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ENERGY TRANSFER IN THE EARTH'S MANTLE

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# ENERGY TRANSFER IN THE EARTH'S MANTLE<sup>1</sup>

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## ABSTRACT

Several processes of energy transfer in the earth's mantle are examined: (1) gray radiation, (2) ambipolar diffusion of electron-hole pairs, (3) exciton transfer, and others. Using Rikitake's values of the electrical conductivity and correcting for the frequency dependence of the conductivity and the variation of the index of refraction with depth, the values for the radiative contribution to the heat flow are found to be appreciably larger than those estimated by Clark. Estimation of contributions from the electronic processes shows that conduction by excitons may play an important role in the lower parts of the mantle.

## INTRODUCTION

In recent years a wide variety of experimental and theoretical work has been performed on the flow of energy in solids. Chandrasekhar (1939) has shown the importance to astrophysics of the flow of radiant energy. More recently certain workers in the glass industry have demonstrated its importance in this area. A recent critical review of much of this work has been published by Gardon (1956). Clark (1956) has applied these concepts to the study of the mantle. In addition, theoretical work has been carried out on various electronic processes (Pikus, 1956). That such contributions exist has been confirmed by experiments of Busch (1954) and Joffe (1956). The purpose of this paper is to estimate these effects in the mantle. It will be shown that these effects can be an order of magnitude greater than the theoretical values of the normal lattice conductivity calculated by Uffen (1954).

## RADIATION TRANSFER

In a recent series of papers Clark has shown that for an absorption coefficient,  $\alpha$ , between 10 and 100  $\text{cm}^{-1}$ , the effect of energy transfer by radiation may be important in determining the earth's temperature gradient (Clark, 1956). He has also shown experimentally that certain minerals, commonly thought to occur at least in the upper portion of the mantle, are at least

this transparent, even allowing for selective  $\text{Fe}^{++}$  absorption (Clark, 1957*a*). In a third paper (Clark 1957*b*), he estimated the increase in absorption at higher temperatures arising from the absorption of light by the "free" electrons of the intrinsically semiconducting "silicate" mantle. From his analysis Clark concludes that at elevated temperatures the enhanced absorption from this process is so high that radiative cooling can be important only in the outer mantle.

Prior to the appearance of the latter two papers, the authors had carried out a similar analysis. This fact would not be worthy of note, particularly since our formulas are identical with those of Clark, if our conclusions were in agreement. As a matter of fact, we have concluded that intrinsic semiconductor-type absorption of radiation cannot limit radiative transfer to a degree that makes it negligible compared to ordinary thermal conduction. Such a limitation to radiation transfer, if it exists, must be the result of other types of absorption, e.g., absorption by  $\text{Fe}^{++}$  ions. As will be seen, the present analysis does not conflict with Clark's conclusions on the upper (say 400-km.) portion of the mantle.

We agree with Clark that the pertinent equations for the "gray" case are

$$\alpha = \frac{120\pi\sigma(\omega)}{n} \quad (1)$$

and

$$K_r = \frac{16n^2 sT^3}{3\alpha}, \quad (2)$$

<sup>1</sup> Manuscript received March 17, 1958.

where  $\alpha$  is the average absorption coefficient for the frequency range of importance at temperature  $T$ ;  $n$  is the refractive index;  $s$  is the Stefan-Boltzmann constant;  $\sigma(\omega)$  is the conductivity in  $\text{ohm}^{-1} \text{cm}^{-1}$ ; and  $K_r$  is the radiative component of thermal-energy transfer. However,  $\omega$  is the angular frequency (not the frequency, as stated by Clark).

Specifically, our disagreement with Clark arises from the following three points.

1. We believe that an extrapolation of deduced conductivities versus depth based empirically on the observed rate of propagation of magnetic disturbances in the mantle is sounder data than that based on the electrical behavior of a few crustal silicates.

2. We do not believe that  $\sigma(\omega) \cong \sigma(0)$ .

3. We do not believe that it is justifiable to neglect the pressure variation of the refractive index. Our method of approach has been to bound (rather than estimate)  $\alpha$  from above and  $K_r$  from below, using solid-state theory. We shall now attempt to substantiate our point of view.

From classical theory,

$$\sigma(0) = \sigma(\omega) \left[ 1 + \left( \frac{\omega}{2\pi\gamma} \right)^2 \right], \quad (3)$$

where

$$\gamma = \frac{e}{2\pi m^* b}, \quad (4)$$

in which  $e$  is the electronic charge,  $m^*$  is the effective mass of the carriers, and  $b$  is the mobility;  $m^*$  approaches  $m$  at high temperatures because of the smearing of band edges, as is known from liquid behavior. Hence we shall take  $m^* = m$  the mass of a free electron, as Clark did. The mobility is given by

$$b = \frac{4el}{3(2\pi mkT)^{1/2}}, \quad (5)$$

in which  $k$  is Boltzmann's constant and  $l$  is the mean free path (Shockley, 1950).

