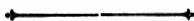


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THE THERMAL CONDUCTIVITY OF ROCKS AND ITS DEPENDENCE UPON TEMPERATURE AND COMPOSITION.

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PART II.

V. DISCUSSION.

The mass of material presented in the preceding section has an immediate value, insofar as it comprises measurements of conductivity of a wide variety of more or less common, "representative" types of rocks over a considerable range of temperature. What is perhaps still more important, the quantity and scope of this material enable us to examine in some detail the relations between conductivity and composition, and to draw some general inferences concerning these relations. We shall discuss the experimental results with the following questions in mind: First, how do the measurements compare with expectations on theoretical grounds? We shall find that the theory is not yet sufficiently advanced to give more than general suggestions, which are, nevertheless, helpful in understanding the character of the results. Second, what are the relations among the conductivities of the rocks, of the monomineral aggregates, and of the single crystals? We shall find that while the conductivities of the rocks reflect clearly the constitution of the rocks in terms of their principal minerals and of the conductivities of aggregates of these minerals, the relations of the latter to the single crystal values remain in doubt, for the good reason that too few of these values have so far been determined.

For the present, we have little to say about the conductivity of such common and highly important materials as the shales, limestones, and sandstones; a study of these rocks, with the introduction of controlled compression, has commenced. The conductivity of the igneous rocks is almost certainly much less dependent upon compression. Bridgman's experiments⁹ show a

rise of conductivity with hydrostatic pressure amounting to about 0.5 per cent per thousand atmospheres for diabasic basalt and hard limestone, as against 1.5 to 3 per cent for such "softer" but still compact materials as talc and pipestone. It is questionable whether these experiments produced quite the conditions in which we are interested; we shall proceed, however, with the assumption that this effect is probably small.

A. Theoretical expectations.

Although no satisfactory calculation of the absolute conductivity of even the simplest dielectric crystals has yet been carried through, the main features of the process of heat conduction appear to be fairly well understood. In general, the transfer of heat in crystals may be traced to the motion of free electrons and of the atomic lattice. For the materials of interest here, there are no free electrons; the transfer of energy is attributable entirely to the motions of the lattice particles.

The thermal motion of the atoms arranged in a crystalline lattice may be conceived as the superposition of a great number of wave-trains that traverse the crystal in all directions. The waves are of two types, familiar in elastic theory: compressional waves and distortional waves, propagated with different velocities. In crystals, the wave-velocities depend also upon the direction of propagation with respect to the crystallographic axes. The frequencies of the waves range from some low value which depends upon the dimensions of the crystal to an upper limit determined by the temperature. When no thermal gradients exist, no net energy is carried by the waves in any direction. In terms of this conception, with the additional restriction to isotropic materials, Debye¹⁴ was able successfully to account for the variation with temperature of the *heat capacity* of simple substances.

The establishment of a thermal gradient perturbs this wave system in such a way as to cause a flow of energy from the region at higher temperature to that at lower temperature; this process requires that there be exchange of energy between the various individual wave-trains. A wave coming from the hotter region, possessing an energy appropriate to that temperature, interacts with the atoms in its path with loss of

¹⁴ Debye, P.: *Vorträge ueber die kinetische Theorie der Materie*, Leipzig-Berlin, 1914.

energy; it will be "scattered." With a steady thermal gradient, there results a steady flow of energy whose magnitude depends upon the velocities of the waves, the heat capacity, and the amount of scattering. The latter factor may be represented by a "mean free path," roughly analogous to the free path between collisions which plays a similar rôle in the kinetic theory of gases. In solids, this free path is the distance in which the energy of the waves is reduced by scattering in the ratio $1/2.718$. . . Debye was able to derive an expression for the conductivity in the form, $K = \frac{1}{4}\sigma V\rho L$, where σ is the heat capacity, V the mean velocity of the waves, ρ the density, and L the free path. Unfortunately, the computation of L is very difficult; the formula is usually turned the other way: to find L , knowing K . This gives a rough idea of the distance of comparatively free passage of the thermal waves. For NaCl, we find that at 0° C. (with our data) $L = 30.10^{-8}$ cm., about eleven times the interionic distance; in quartz, parallel to the axis, $L = 60.10^{-8}$ cm., at 0° C. Using the experimental data, we see that for these crystals, L decreases rapidly as the temperature and consequently the amplitude of motion of the lattice particles increase. This decrease of L with increasing temperature is also given theoretically.

The most illuminating discussion of the factors that determine the conductivity of real crystals has been given by Makinson,¹⁵ still in terms of an isotropic crystal. In addition to the scattering of the thermal waves by their mutual interaction, which is present in the most perfect crystal, Makinson considers the scattering produced by irregularities in the lattice of atomic dimensions, such as would be caused by impurities, and by large-scale interruptions of the lattice, such as grain boundaries. A free path is defined for each of these sources of scattering. At high temperatures the effective wave-length of the thermal waves is so short that the various lattice defects are almost without influence upon the scattering, which is then determined principally by the lattice motion. Peierls¹⁶ and Debye have concluded that the conductivity will then be approximately inversely proportional to the absolute temperature. At lower temperatures, the effective wave lengths increase, the scattering by the lattice motion diminishes and

¹⁵ Makinson, R. E. B.: Proc. Camb. Phil. Soc. 34, 482, 1938.

¹⁶ Peierls, R.: Ann. Phys. 3, 1055, 1929; Ann. Inst. H. Poincaré, 5, 177, 1935.

conduction is limited, first by the small scale irregularities, and finally, at very low temperatures, by the size of the crystal itself: the free path cannot exceed the crystal diameter. This remarkable prediction of the theory has been confirmed by experiments¹⁷ with small sylvine crystals in the neighborhood of 5° absolute, with quartz crystals at about 15° absolute. At these temperatures, the free path is of the order of one millimeter.

