measurements indicated no change in the results, and he therefore assumed that his apparatus was free from convection. However, from the convection relations, with b assumed equal to $1/6$, the change in convection loss due to halving the temperature is only 12 percent. As indicated in Table I, the total difference in heat loss, when convection is hindered by the presence of asbestos floss lagging about the specimen and when no lagging is present, is 16.6 percent. Under the assumption that this heat loss is completely due to convection, halving the temperature difference would reduce this by 12 percent or a total heat loss reduction of 2 percent. Since the precision of Bridgman's measurements was not very high, such a small change may have passed unnoticed. That such a change does occur is indicated by the experimental results shown in Table I and Fig. 2.

⁵ J. K. Roberts, *Heat and Thermodynamics*, p. 234 (Blackie & Son, 1928).

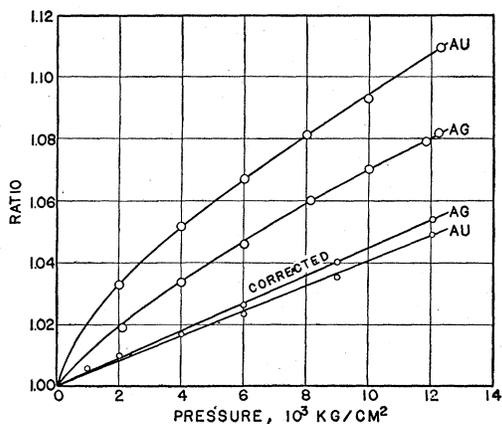


FIG. 4. Ratio of heat input to temperature drop (W/θ), in relative units, as a function of pressure for silver and gold specimens.

As a final test that the analysis of the convection effect was correct, measurements of the pressure coefficient of thermal conductivity were made on two copper specimens, one 2.3 cm long and the other 1.1 cm long. The specimens were surrounded by asbestos floss lagging in each case. Since some of the heat losses and corrections vary approximately as the square of the length, and some approximately as the length, the relationship between the various losses and corrections, and the heat input is different for two specimens. Any error or omission in the analysis of the correction to be applied to the measurements would thus be shown by a discrepancy in the results. The results of the measurements are shown in Fig. 3. After applying all the corrections discussed under experimental procedure, the pressure coefficient determined for the two specimens was the same, within the experimental error. This result conclusively indicates that the asbestos floss lagging has removed the convection error.

The effect on the results of the pressure coefficients of thermal conductivity of the asbestos floss lagging can be shown to be less than the experimental error of the results. As determined by direct measurement, the asbestos floss forms about 7 percent of the total volume of the specimen; petroleum ether the remainder. Assuming

TABLE II. Summary of results. Pressure coefficients $\times 10^6$.

METAL	COEFFICIENT OF THERMAL CONDUCTIVITY	COEFFICIENT OF ELECTRICAL CONDUCTIVITY	COEFFICIENT OF WIEDEMANN-FRANZ RATIO	AVERAGE VOLUME COMPRESSIBILITY
Copper	3.0 ± 0.3	1.86	1.1 ± 0.3	0.69
Silver	4.5 ± 0.3	3.44	1.1 ± 0.3	0.94
Gold	4.0 ± 0.4	2.98	1.0 ± 0.4	0.55
<i>Radial Method (Bridgman):</i>				
Tin	13.2 ± 0.7	10.13	2.8 ± 0.6	1.79
Lead	17.3 ± 0.4	13.79	3.1 ± 0.3	2.20

that the thermal conductivity pressure coefficient of the asbestos minerals is of the same order of magnitude as that of silica, the total effect of the asbestos is equivalent to less than 2 percent of the pressure coefficient of the liquid, or to about 0.1 percent in the final result. The results shown in Fig. 3 substantiate this also.

RESULTS

The experimental determinations for copper, silver, and gold are shown in Figs. 3 and 4. The copper used was doubly deposited electrolytic copper with a spectrographically indicated purity of better than 99.999 percent. The silver and gold specimens were made from commercially pure materials, the silver 99.95 percent pure, and the gold 99.97 percent pure.

The results are summarized in Table II. Bridgman's radial flow determinations are also included, since these are not open to the convection error criticism and therefore are reliable.

These results indicate that the Wiedemann-Franz ratio for the metals and the pressure range investigated has a very small positive pressure coefficient. It is reasonable to suppose that this positive coefficient is due to the nonelectronic part of the thermal conductivity, and this assumption is further supported by the correlation between the positive coefficient and the compressibilities.

The writer is indebted to Professor P. W. Bridgman for his support of this research and to Harvard University for the use of their physics laboratories.