An estimate of the minimum value of  $b$  may be made by taking  $l = l_0$ , the minimum possible distance between scattering centers, i.e., of the order of magnitude of

a few angstroms. This minimum value  $b$  turns out to be about 1 cm/sec/volt/cm. Even for this low value of  $b$ , for optical frequencies,  $\sigma(\omega)$  will be appreciably less than  $\sigma(0)$ .

To obtain a more realistic estimate of  $l$ , we use the relation, derivable from deformation potential theory (Shockley, 1950),

$$l_n = \frac{\pi \hbar^4 c_{11}}{\mathcal{E}_{1n}^2 k T m_n^2}, \quad (6)$$

where  $\mathcal{E}_{1n}$  is the logarithmic derivative with respect to the volume of the energy of the bottom of the conduction band, and  $c_{11}$  an elastic constant. The subscript  $n$  refers to electrons; a similar expression with  $n$  replaced by  $p$  is valid for holes. We here assume, for simplicity,  $l_n = l_p$ .

Let us choose some nominal depth below the crust, which we shall call the "surface,"  $s$ , where the melting point  $T_{ms}$  may be estimated. For  $s = 100$  km,  $T_{ms} = 1,800^\circ \text{K}$ , according to Gutenberg (1939). For this value of  $s$ , we shall take  $l_{ms}$ , the mean free path at  $T_{ms}$ , equal to its minimum value  $2.76 \text{ \AA}$ , i.e., twice a nominal oxygen ion radius. Then, for the actual temperature  $T_s$  of this surface, the mean free path according to equation (6) is related to  $l_{ms}$  by the inequality

$$l_s > \frac{l_{ms} T_{ms}}{T_s}, \quad (7)$$

since the elastic constants increase with decreasing temperature. At any other depth, assuming that  $\mathcal{E}_{1n}$  is independent of volume, we have

$$l \geq \frac{l_{ms} T_{ms} c_{11}}{T c_{11s}} \quad (8)$$

or

$$l \geq \frac{l_{ms} T_{ms} \rho v_L^2}{T \rho_s v_{Ls}^2}. \quad (9)$$

A more stringent estimate of a minimum  $l$  may be obtained by assuming only that  $\mathcal{E}_{1n}$  is independent of temperature in the following way. Assume that the mean free path  $l_m$  at the melting point corresponding



to the depth in question is the oxygen spacing at that depth. Then

$$l_m = l_{ms} \left( \frac{\rho_s}{\rho} \right)^{1/3} \quad (10)$$

and again, by equation (6) as before,

$$l > \frac{T_m l_n}{T}. \quad (11)$$

Now according to Gilvarry (1957), from the Lindemann theory of melting, we have  $T_m$  proportional to  $c_{11}/\rho$  or the velocity of sound squared. Hence we have

$$l > l_{ms} \left( \frac{\rho_s}{\rho} \right)^{1/3} \frac{T_{ms} v_L^2}{T v_{Ls}^2}. \quad (12)$$

In calculating the values of  $l$  for various assumed temperature distributions, we have empirically taken  $l$  to be between the values of equations (9) and (12), according to the formula

$$l = l_{ms} \left( \frac{\rho}{\rho_s} \right)^{2/3} \frac{T_{ms} v_L^2}{T v_{Ls}^2}. \quad (13)$$

In deriving equation (12), we have neglected a possible 10 per cent variation in an empirical constant in the Lindemann equation that is related to the packing of the structures and that might change if phase transformations occurred.

We estimate  $n$  from a commonly used empirical equation,

$$n = c\rho + 1, \quad (14)$$

where  $c$  is a constant adjusted to give  $n = 1.70$  at the 33-km. level. For our purposes, this estimate of  $n$  is superior to the Clausius-Mosotti relationship, since it is lower and presumably approximates better the change in the polarizability which decreases with pressure. For comparison (14) leads to  $n = 2.205$  at 2,900 km., while the Clausius-Mosotti gives  $n = 2.6$  at that level. Equation (14) also underestimates  $n$  for substances which undergo a polymorphic transition with pressure, since their index is higher because of their greater density.

Using data from magnetic disturbances, Rikitake (1950-1951, 1951, 1952) has calculated the electrical conductivity in the mantle to the 1,200-1,400-km. level. His equation of best fit is given as  $\sigma = 10^{-3} (r/a)^{-11}$  mho, in which  $a$  is the earth's radius and  $r$  the radial distance from the center. This leads to an extrapolated value of 0.79 mho at the core boundary. Runcorn's (1955) estimate of 1 mho through the lower 2,000 km. of the mantle may be regarded as confirming evidence. Densities and longitudinal wave velocities have been taken from Bullen (1953). The quantity  $\omega$  is taken equal to the angular frequency of maximum density of radiation energy and may be calculated from Wien's law.

Values for  $\alpha$  calculated from equations (1), (3), (4), (5), (13), and (14) are given in table 1. Corresponding values for  $K_r$  are given in table 2 and illustrated in figure 1.

As may be seen, the  $K_r$  is sufficiently high in all parts of the mantle to dominate the thermal conduction mechanism. If intrinsic semiconductor radiation absorption is the only significant mechanism, we are forced to the conclusion that the mantle is highly conducting of heat, much more so than previously supposed, or that the temperatures are much lower.