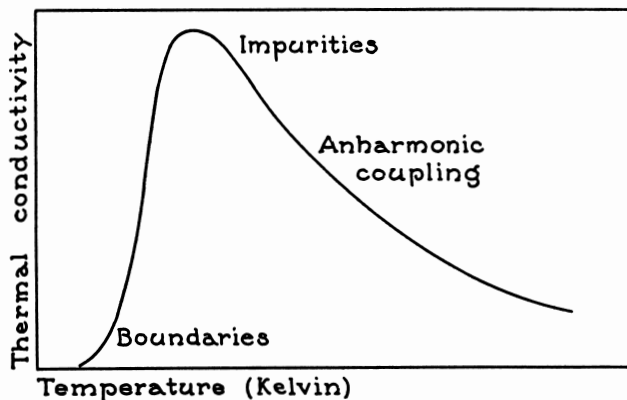


Fig. 9. Variation of conductivity with temperature in dielectric crystals, after Makinson.

The general form of the variation of conductivity with temperature is suggested by Fig. 9, taken from Makinson's paper. At high temperatures, the conductivity is shown as inversely proportional to the absolute temperature; this is the region labelled "anharmonic coupling." This term refers to the kind of interaction between the lattice particles which is required to give scattering by lattice motion. At very low temperatures, the conductivity is limited by reflection of the thermal waves at the boundaries of the crystal grain; the smaller the grain, the higher is the temperature at which this limitation commences to be important. At some intermediate temperature, scattering by impurities or by irregularities of atomic dimensions reduces the conductivity below the value which it would have if the lattice motion alone were responsible for the scattering. It is not possible to fix the precise temperatures at which these various effects should take place for real

¹⁷ deHaas, W. J., and Biermasz, T.: *Physica* 5, 47, 1938; 5, 320, 1938.

crystals, and the proportions of the curve may be very different from those shown in the Figure. The experiments cited showed the abrupt fall of conductivity due to reflection at the grain boundaries occurring at temperatures below 20° absolute for certain crystals about one millimeter long. For much smaller crystals, or for crystals with many fine-scale defects, the region marked "boundaries" would be extended toward higher temperatures.

B. Comparison of theory and experimental results.

Experimental material for the verification of these theoretical predictions for dielectric crystals at higher temperatures has been scanty, consisting chiefly of Eucken's measurements¹ between -190° C. and 100° C. for a few natural crystals. Eucken's results are given in Table 9; since they were intended to show that the conductivity was inversely proportional to the absolute temperature, we have listed merely the ratios of conductivity at the various temperatures to the conductivity at 0° C. (273 absolute) and in another column the ratio of 273 to the absolute temperature of the measurements. These columns would be identical if the relation, $K = A/T$ were exact. (A is a constant.) Although these results have generally been accepted as establishing the correctness of this relation at high temperatures, it is clear that the agreement is very rough. If instead of forcing the measurements into this form, we plot *resistivity* against absolute temperature, we find that the points at the three higher temperatures fall on good straight lines for NaCl and KCl, heading toward zero resistivity at about 40° abs. The points at -190° C. lie off this line, toward the side of higher resistivities, as we now expect. For the other crystals, the results are less regular. Our own resistivity values for rocksalt, from 0° to 400° C., a considerably larger temperature range, fall on a straight line which intersects the temperature axis at 66° absolute. In the later work by Eucken and Kuhn only two temperatures were used. The shape of the curves is thus undetermined, but the ratios of conductivity at the two temperatures varied in both directions from the ratio of the absolute temperatures. A more accurate statement of the experimental results at relatively high temperatures is that resistivity tends to increase linearly with the temperature; it is not, however, directly proportional to the absolute temperature.

TABLE 9.

Temperature		Relative Conductivity, K_T/K_{273} (Eucken).						
°C	°Abs.	$\frac{273}{T}$ abs.	KCl	NaCl	CaF ₂	CaCO ₃	SiO ₂	
						⊥		⊥
100	373	0.742	0.706	0.695	0.774	0.830	0.662?	0.770
0	273	1	1	1	1	1	1	1
— 78	195	1.400	1.492	1.497	1.459	1.342	1.437	1.392
—190	83	3.289	3.015	3.816	3.776	3.684	3.600	3.385

The resistivity of our quartz crystal (parallel to the optic axis) also increases linearly with temperature from 0° to 400° C.; this line intersects the temperature axis at about 31° abs. For the other direction in the quartz, the resistivity is linear above 100° C. For nearly all of our other materials the resistivity may be said to be roughly a linear function of the temperature, satisfying approximately our expectations for such materials. There are two surprising features, however, not readily accounted for. One is the failure of the conductivity to decrease as rapidly as the theory would appear to demand, as the temperature increases; this fact may also be expressed by saying that the curves of *resistivity* versus temperature tend to be *concave* toward the temperature axis. This effect is most pronounced for the calcite, limestone, and dolomite specimens. The same tendency is shown by Eucken's observations on calcite between —190° C. and 100° C., although his absolute values are different from ours. If Fig. 9 really gave the shape of the conductivity-temperature curve, then the resistivity-temperature curve should be *convex* toward the temperature axis. There appears to be some factor at work here which is not included in the theory.

The other and perhaps more important departure from expectation is the increase of conductivity with temperature shown by three of the feldspar aggregates. That this effect is probably inherent in the crystals and not the result of aggregation is suggested by Eucken and Kuhn's observations of a similar variation between —190 and 0° C. with a number of single crystals: orthoclase, analcime, and tourmaline; beryl showed an increase of conductivity at —190° of only six per cent over the value at 0° C. This anomalous effect can thus persist to very low temperatures. What interpretation can be found for it? The tentative explanation which we advance is that the effect must be traced to some variety of crystalline imperfection.