#### EFFECT OF ALTERNATIVE SCATTERING MECHANISMS ON $b$

In the previous discussion, we have calculated the mobility  $b$  as if the mean free path of the electrons (and also the holes) were determined solely by the thermal scattering. Actually, it is necessary to consider alternative scattering processes such as those arising from impurities. Furthermore, we have assumed that the semiconducting mantle is nondegenerate. We shall now examine critically both these assumptions.

To study the possibility of degeneracy, let us assume in the earth's mantle that we have present at least 1 per cent impurities which can act as either donors or acceptors. Then, according to Johnson and Lark-

Horowitz (1947), for a degenerate semiconductor the conductivity is given by

$$\sigma = \frac{n^{1/3}}{6,270} \text{ ohm}^{-1} \text{ cm}^{-1}, \quad (15)$$

where  $n$  is the volume density in  $\text{cm}^{-3}$  of effective impurities. If at the base of the mantle we assume that the molal volume is approximately  $15 \text{ cm}^3$ , then  $n = 4 \times 10^{20}$  and  $\sigma = 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ . For a higher density of impurities,  $\sigma$  is correspondingly higher. Since  $\sigma$  is already a factor of a thousand

where  $\epsilon$  is the dielectric constant and  $N$  is the volume density of neutral impurities. Suppose we assume that the composition of the deep mantle is the same as olivine (although the packing and chemical arrangement may be different). Deep in the mantle the iron should be completely converted to the divalent state. If it is scattered at random as a substitutional impurity on divalent magnesium sites, it will act as a neutral impurity. For 20 per cent  $\text{Fe}^{++}$  and 80 per cent  $\text{Mg}^{++}$ , which seems to

TABLE 1  
MAXIMUM VALUES OF  $\alpha$ , THE "GRAY" ABSORPTION COEFFICIENT  
(IN  $\text{CM}^{-1}$ ) FROM ELECTRONIC SCATTERING

$d$ (Km.)	1,000	1,500	2,000	$T$ ( $^{\circ}\text{K}$ )			
				2,500	3,000	4,000	5,000
413.....	0.096	0.130	0.158	0.181	0.201	0.233	0.257
600.....	0.073	0.104	0.130	0.154	0.176	0.214	0.246
800.....	0.073	0.105	0.134	0.161	0.186	0.232	0.271
1,000.....	0.092	0.133	0.171	0.207	0.240	0.301	0.354
1,400.....	0.157	0.229	0.296	0.360	0.422	0.538	0.639
1,800.....	0.314	0.461	0.600	0.734	0.864	1.11	1.33
2,200.....	0.678	1.00	1.31	1.60	1.90	2.45	2.96
2,600.....	1.68	2.49	3.27	4.02	4.77	6.19	7.51
2,900.....	3.78	5.60	7.34	9.05	10.8	14.0	17.0

TABLE 2  
VALUES OF EFFECTIVE RADIATIVE COMPONENT OF THERMAL ENERGY IN  
 $\text{CAL}/^{\circ}\text{C}/\text{SEC}/\text{CM}$  IF LIMITED ONLY BY ELECTRONIC SCATTERING

$d$ (Km.)	1,000	1,500	2,000	$T$ ( $^{\circ}\text{K}$ )			
				2,500	3,000	4,000	5,000
413.....	0.250	0.624	1.22	2.07	3.22	6.59	11.7
600.....	0.366	0.873	1.64	2.70	4.09	7.98	13.6
800.....	0.397	0.932	1.72	2.80	4.19	7.96	13.3
1,000.....	0.328	0.764	1.41	2.28	3.39	6.41	10.7
1,400.....	0.202	0.467	0.853	1.37	2.02	3.76	6.18
1,800.....	0.105	0.243	0.441	0.704	1.03	1.91	3.11
2,200.....	0.051	0.116	0.211	0.335	0.491	0.900	1.46
2,600.....	0.021	0.049	0.088	0.140	0.203	0.371	0.637
2,900.....	0.010	0.022	0.040	0.061	0.093	0.170	0.272

greater than the highest observed conductivity even if only 1 per cent effective impurities are present, it seems unlikely that the mantle ever acts as a degenerate semiconductor.

We must nevertheless consider the effect of neutral impurity scattering centers. Then, according to Erginsoy (1950), the mobility is limited by such centers to

$$b_n = \frac{m e^3}{20 N \epsilon \hbar^3}, \quad (16)$$

be a reasonable distribution to assume,  $b_n = 56 \text{ cm}^2/\text{sec}/\text{volt}/\text{cm}$ . Since this is a much higher mobility than those estimated from thermal scattering, it seems that neutral impurities could play a significant role only in the outer portions of the mantle.

#### ABSORPTION BY TRANSITION METAL IONS

In the foregoing, the only absorption process considered has been that arising from the free carriers. As a matter of fact,



characteristic absorption bands arising from the presence of  $\text{Fe}^{++}$  ions are known to occur in a wide variety of liquid and solid solutions. The origin of this absorption has been the subject of extensive theoretical analysis, the most recent of which is reported by Dunitz and Orgel (1957). In brief, the

levels of the unfilled  $d$ -shells of the iron ion are split by the crystalline field. Transitions between some of these split levels are allowed and lead to a strong absorption of  $\text{Fe}^{++}$  at approximately  $10,500 \text{ cm}^{-1}$  in oxides and hydrates. Clark (1957*a*) has observed this band in some minerals and has

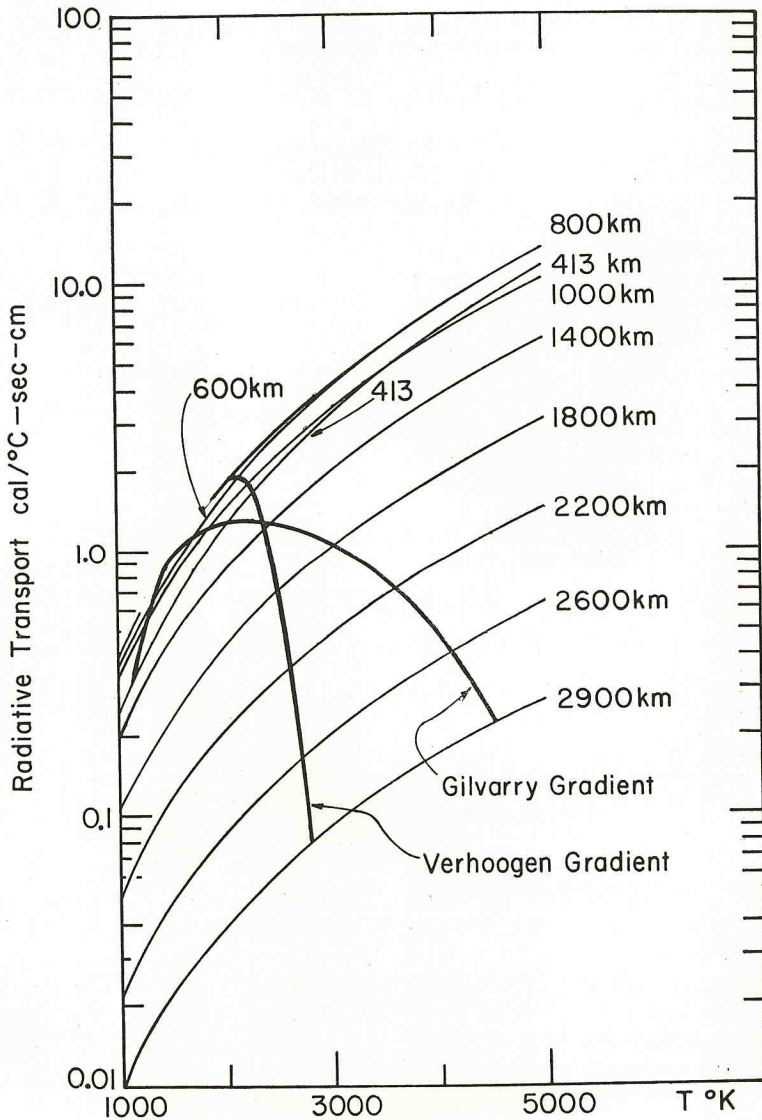


FIG. 1.—Radiative transport coefficient  $K_r$ , calculated from equation (2) as a function of temperature for various depths. The parabolic-type curves indicate possible values for  $K_r$  as a function of depth for two assumed temperature distributions.

shown that the presence of the band does not materially affect the conclusion that radiative transfer is important, if the band is not materially shifted or enhanced by pressure.

As a matter of fact, it is likely that the nature of the optical absorption in the minerals composing the mantle varies with depth for a variety of reasons discussed below, and the information obtained from minerals available at the surface of the mantle may be misleading.

The problem of absorption by  $\text{Fe}^{++}$  ions

in an octahedral field has been treated by Furlani and Sartori (1957) and by Tanabe and Sugano (1954). Using Slater  $F$ -functions for the free ion as a starting point, they calculated the matrix elements for a perturbing octahedral field of a given value of the field strength. We have extended these results by the use of second-order perturbation theory to derive approximate curves for the dependence of the energy levels on field strength. The resulting curves are shown in figure 2. Such curves permit certain qualitative conclusions to be drawn