C. Effect of imperfections of crystals.

Although the existence of fine-scale imperfections in crystals is generally recognized, there is serious disagreement concerning the nature of the imperfections, which are variously described in terms of "mosaic," "block," "secondary," or "lineage" structures. The absolute size, degree of regularity, amount of disorientation of the domains in which the lattice is considered to be perfect, are matters on which research is centered at the present time, without as yet any generally accepted conclusions, except, perhaps, the conclusion that these factors are dependent upon the conditions of crystal growth and upon the subsequent mechanical and thermal history. There is some evidence that such imperfections play an important part in determining the thermal conductivity of certain crystals, but in these instances, the effect of temperature was not reversed. On the other hand, we know very little about the fine-scale imperfections of the crystals showing the abnormal temperature effect. As Makinson points out, the result of fine-structure, in a general way, would be to extend the portion of the conductivity curve marked "boundaries" but we are unable to say to what temperature such an extension might reach. To account for the observed results on the feldspars, we must imagine this curve so flattened and stretched as to give a low maximum of conductivity above 400° C., with a subsequent slow decline at still higher temperatures. The position of this maximum would depend upon the number or spacing of imperfections and upon their character; we might thus allow for the fact that the feldspar aggregate containing the greatest proportion of albite shows a small decrease of conductivity as the temperature increases; the maximum for this material appears to lie at lower temperatures. We must admit, however, that at present this interpretation is quite without experimental verification.

Our measurements for rocksalt indicate that the observations are in a range of temperature where impurities and imperfections are of little importance for the conductivity, for the resistivity is very accurately a linear function of temperature from 0° to 400° C. It is therefore surprising that the absolute value for our crystal is so much lower than values (about 0.024 at 0° C.) found by Eucken and Kuhn for crystals grown artificially from melts and from solutions. It is known that rock-

salt crystals grown from melts may be exceptionally free from "mosaic" structure, but if the difference in absolute value is to be attributed to finer "mosaic" structure in our specimen, then we must conclude that the effect of this structure may persist to very much higher temperatures than has been supposed.

There is some evidence that the conductivity is in fact dependent upon the fine-structure even at high temperatures. The thermal resistance of certain micas across the basal planes has been found by Powell and Griffiths¹⁸ to decrease as these planes are forced together by mechanical pressure; irreversible decreases of conductivity on heating mica to about 200° C. led to an X-ray examination by Wood,¹⁹ who concluded that the original mica structure had broken down into a group of small domains tilted from their original positions by as much as 5°. There was a tendency toward recovery of the original structure. Apparently no dehydration took place. Aside from this example, the question of the relation of conductivity to fine-structure remains unfortunately obscure.

D. Conductivity and crystal structure.

An attempt has been made by Wooster²⁰ to correlate the thermal conductivity of crystals with their structure; so few data are available that the success of this effort is not easily judged. The simple Debye theory gives a conductivity proportional to the velocity of the elastic waves, density, heat capacity, and mean free path; but there is no way of predicting the free path in complicated crystals. The large increase in conductivity on substituting magnesium for calcium in carbonate crystals may be correlated with the increase in velocity and density on passing from limestone to dolomite. The dense ultrabasic minerals, with high elastic constants and high velocities, give high conductivities with respect to the feldspars, though not with respect to quartz. How much of the difference may be laid to greater perfection of the quartz crystal as it generally occurs is not yet known. Eucken and Kuhn have given a few measurements, for unspecified directions in silicate single crystals; these values, at 0° C. are: orthoclase, 0.0099, beryl, 0.020, tourmaline, 0.011, analcime, 0.008, andalusite,

¹⁸ Powell, R. W., and Griffiths, E.: *Proc. Roy. Soc.* 163, 189, 1937.

¹⁹ Wood, W. A.: *Proc. Roy. Soc.* 163, 199, 1937.

²⁰ Wooster, W. A.: *Zeit. f. Krist.* 95, 138, 1936; *Crystal Physics*, p. 85. (Cambridge, 1938.)

0.026, topaz, 0.056 (in cal./cm.sec.deg.). The value for orthoclase is about double the value that we find for an orthoclase aggregate; it is quite possible that measurements upon selected single crystals of pyroxenes, olivine, and feldspars will show conductivities appreciably higher than those of aggregates of these minerals.

As the temperature increases, crystal anisotropy appears to decrease; the conductivities in the different directions in quartz become much more nearly equal; the same is true of the calcite. The relations are shown in Fig. 10.

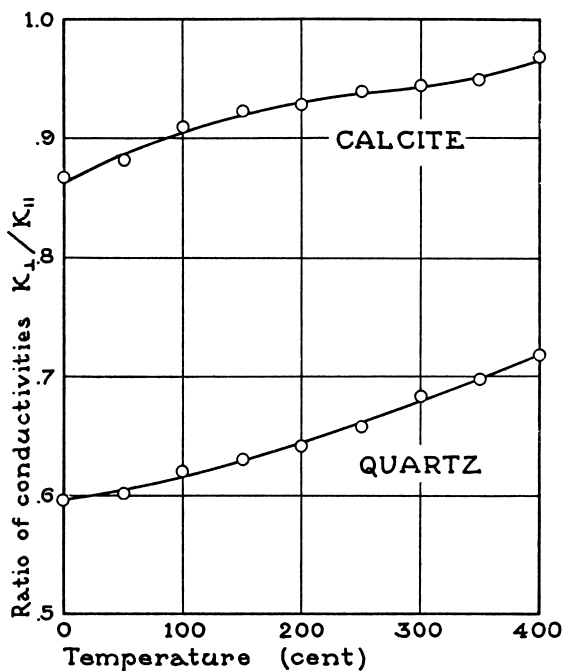


Fig. 10. Variation with temperature of the ratio of conductivities, perpendicular and parallel to the optic axis, in quartz and calcite.