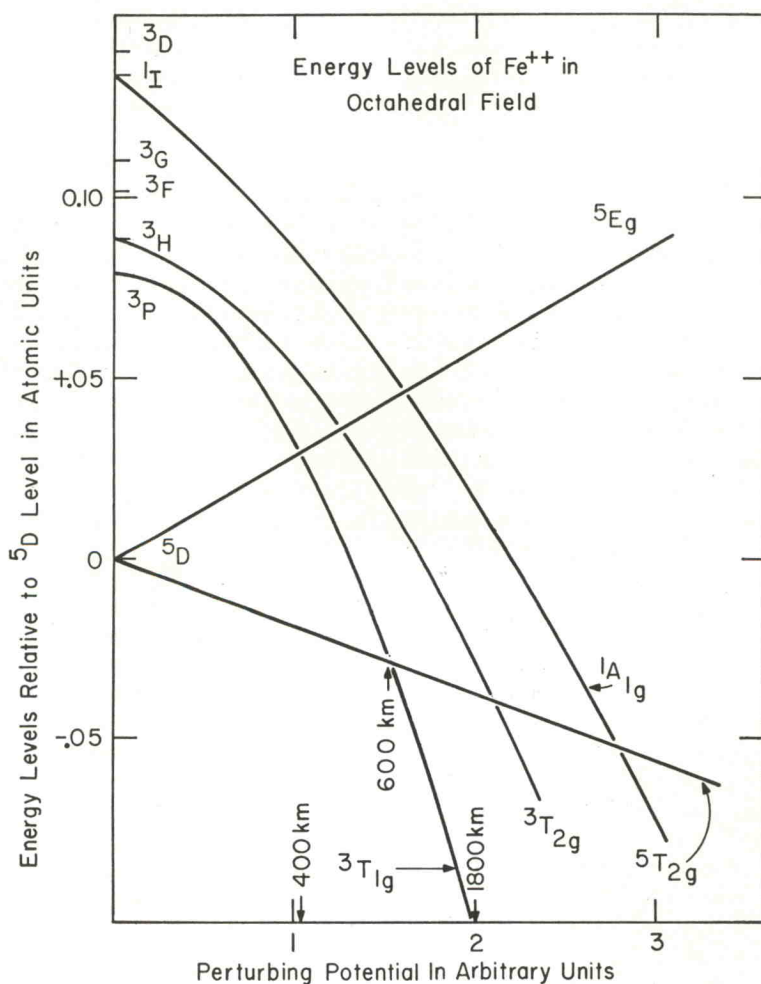


FIG. 2.—An Orgel-type diagram for  $\text{Fe}^{++}$  calculated from Furlani's matrix elements. The arrows indicate depths within the earth on the basis of the reasonable assumption of an absorption band at  $10,500 \text{ cm}^{-1}$  near the surface. The diagram may be scaled for any other desired assumption.



about the change in absorption as a function of depth in the mantle.

To utilize figure 2, we must interpret the units on the abscissa. The field strength  $F$  may be calculated from a function given by Hartmann and Ilse (1951), which (to a degree of approximation satisfactory for our purposes) is given by

$$F = \text{Const. } R^{-6}, \quad (17)$$

where  $R$  is the distance between the  $\text{Fe}^{++}$  ion and the units producing the octahedral field. The constant in equation (17) may be evaluated empirically by setting the observed spacing of the  ${}^5E_g$  and  ${}^5T_{2g}$  levels equal to the observed  $h\nu$  of the principal absorption peak of a suitable ferrous-bearing mineral. We have already remarked that this spacing is approximately  $10,500 \text{ cm}^{-1}$  in hydrates. Clark (1957*a*) finds the absorption peak in diopside and olivine at  $9,000 \text{ cm}^{-1}$ . If, for example, we assume  $10,500 \text{ cm}^{-1}$  as the position of the peak of the  $\text{Fe}^{++}$  absorption band at 413 km., then the perturbing potential in arbitrary units corresponding to this is shown in figure 2. For a different position of the peak, the appropriate corresponding potential must be chosen proportionately to the level spacing. Assuming that the level spacing varies as the inverse square of the density, we observe that the absorption peak moves to the ultraviolet until a depth of approximately 600 km. is reached, when the  ${}^3T_{1g}$  level crosses the  ${}^5T_{2g}$  level and becomes the lowest state. At this point a new band will appear in the infrared corresponding to  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  transition of approximately the same intensity. (Note the  ${}^3T_{1g} \rightarrow {}^5E_g$  is spin forbidden and any absorption from such a transition will be one or two orders of magnitude lower than for the  ${}^5T_{2g} \rightarrow {}^5E_g$ .) As one goes deeper into the mantle, this band will gradually increase in intensity as the first band dies out, owing to the change in relative thermal excitation of the two states. In addition, this new band will rapidly shift farther into the ultraviolet, with further increase in depth. Even after the crossover in levels occurs, the two bands

should always be on the ultraviolet side of the absorption peak at atmospheric pressure. This conclusion is valid even if a phase transformation occurs, provided that the higher-density modification has at least as high an octahedral perturbing field as the low-density phase and no other types, e.g., tetrahedral, of field splitting are introduced. Consider as a prototype mineral an iron magnesium silicate such as olivine. Presumably this will transform at a depth of several hundred kilometers to the spinel modification reported by Ringwood (1958).

If the compressed olivine structure is a normal spinel, the  $\text{Fe}^{++}$  ions will all occur in octahedral sites. If it is inverted, half the  $\text{Fe}^{++}$  ions will occur on tetrahedral sites. In general, according to McClure (1957), the absorption of  $\text{Fe}^{++}$  on tetrahedral sites will occur at about four-ninths of the wave number associated with the octahedral sites. This absorption, if it occurs, would radically alter the conclusions concerning the importance of radiative transfer in the mantle. No detailed information is available for dependence of such absorption lines with depth (i.e., pressure). McClure has shown that  $\text{Fe}^{++}$  in spinel is more stable on octahedral sites, and so the olivine spinel is presumably normal.<sup>2</sup>

In the foregoing discussion, we have neglected the effects of pressure on the free ion wave functions and also assumed that the crystal is ionic. As the crystal is compressed, the binding becomes less ionic and more homopolar. This requires the replacement of the constant of equation (12) by a monotonically decreasing function with pressure. The net effect is to cause the crossing of the  ${}^5T_{2g}$  and the  ${}^3T_{1g}$  terms to occur at a greater depth, since the tendency to homopolar binding is to decrease the electrostatic field.

It is, of course, conceivable that a  $3d$  electron is squeezed out of the iron at high pressures, resulting in a change in the elec-

<sup>2</sup> S. P. Clark has kindly called to our attention the fact that, since the silicon ions would occupy octahedral sites in an inverse structure, this structure is most improbable.



tronic configuration of the free ion. Such a transition would correspond to the creation of  $\text{Fe}^{+++}$  ions from  $\text{Fe}^{++}$ . The smaller size of the  $\text{Fe}^{+++}$  ion would favor its appearance under pressure. However, the strongly reducing atmosphere at the base of the mantle has led most chemists to believe that the  $\text{Fe}^{++}$  state is favored (Urey, 1952). The  $\text{Fe}^{+++}$  absorption is much farther from the infrared. Again, in this case, no detailed information is available to predict the absorption as a function of depth. The presence of an appreciable amount of both  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$  states would presumably lead to a charge-transfer mechanism of conductivity, resulting in a much higher  $\sigma$  (such as that of magnetite) than is inferred from magnetic measurements.

Our discussion of absorption by transition metals has been limited to the case of iron. In principal, similar discussions can be carried out for other ions such as  $\text{Mn}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ , etc. In general, however, the absorption peaks of these ions lie much farther in the ultraviolet. In addition, the abundance of these elements is lower. For this reason, they will not be considered in detail here.

We have noted that the  $\text{Fe}^{++}$  absorption, if unaltered in position and intensity by depth, would not materially affect the radiant-energy flux. It is now necessary to consider the change in intensity of a given absorption peak with depth. If the absorption increases sufficiently rapidly with depth, this may outweigh the decrease in absorption due to the blue shift. Two theoretical statements may be made. According to Orgel (1955), the half-width of the absorption band is related to the rate of change of the energy gap with respect to the strength of the octahedral field. As may be seen in figure 2, since both  ${}^5T_{2g}$  and  ${}^5E_g$  are linear functions of the field parameter, the band width should be constant to a first approximation if we ignore the small smearing due to temperature effects and assume that the degeneracy of the levels is not destroyed by deviations from a true cubic-field symmetry. This statement holds

until the crossover in levels occurs. Assuming constant band width, the only other factor needed for an estimate of absorption intensity is the molar extinction coefficient  $\epsilon_{\text{max}}$  at the frequency of maximum absorption  $\nu_{\text{max}}$ .  $\epsilon_{\text{max}}$  may be estimated by a formula given by Ballhausen (1955). By reworking his equations (1) and (4), we find

$$\epsilon_{\text{max}} = \frac{21.7 (\tau/2)^2 \nu_{\text{max}}^3}{\nu^+ \Delta\nu}, \quad (18)$$

where  $\tau$  is the ligand distance in Å,  $\Delta\nu$  is the half-width of the absorption band, and  $\nu^+$  is the frequency of the transition from the ground state to the first state of opposite parity (in the sense of Laporte's rule) in the free ion. Typical values for  $\nu^+$  are given by Ballhausen (1955) and yield values for  $\epsilon_{\text{max}}$  of the order of 10 for the observed values of  $\Delta\nu/\nu_{\text{max}}$  of 25 per cent. Since  $\nu_{\text{max}}$  varies as  $r^{-6}$ , the resultant increase in intensity is a factor of 2 in going from 400 to 600 km. assuming constant composition. These numbers are in rough agreement with measurements of Drickhamer (1958) to 200,000 bars on absorption by transition metal complexes.

It remains to discuss the effect of  $\text{Fe}^{++}$  absorption on the radiative flux of energy. It may easily be shown that, for the highest temperature (4,500° K) under consideration here and the lowest absorption peak of  $9,500 \text{ cm}^{-1}$ , the radiant flux is reduced by only 15 per cent if the band width is approximately the same as at atmospheric pressure. This is true even if  $\alpha$  is assumed  $\infty$  within the band. As mentioned above, we believe that the absorption peak is farther in the blue at great depths and hence that absorption by  $\text{Fe}^{++}$  ions is unappreciable.