E. Conductivity of aggregates.

The inadequacy of our present information concerning single crystals is evidently a serious handicap when we attempt to discuss the conductivity of aggregates of crystals. We shall commence with homogeneous aggregates of crystals of known conductivity, such as quartzites and limestones, and then pass to the consideration of the heterogeneous aggregates, with the

hope of establishing a reasonably good working correlation between conductivity and composition.

The conductivity of a homogeneous aggregate must depend primarily upon the conductivity of the crystal, and upon the thermal contact between the crystals. The individual crystals of these rocks are all more or less anisotropic with respect to the flow of heat. Even with perfect contact between the grains, the rigorous computation of the average conductivity of a specimen comprising a large number of crystals oriented at random would be impracticable. For crystals of relatively simple symmetry, such as quartz and calcite, an average value for random orientation may be found by taking this equal to the average value of the conductivity over all directions for a single crystal. Some ambiguity still exists, because the average conductivity over all directions for a crystal is not in general the reciprocal of the average resistivity over all directions. For example, the average conductivity of quartz at 0° C. is 0.020, while the reciprocal of the average resistivity is 0.0188. This difference is not very important for quartz and it is even less so for calcite, where the principal conductivities are much more nearly equal. Kaye and Roberts²¹ found that the measured conductivity of polycrystalline bismuth was 0.0193, while the reciprocal of the mean resistivity of single-crystal bismuth was 0.0195; but the mean conductivity of the single crystal is 0.020, which differs from the measured value by little more than the experimental uncertainty.

For crystals having a principal axis, the conductivity in any direction is given in terms of the two principal conductivities, K_{\perp} and K_{\parallel} by the expression²², $K_{\beta} = K_{\perp} \sin^2\beta + K_{\parallel} \cos^2\beta$, where β is the angle between the principal axis and the given direction. The average value of K is found by taking the averages of $\sin^2\beta$ and of $\cos^2\beta$ over all directions: $(\sin^2\beta)_{av} = 2/3$; $(\cos^2\beta)_{av} = 1/3$. This is of course not rigorously equal to the conductivity of a random aggregate; it is equal to the mean conductivity of a single layer of crystals, oriented at random, with the heat flow perpendicular to the plane.

The mean resistivity over all directions can be found from an expression analogous to the one above for mean conductivity; the reciprocal of this mean resistivity is the conductivity of a filament of crystals placed one on top of the other with

²¹ Kaye, G. W. C., and Roberts, J. K.: *Proc. Roy. Soc.* 104, 113, 1923.

²² Voigt, W.: *Lehrbuch der Kristallphysik*, Leipzig and Berlin, 1928.

random orientation, with the flow of heat along the filament. An aggregate may be considered as composed of a great number of such filaments placed side by side, or as a large number of layers, one upon the other. Needless to say, both of these methods of treating random aggregates are justified chiefly by their simplicity; they approach one another as the individual crystals become more nearly isotropic; they become very different when applied to heterogeneous aggregates of minerals of very different conductivities. Eucken and Kuhn have used still another mean for calcite aggregates, given by $(K^2 \perp K \parallel)^{1/3}$, for which there seems to be no very good justification; for calcite, all of these mean values are practically indistinguishable.

The calcite aggregates, Vermont marble and Solenhofen limestone, are of special interest; they contain very little material other than calcite, and we have measurements for the calcite single crystal over the same temperature range. In Table 10 are shown the mean resistivity R_c of an ideal calcite aggregate, calculated from $R_c = \frac{1}{3}R \parallel + \frac{2}{3}R \perp$, where $R \parallel$ and $R \perp$ are taken from Table 7. R_m is the mean resistivity of the marble, R_l of the limestone.

TABLE 10.

Comparison of resistivities of marble, limestone, and an ideal calcite aggregate.

Resistivity in cm.sec.deg./cal.							
°C.	R_c	R_m	R_m/R_c	$R_m - R_c$	R_l	R_l/R_c	$R_l - R_c$
0	115	138	1.20	23	139	1.21	24
50	134	157	1.17	23	163	1.22	29
100	149	173	1.16	24	181	1.21	32
150	162	186	1.15	24	197	1.22	35
200	172	196	1.14	24	210	1.22	38

Eucken and Kuhn have sought to interpret their measurements on two fine-grained marbles in terms of the conductivity of calcite, using a relation of the form, $R = R_c (1 + nB)$ where n is the number of crystals per cm. in the marble, or the reciprocal of the mean grain diameter, and B is the ratio of the temperature drop at one intercrystalline contact to the mean temperature drop per cm. This relation is seen to fit the present measurements for marble very well, with $nBR_c = 24$ over the whole range of temperature. Since n for our marble is about 30/cm., we find $B = 0.0065$ at 0° C. Eucken and Kuhn

found a common value, $B = 0.0027$ at 0° , 0.029 at -190° . The difference between the resistivity of the Solenhofen limestone and the ideal calcite aggregate is, however, not very different from that between the marble and calcite resistivities; since the grain is much finer and thus n much greater in the limestone, B would thus be very much smaller. It is therefore questionable whether this mode of treatment has much validity, since B , which should be a constant for a given temperature, turns out to be roughly proportional to the crystal size. The agreement found by Eucken and Kuhn for their two marbles seems to be a result of their use of marbles with nearly equal values of n , 103 and 138.