#### RESTSTRAHLUNG AND ULTRAVIOLET ABSORPTION

Two final sources of absorption remain to be considered. Clark (1957b) has already concluded that the encroachment of the lattice absorption bands is not an important effect. If one were to accept Runcorn's

(1955) estimate of the semiconductor gap  $\Delta E$  for the base of the mantle of 0.92 eV (for 2,600° K), the fundamental absorption band would almost coincide with the Wien law maximum wave length. However, using Rikitake's value for the conductivity of the mantle, we may estimate *minimum* values of the thermal activation energy  $\Delta E$  from the formula  $\sigma = 2 neb$  by setting  $b = 1$ . We obtain  $\Delta E = 1.34$  eV, 1.87 eV, and 2.41 eV for assumed temperatures of 2,500°, 3,500°, and 4,500° K, respectively. The values of  $b$  as given by equation (5) would increase these  $\Delta E$  values by only a few per cent. However, because of the ionic character of the bonding, the optical

tional contribution to the heat conductivity  $\Delta \kappa_p$  from this source is given by

$$\Delta \kappa_p = 2L \frac{\sigma_+ \sigma_-}{\sigma_+ + \sigma_-} \left( \frac{\Delta E}{2kT} + 2 + r \right)^2 T, \quad (19)$$

where  $\sigma_-$  is the electron conductivity,  $\sigma_+$  the conductivity due to holes,  $\Delta E$  the gap energy, and  $r$  a measure of gap change with temperature and pressure;  $L$  is the Lorenz number equal approximately to  $(k/e)^2$ , where  $k$  is Boltzmann's constant and  $e$  the electronic charge. We set  $\sigma_+ = \sigma_-$  and  $r = 0$ . With the largest  $\Delta E$  estimated above and  $T = 4,500^\circ$  K, we obtain  $\Delta \kappa_p \cong 7(10)^{-4}$  cal/°C/cm/sec which is not large enough to affect materially our previous conclusions. In fact, Joffe has pointed out that this effect is several orders of magnitude less than the observed increase in thermal conductivity in InSb, although in certain materials the formula appears to account for the experimental data.

Another electronic process capable of transferring energy is the transport of excitation energy by excitons. This mechanism was suggested by Fröhlich and Kittel (1954) to explain the anomalously high heat conductivity observed in InSb by Busch and Schneider (1954). This process has been considered in detail by Pikus (1956), who shows that

$$\Delta \kappa_{ex} = 6.64 (10)^3 l_0 T^2 \times \left[ \left( \frac{E_{ex}}{kT} + 2 \right)^2 + 2 \right] e^{-E_{ex}/kT}, \quad (20)$$

where  $l_0$  is the mean free path of the excitons and  $E_{ex}$  is the excitation energy. Joffe (1956) suggests that this process can explain enhanced heat conductivities in a number of substances studied by him. In table 3 are given a few values for  $\Delta \kappa_{ex}$ , the portion of the heat conductivity given by exciton flow for  $E_{ex} = 0.31$  eV and  $E_{ex} = 1.19$  eV. These numbers are actually taken from Clark's (1957a) olivine data but should be taken only as representatives of exciton energy levels, since the identification by Clark of certain peaks as arising from exciton levels is uncertain. Because the maxi-

TABLE 3  
VALUES OF  $\Delta \kappa_{ex}$ , EXCITON CONTRIBUTION TO THERMAL CONDUCTIVITY FOR TWO ASSUMED EXCITON LEVELS (IN CAL/°C/SEC/CM)

T (° K)	$\Delta \kappa_{ex}$	
	( $E_{ex} = 0.31$ eV)	( $E_{ex} = 1.19$ eV)
1,000	0.06	0.002
2,000	0.072	0.02
3,000	2.2	0.27
4,000	4.5	1.2

activation energy is greater than the thermal activation energy by approximately the factor  $\epsilon/n^2$ , where  $\epsilon$  is the static dielectric constant (for a discussion of this point see Dekker, 1957). The maximum effect of fundamental absorption on radiant flux is only 15 per cent for  $\Delta E = 1.34$  and  $T = 2,700^\circ$  K. For higher assumed temperatures,  $\Delta E$  is larger, and the absorption is less. Because of the expected difference in thermal and optical activation energy, fundamental absorption is probably negligible.

#### ELECTRONIC TRANSFER OF ENERGY

A number of electronic processes of heat transfer operate in semiconductors. These have been reviewed recently, and experimental data given by Joffe (1956). The processes include electron-hole ambipolar pair diffusion in a thermal gradient. The addi-



imum energy gap for exciton levels must at all times be less than the conduction gap, it is to be noted that even for  $E_{ex} = 1.19$  ev, which is a reasonable value near the base of the mantle, the contribution from exciton flow can be very appreciable. For smaller  $E_{ex}$  (at constant temperature) it becomes even larger.

The authors (1958) have reconsidered the analysis by McQuarrie (1954) of the

data on the heat conductivity of  $MgO$ ,  $Al_2O_3$ , and  $BeO$  as a function of temperature. McQuarrie established the existence of an enhanced conductivity at high temperatures which he found to vary as  $T^{-10}$  and which he believed was radiative in origin. The data, however, fit equally well to a linear dependence of  $\log \Delta\kappa_{ex}$  versus  $1/T$ . For this reason the authors believe the enhanced conductivity to be a result of conduction