A more useful way of accounting for the reduced conductivity in such aggregates might be to think of a reduction of effective cross-section, to be traced to spaces of relatively low conductivity between some of the crystals, which are imagined to be in good contact over the rest of the area. We thus easily account for the nearly constant ratios of rock resistivity to calcite resistivity shown in Table 10. Eucken and Kuhn's ratios at 0° are: for $n = 103$, $R_m/R_c = 1.28$; for $n = 138$, $R_m/R_c = 1.37$; using their values for calcite as well as for the marbles. (At -190° , their ratios have risen to 3.88 and 5.16, respectively.) Some change in this ratio is likely to result from the change in size and shape of the individual crystals with temperature. We know²³ that a considerable compression of marble can be produced with very little stress, the probable initial effect being largely to close narrow, wedge-shaped spaces between the crystals. It is possible that this process is accompanied by a marked increase of conductivity. On the other hand, the Solenhofen limestone, though possessing a much greater porosity than the marble, is less easily altered in this respect by the application of stress; we hope to perform experiments to test these points.

The Pennsylvania limestone contains about 20 per cent of carbonaceous material which is evidently a fairly good conductor; the variation of conductivity with temperature is smaller than that of the nearly pure calcite aggregates, a fact perhaps ascribable to the small effect of temperature upon the conductivity of graphite. There is a large difference of conductivity in the directions parallel and perpendicular to the bedding planes, which may conceivably disappear under stress.

²³ Zisman, W. A.: Proc. Nat. Acad. Sci. 19, 653, 1933.

Our quartzite contains about seven per cent sericite, six per cent microperthite and microcline, and seven per cent magnetite. A direct correlation with the conductivity of quartz is therefore inappropriate. The conductivity of a pure quartz aggregate would be about 0.019 to 0.020 at 0°, as against 0.0133 for the quartzite (mean of the two samples). To deal with this more complex situation, we must introduce a method of combining the conductivities of the various components.

Let us consider an aggregate of several types of crystals, A, B, and so on, occurring in the proportions by volume, $x(A)$, $x(B)$, . . . Each kind of crystal will have a mean conductivity, denoted by $K(A)$, $K(B)$. . and a mean resistivity, $R(A)$, $R(B)$, . . . Let us imagine a highly idealized model consisting of equal cubes, stacked regularly together; this idealized aggregate may be dissected into filaments or piles of crystals, each pile one crystal thick. With random distribution of the constituents and a path of sufficient length, each pile will contain the constituents in the same proportion in which they occur in the whole mass. The next step is to identify these piles with the "tubes of flow" of heat. A tube of flow is generated by lines of flow, which are everywhere normal to the isothermal surfaces; no heat flows in or out across the sides of the tube; the flow across any cross-section of the tube is everywhere the same. Now if the different crystals possess different conductivities, the single crystal piles would really be tubes of flow only if they were insulated from each other, so that no lateral flow could take place; the real tubes of flow expand and contract in section as they progress through materials of different conductivities. Nevertheless, the approximation is not necessarily a bad one, for there will be a tendency for heat lost from one of the piles at one level to be balanced by inflow of heat at another. The resistance per unit area of each pile will thus be approximately $x(A) R(A) + x(B) R(B) + \dots$ and this will also be the mean resistivity of the aggregate. Such a treatment may be termed the "series" arrangement of elements: a given quantity of heat, in flowing from one isothermal surface to a distant one, is supposed to traverse a path in which the constituents occur in proportion to their volume distribution in the whole mass.

On the other hand, for two isothermal surfaces that are separated by a distance of the order of the mean crystal size, the treatment of elements as in series is clearly inappropriate.

We have now a layer of crystals across each of which there exists the same difference of temperature. The flow of heat across an area comprising a large number of crystals is the sum of the flow across the individual crystals and the mean conductivity of the layer is $x(A) K(A) + x(B) K(B) + \dots$. In the electrical terminology, the elements are in parallel.

The flow of heat in real aggregates must be much more complicated than either of these simple approximations contemplates. But as we shall see, the treatment of elements in series is remarkably successful except for a single instance in which the thickness of the specimen is clearly too small with respect to the crystal size. In this instance, the parallel treatment accounts for the apparent conductivity.

These approximations will be least suitable when there is a regular orientation of crystals of pronounced thermal anisotropy or when the different kinds of crystals occur in very different grain sizes. In the quartzite, the two samples with different orientations with respect to the bedding show differences of only three or four per cent; there is probably no significant departure from random orientation. In the marble specimens the difference is also slight, but the calcite crystal is so nearly thermally isotropic that even a marked orientation of the crystals would have relatively little effect.

We do not know the conductivities of a number of the minor constituents; the best alternative is to lump the minor constituents with the major ones which they probably resemble with respect to conductivity. Thus we group the magnetite, whose conductivity is probably at least as high as that of the quartz, with the quartz, and the sericite with the feldspar, obtaining the rounded composition, 87 per cent "quartz," 13 per cent feldspar. Taking the mean conductivities at 0° C. as 0.019 for the quartz and 0.0045 for the feldspar, we find that the series computation gives a conductivity of 0.0133, the parallel computation, 0.0171. The agreement with the series computation is obviously better than the data warrant; the result of the parallel computation is too high, as will always be the case except when the specimen is not much thicker than the mean grain size. At 200° C., the mean measured conductivity of the quartzite is 0.0088; the computed series conductivity, 0.0093. The assumption that the elements are effectively in series appears to be roughly justified in this instance.