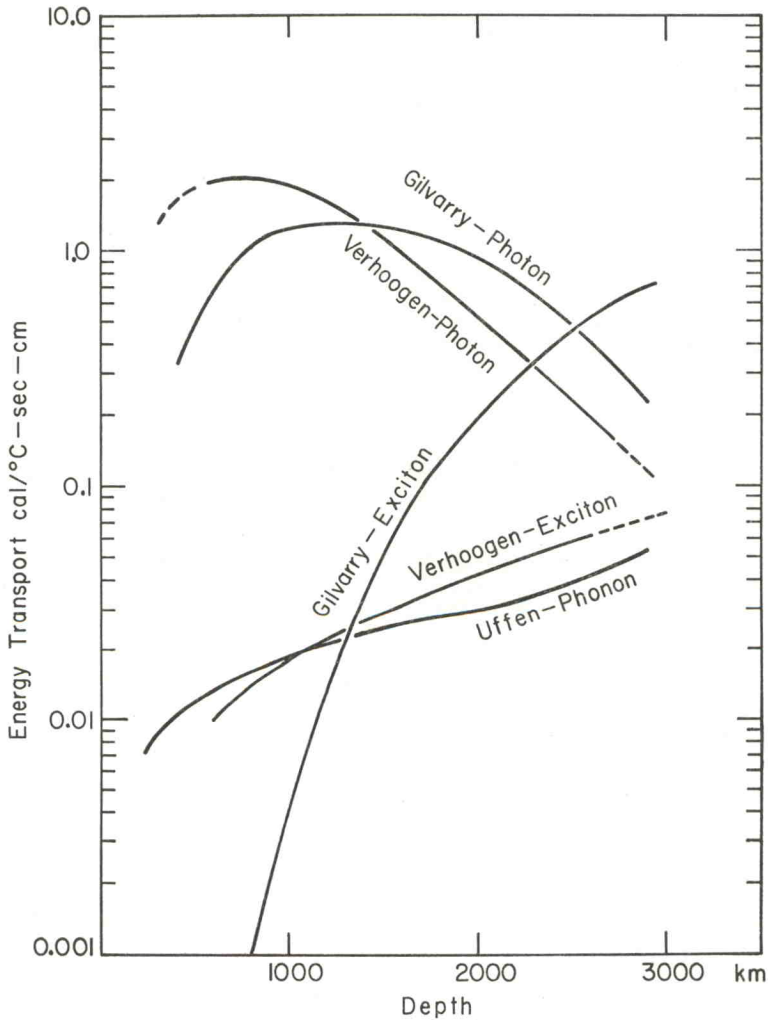


FIG. 3.—Summary of the contributions made by phonons, photons, and excitons for the energy transport in the earth's mantle. The photon contribution is obtained from equation (2). The exciton contribution has been estimated by extrapolating observed data on the heat conductivity of  $MgO$ . The total heat transport is the sum of the appropriate curves for the assumed temperature distribution.



by excitons. For MgO, the data fit equation (20) with  $l_0 \cong 10^{-5}$  cm. We have therefore used this value in preparing table 3. (Dekker, 1957, quotes a figure of  $l_0 \leq 10^{-4}$  cm.)

#### DISCUSSION

We have shown above that the principal limitation on radiative flux is provided by free-electron absorption. When this absorption is corrected for the frequency variation of the conductivity and the variation of the index of refraction with pressure, it is found that the radiative flux may be appreciable in the earth's mantle. Since the radiative flux depends on the absolute temperature cubed, it is necessary to assume a temperature distribution within the earth in order to estimate the effective contribution to the heat conductivity at any depth. Using Verhoogen's temperature distribution as quoted by Jacobs (1956) and Gilvarry's (1957) distribution, we have estimated, by means of figure 1 (which shows the variation of  $K_r$  with  $T$ ), the variation of  $K_r$  as a function of depth in the mantle. This variation is plotted in figure 3. The two temperature distributions considered here were used because they cover the extremes in temperature currently considered admissible within the mantle (Verhoogen, 1956). The two values of  $K_r$  so obtained are compared with the phonon transport estimated by Uffen (1954). It should be pointed out that the validity of all the formulas used above involves the assumption that the mean free path is not limited by grain size. The largest

mean free path involved is for radiation near the top of the mantle, where the mean free path is of the order of centimeters. Also plotted in figure 3 for the two temperature distributions is the *extra* conductivity of MgO extrapolated from lower temperatures ( $\sim 2,000^\circ$  K). If the  $E_{ex}$  for the material composing the mantle is larger or smaller, the exciton contribution will vary accordingly in the manner suggested by table 3. Since the gap energy apparently decreases with depth, it is probable that the data in figure 3 are not far from minimum values.

The contribution of electron-hole pairs is negligible and has not been included in figure 3.

It is seen that the effective conductivity of the earth's mantle can be of the order of magnitude of 0.5–2.0 cal/ $^\circ$  C/sec/cm from about 400 km. to the base, i.e., of the same order of magnitude as the liquid core.

Such a high effective conductivity raises interesting questions concerning the thermal history of the earth and the compatibility of assumed gradients of temperature within the core. These problems are, however, beyond the scope of this investigation.

Inasmuch as the conclusions drawn here depend to a large extent on the reliability of the estimates of the electrical conductivity within the mantle, the desirability of more accurate data is immediately apparent.

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