Measurements of the conductivity of 17 specimens of the Witwatersrand quartzite have recently been published by Bullard.²⁴ The quartz content of 8 of the specimens was determined from thin sections, and an expression derived giving the conductivity as a function of quartz content alone. It is clear, however, from further discussion by Bullard that the character of the other constituents cannot be neglected. The 17 specimens could be classified in 3 groups as "feldspathic," "non-feldspathic" and "chloritoid bearing," with "no evidence for a difference between the chloritoid-bearing and the non-feldspathic groups," but with the conductivity of the feldspathic specimens "definitely lower than either of the others." It is likely that the conductivity of the chloritoid and similar minerals is very nearly as high as that of the quartz; the relatively low conductivity of the feldspars accounts for the difference between these groups. A more complete analysis is necessary for closer correlation with composition. Incidentally, the value (0.022) which would be found from Bullard's formula (page 481) for the conductivity of a quartzite with 100 per cent quartz at 25° C. is improbably high, unless the crystals were predominantly oriented with their optic axes parallel to the direction of mean heat flow. At 25° C., the conductivity of the quartz crystal parallel to the axis is only 0.0246. The considerably lower value computed for a quartz aggregate (0.017 to 0.018 at 25° C.) would probably fit with Bullard's data almost as well.

The correlation with composition for the igneous rocks depends upon the use of the measurements on the monomineral aggregates. These should first be corrected for the presence of minor constituents: the anorthosites contain small quantities of pyroxene, the pyroxenites small amounts of feldspar. There are small quantities of minerals for which we have no data, but we group hornblende and magnetite with olivine or pyroxene, sericite with feldspar. No correction is made for the three per cent of serpentine, chromite, etc. in the dunite. The corrected values, assuming series arrangement of elements, are shown in Table 11; they will be used to compute the conductivities of the rocks composed chiefly of feldspar, pyroxene, and olivine. They represent mean values for these kinds of crystals as they occur in rocks, with their natural imperfections, impurities, cleavages, twinning, and intercrystalline resistances.

²⁴ Bullard, E. C.: Proc. Roy. Soc. A 173, 474, 1939.

TABLE 11.
Corrected conductivities of monomineral aggregates.
Cal./cm.sec.deg.

		Temperature °C.			
		0	50	100	200
Olivine0124	.0105	.0094	.0081
Bronzite012	.0098	.0090	.0080
Hypersthene011	.0100	.0093	.0087
Pyroxene (mean of two above)0115	.0099	.0092	.0084
Plagioclase feldspar					
Albite	Ab ₈₈ An ₁₂0048	.0048	.0047	.0047
Anorthosite	Ab ₂₀ An ₈₀0044	.0044	.0045	.0046
Transvaal					
Anorthosite	Ab ₄₀ An ₆₀0041	.0042	.0042	.0043
Quebec					
Anorthosite	Ab ₃₅ An ₆₅0040	.0040	.0041	.0043
Montana					

The agreement between the values for the labradorite in the Quebec and Montana anorthosites, of quite different grain size, is reasonably good. The pyroxenes do not differ greatly from one another, nor from the olivine; this close similarity of properties has also been noted with respect to elasticity.

In Table 12 are given the computed and measured conductivities of the rocks of gabbroic composition at 50° C. and 200° C.; the compositions given in Table 4 have been rounded to those shown in Table 12. The computations were all based on the series arrangement of components. The greatest discrepancies, not over ten per cent, occur for the rocks having the largest proportion of pyroxene, the French Creek gabbro and the Maryland diabase. In these cases, as indeed in some of the others as well, much of the pyroxene is actually augite, which may have a somewhat lower conductivity than bronzite or hypersthene. On the other hand, the relatively good agreement for the Westfield diabase, where the pyroxene is all augite, suggests that this difference is not large. No correlation is evident between the discrepancies and the mean grain size. In view of the uncertainties of analysis, and the roughness of the computation, it seems a fair conclusion that not only the absolute value of the conductivity but also its variation with temperature are to a reasonably good approximation accounted for in terms of the conductivities of the plagioclase and pyroxene aggregates. The decreasing conductivity of the pyroxene is very nearly compensated by the slightly increasing conductivity of the plagioclase. Rocks of this type may show either small positive or small negative temperature coefficients.

TABLE 12.
Measured and computed conductivities of gabbroic rocks.
[Cal./cm.sec.deg.]

	50° C.		200° C.	
	meas.	calc.	meas.	calc.
French Creek Gabbro00537	.00570	.00513	.00562
52 Ab ₃₅ An ₆₅				
48 pyroxene				
Wisconsin Gabbro00470	.00490	.00476	.00493
73 Ab ₁₀ An ₉₀				
15 pyroxene				
12 olivine				
Westfield Diabase00502	.00515	.00501	.00515
67 Ab ₄₈ An ₅₄				
33 pyroxene				
Vinal Haven Diabase00515	.00532	.00503	.00530
62 Ab ₄₅ An ₅₅				
25 pyroxene				
13 olivine				
Maryland Diabase00544	.00590	.00537	.00576
48 Ab ₁ An ₂				
52 pyroxene				

Published values for rocks characterized as "trap," lava, basalt, diabase, gabbro, fall between 0.003 and 0.009. The descriptions are usually quite inadequate for the purpose of accounting for these conductivities. It seems likely that, as in the lavas studied by Bullard, high conductivities are associated with the presence of amygdales of high conductivity, such as the quartz, chlorite, and calcite in the Ventersdorp lavas. Unusually high content of pyroxene or olivine will result in high conductivity; it is difficult to account for values below 0.004 except in terms of glass content, alteration, porosity, fracturing, or other factors that have not as yet been studied. A glassy basalt might have a conductivity below 0.003.

In some of the remaining rocks, the amount of accessory minerals becomes embarrassingly large: there is 15 per cent of biotite in the tonalite, 12 per cent in the Barre granite. We have no independent data for orthoclase, nor for such intricate aggregates as micropertthite. A value for an orthoclase aggregate may be obtained from the measurements on the augite syenite; this is mainly (84 per cent) an intergrowth of albite and orthoclase. The chemical analysis gives a ratio of albite to orthoclase equal to 1.45, so that the composition may be reduced to augite (plus three per cent olivine) 16 per cent,

albite 51 per cent, orthoclase 33 per cent. Taking the conductivity of albite as .005, we find for orthoclase, .0046 at 50°, .0045 at 200°; these values are much like those for the other feldspars. An average value for the biotite is not easily found from these measurements, as it never exceeds about 15 per cent of the volume. From the small resistance remaining to be attributed to this component in the tonalite, Westerly granite, and Barre granite, it appears that the biotite is a relatively good conductor, and we shall take its mean conductivity as equal to that of the pyroxenes. This does not mean that the conductivity of biotite is high in all directions. For muscovite mica, for example, the conductivity across the cleavage planes is about 0.002, but in the directions at right angles, it is from five to six times as great. Measurements upon biotite are desirable. Table 13 shows the measured and calculated conductivities, at 50° and 200°, for the other rocks.

TABLE 13.

Measured and computed conductivities of quartz-bearing rocks.
[Cal./cm.sec.deg.]

	50°		200°	
	meas.	calc.	meas.	calc.
Tonalite0062	.0064	.0055	.0061
28 quartz				
50 Ab ₅₆ An ₄₄				
22 "pyroxene" (15 biotite, 7 hornblende)				
Quartz monzonite0070	.0063 (.0086)	.0059	.0058 (.0070)
34 quartz				
27 orthoclase				
33 Ab ₇₂ An ₂₈				
6 "pyroxene" (biotite and hornblende)				
Westerly granite0056	.0058	.0051	.0054
19 quartz				
41 albite				
33 orthoclase (microcline)				
7 "pyroxene" (biotite)				
Barre granite0063	.0064	.0055	.0058
26 quartz				
37 albite				
25 orthoclase				
12 "pyroxene" (biotite)				
Rockport granite0081	.0064 (.0083)	.0066	.0058 (.0068)
30 quartz				
64 micropertthite (.0048)				
6 "pyroxene" (amphibole)				

The outstanding discrepancy here is for the Rockport granite; fortunately, the interpretation seems clear. In this rock, the large quartz crystals form long chains which, in specimens of this size, short-circuit the feldspars. If the computation is made on the assumption of parallel flow, we find the values given in parentheses, which are in good agreement with the measured values for the granite; much less so for the quartz monzonite, which is of somewhat finer grain. In the Rockport granite the connected chains of quartz crystals are easily visible, some of them several inches long. We find moreover, a close correlation between the difference in conductivity of the two samples and their quartz content. A careful study of the surfaces of these specimens was made by Dr. E. B. Dane; the average proportion of the area occupied by quartz crystals was 25.1 per cent for specimen 1, 32.8 per cent for specimen 2. Computing the conductivities assuming *parallel* elements, we obtain the results shown in Table 14:

TABLE 14.
Apparent Conductivity of Rockport Granite.
[Cal./cm.sec.deg.]

	Specimen 1 25% quartz		Specimen 2 33% quartz	
	meas.	calc.	meas.	calc.
50°0078	.0078	.0083	.0086
200°0065	.0065	.0068	.0071

Measurements on specimens of the Rockport granite three quarters of an inch thick gave conductivities in close agreement with those for the thin specimens, but it is questionable whether even the three quarters of an inch specimens were thick enough to be representative of a large mass of this material. As the thickness of the specimen increases, sooner or later it will exceed the average length of the connected chains of quartz crystals and the effective conductivity will be reduced, since some quantity of feldspar must intervene in every tube of flow. Whether the conductivity would ever fall as low as that of the Barre granite, it is not possible at present to say.

Bullard reports the mean conductivity of four specimens of Dubbeldevlei granite as .0068 at 25° C.; the composition, from thin sections, was about 30 per cent quartz, 64 orthoclase, six per cent mica, and the grain size was apparently much the same as that of the Rockport granite. The computed conductivity

would be, for series elements, .0062; for parallel elements, 0.0086. It is quite likely that here also the specimens were somewhat too thin for such coarse-grained material. The same consideration may account for the high values for granite given by Nancarrow²⁵ (.0081) and in some of the older researches.

Other factors being the same, the grain size should not be of importance unless an appreciable proportion of the thermal resistance occurs at intercrystalline contacts. Most of the present evidence suggests that in relatively fresh igneous rocks, at least, the intercrystalline resistance is low. In the few cases where significant differences exist between fine-grained and coarse-grained samples of approximately the same composition, the difference is apparently traceable to the inadequate size of the coarse-grained sample. The question cannot be considered closed, however, until measurements on specimens of suitable size of the Rockport granite, for example, have been made. It is our belief that the apparent conductivity will decrease as the size of the sample increases until a value not far from the computed series value (0.0064 at 50°) has been reached. The effect of serious alteration by weathering, leaching and so on, has not been studied; it seems most likely that these processes would lower the conductivity.

The good thermal contact between crystals, in the igneous rocks, may be in part maintained by adsorbed films of water. Such films are probably firmly held, and do not begin to come away until the rocks are heated to 300° or 400°; furthermore, they are not readily replaced. The loss of this moisture and the development of imperfections may account in part for the "permanent" decreases of conductivity on heating above 300° at low pressure. Loss of water films cannot be entirely compensated by the presence of helium in these experiments, although the decrease of conductivity from this cause is undoubtedly smaller in the helium atmosphere than it would be in air. A few experiments which we have not described were made with rocks that had been soaked in water after pumping off the air and whatever else would come at ordinary temperature. The interpretation of the measurements was difficult, for in some cases, water that had been soaked up by the rock reappeared at the surface of contact with the copper plates of the apparatus, so that the usual method of computation

²⁵ Nancarrow, H. A.: Proc. Phys. Soc. Lond. 45, 447, 1933.

could not be used. There was no evidence, however, that the conductivity of the igneous rocks could be increased by this means; the results for a few other samples were more ambiguous and require further experimental clarification.

F. Conductivity of glass.

The conductivity of the glasses is found to increase with temperature over the whole range, in agreement with the results of other observers. Bridgman²⁶ has given a simply derived expression for the thermal conductivity of liquids, which successfully correlates this property with the density, molecular weight, and velocity of sound, and has suggested that the same expression may be valid for glasses. The application to glasses is not quite straightforward, since the molecular weight of a glass is a rather vague concept; there are moreover two velocities of sound in glass. The relation may be turned around to find the mean distance between the particles or groups of particles that are active in the propagation of thermal energy, using a mean velocity; we have taken the mean velocity to be $\frac{1}{3}(V_1 + 2V_t)$, where V_1 and V_t are the velocities of longitudinal (compressional) and distortional waves, respectively. The relation is $K = 3kV/\delta^2$, where $k = 1.35 \cdot 10^{-16}$, the gas constant, V is the velocity, and δ the mean distance between "molecules" or groups of ions. Using the measured values of the conductivity at 50° C., we find the distances δ shown in Table 15.

TABLE 15.
Application of Bridgman's formula to glasses.

Glass	V cm./sec.	K (meas.) ergs./cm.sec.deg.	δ (calc.) cm.
Silica	4.4·10 ⁵	14.4·10 ⁴	3.5·10 ⁻⁸
Pyrex	4.1	12.6	3.6
Obsidian	4.2	14.0	3.5
Diabase	4.5	12.0	3.9

The distances δ are thus all of the order of the distance between nearest silicon atoms in silica glass, which is 3.3 Å. This suggests, what we might have suspected, that the relatively heavy silicon atoms or the SiO₄ tetrahedra play a predominant part in the exchange of energy in these glasses. The formula is not successful in predicting the effect of temperature upon

²⁶ Bridgman, P. W.: Proc. An. Acad. 59, 141, 1923.

the conductivity of glasses. In all four glasses, the conductivity increases with the temperature considerably more rapidly than does the velocity, which in fact decreases as the temperature rises for the diabase glass. The conductivity of silica glass increases 29 per cent between 50° and 400°; the velocities increase by less than 2 per cent, and the increase in δ , if given by the thermal expansion, is only a fraction of one per cent.

The Debye formula may be used in the same way, and affords somewhat greater distances for the "mean free path" of the thermal waves (8.5 Å for silica glass, 4.9 Å for diabase glass). It seems clear that the propagation of energy in glasses is chiefly by an atom-to-atom exchange, much as in ordinary liquids. The random assembly of ions effectively scatters the thermal waves in such short distances that the wave concept seems nearly useless for this material. For the same reason, small amounts of "impurities" probably have little influence upon the thermal conductivity of glass.

VI. SUMMARY AND CONCLUDING REMARKS.

The conductivity of a number of igneous and other rocks has been found to vary appreciably with the temperature between 0° C. and 400°. The variation is such that the values for the different kinds of rocks tend to converge as the temperature increases: at 0° the conductivity for all of the rocks lies between 0.014 and 0.004 cal./cm.sec.deg.; at 200°, all values are between 0.009 and 0.004. The poorest conductors, the feldspar aggregates, show conductivities that increase with the temperature. The conductivity of all of the other crystalline materials decreases as the temperature increases. The highest conductivities are found for the ultrabasic rocks, hitherto unstudied. The exceptional behavior of the feldspars is tentatively ascribed to fine-scale imperfections; the possibility exists that under different circumstances,—under pressure, perhaps,—the conductivity of these minerals will be as high as that of the other silicates. While the differences between the conductivities of different classes of rocks are important at the temperatures at which measurements of the geothermal gradient are likely to be made, they become less so at depths of the order of 10 to 20 km.

A simple method of computation permits a calculation of the conductivity of fresh igneous rocks in terms of their mineral composition with an error usually less than five per cent, at

all temperatures between 0° and 200° C. This method may prove useful in the discussion of temperature measurements in rocks where the conductivities have not been measured. For example, observations in masses of pyroxenite and peridotite rocks have been reported to give geothermic "steps" of from 144 to 170 meters /° C.; the actual temperatures were not over 5° C.²⁷ Our values for such rocks afford an estimated value of the heat flow of about $0.8 \cdot 10^{-6}$ cal./cm².sec. This is not very far from the value of heat flow found by Benfield in England and by Bullard and Krige in South Africa,²⁸ in a beautiful series of measurements. Up to the present time, most geothermal observations have been made in sedimentary rocks, whose conductivities cannot as yet be estimated with precision. An increasing number of measurements are being made in igneous rocks, however, and the possibility of arriving at a good approximation to the conductivity of such rocks on the basis of thin-section analyses rather than on laborious conductivity studies may encourage attempts to make the fullest use of such material.

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²⁷ Vladimirov, O., Kraskovski, S., and Semenov, A.: C. R. Acad. Sci. U. R. S. S. 23, 355, 1939.

²⁸ Benfield, A. E.: Proc. Roy. Soc. A 173, 428, 1939; Krige, L. J.: *idem*. 173, 450, 1939.