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Abstract

The theories of heat transfer in insulators are reviewed and discussed revelant to UO_2. As the rate of heat transfer from a reactor core is determined largely by the thermal conductivity of the fuel, this coefficient is of paramount importance to improving the efficiency of an installation. There is no theoretical basis to expect small or moderate chemical additions to increase the thermal conductivity of UO_2 when the oxide is classed as an insulator. Large additions of a phase having a high thermal conductivity have been found to increase the net conductivity. Such systems were two phase and had poor sintering characteristics.

Considering UO_2 as a potential oxidic semiconductor there is a possibility of increasing the thermal conductivity by proper doping. Thermal conduction by intrinsic carriers has been treated experimentally and theoretically and the conductivity values of the two cases do not presently agree, i.e., the

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Wiedemann-Franz law is not obeyed. The extrinsic case such as a doped oxide has not been treated theoretically. Recent measurements indicate that doping UO_2 with Y^{+3} and Nb^{+5} increases the thermal conductivity. This data is sparce, the magnitude of the increase and its dependence upon impurity concentration and temperature have not been determined.

Introduction

The past few years have witnessed great strides in reactor technology. The core temperatures of power reactors have steadily been increased to the point where their advancement is limited primarily by the physical properties of the materials constituting the core. In general, reactor efficiency increases as a function of the temperature differential between the core and its environment, hence the importance of high core temperatures is evident.

This striving for higher operating temperatures has led to the use of ceramic cores. One of the first ceramics investigated for this application was sintered UO_2 and it is presently being used as the fuel material in some reactors in the form of canned cylindrical pellets. One of the major disadvantages of UO_2 as a core material is its low thermal conductivity. Since a low conductivity limits the rate at which heat can be removed from the core it is obvious that this property of the ceramic is one of the major limitations on the operating temperature and subsequently the efficiency of a reactor installation.

This survey was made to elucidate the present theories on thermal conduction in solids, primarily the class including UO_2. Thermal conduction in insulators is discussed in detail since UO_2 might be classed in this group of solids. Thermal conduction in semiconductors is also considered since with the proper impurity additions, UO_2 becomes an extrinsic semiconductor.

Summary

Considering UO_2 as an insulator, there is no theoretical reason to expect either moderate or small additions of oxides or other compounds to increase the thermal conductivity of sintered UO_2. The improvement noted by McCreight(29) with large additions of BeO were undoubtedly due to a continuous BeO phase being present although no X-ray analyses were made of the resulting bodies. If small amounts of foreign ions enter the UO_2 lattice they would act as scattering centers and decrease the conductivity. On the other hand, if the additions would not react with the UO_2 at the sintering temperature they would be present on the grain boundaries as a second phase and inhibit the thermal flow by a more macroscopic process. The formation of a solid solution would also decrease the phonon conductivity by disrupting the periodicity of the lattice.

Considering UO_2 as a potential semiconductor there is a possibility that the thermal conductivity could be increased particularly at elevated temperatures. No indication was found in the literature that an electronic component of thermal conductivity has been induced in an oxide, but it is the author's belief that this effect has not previously been looked for in sintered oxides which have been doped. Recent work has indicated that tentatively an increase in the thermal conductivity of UO_2 occurs at 500°C with yttrium (Y^{+3}) additions.

The theory of heat transport in semiconductors does not presently describe satisfactorily the behavior of such thoroughly studied materials as silicon and germanium, hence no qualitative estimates of the required impurity density or expected magnitude of the electronic thermal conductivity component can be made for an oxide such as UO_2. This could be verified only by physical measurements of the conductivity of doped samples at elevated temperatures.

Theory of Heat Transfer in Solids

As noted in the introduction a survey of the literature was made to review the theories of heat transfer in crystalline solids and an effort made to determine whether the possibility exists of increasing the thermal conductivity of an essentially pure insulator.

A theory of the thermal conductivity of insulators was developed in 1914 by Debye(1); as in his theory of the specific heat (1912), he assumed that the lattice vibrations may be described by a model in which elastic waves are propagated through a continuum. Since solids expand upon heating, these waves cannot be purely harmonic but must be anharmonic. This anharmonicity was according to Debye, the source of coupling between the lattice waves, so that mutual scattering of the waves becomes possible. (He pointed out that mutual scattering is not possible for purely harmonic waves). As a measure of the coupling, Debye introduced a mean free path ℓ, which measures the distance of travel of a wave required to attenuate its intensity by a factor e. The thermal conductivity, k, is then given by the equation,

$$k = 1/4\ cvl \qquad (1)$$

where c is the specific heat per unit volume and v is the wave velocity.

These ideas were extended by Peierls and translated in terms of phonon-phonon interaction(2). In Peierls' theory a crystal is treated as a lattice of atoms rather than a continuum. The coupling between normal modes of vibration is ascribed to anharmonicities arising from third and higher order terms in the potential energy of a displaced atom. The part played by these terms is analogous to that of collisions in the theory of a perfect gas; though introducing only a small perturbation of the motion they are responsible for the coupling between the normal modes which is essential in producing thermal equilibrium. In Peierls' theory the normal modes of vibration are quantized and, by analogy with the photons of radiation theory, these quanta are now called phonons. For a phonon associated with an angular frequency ω and wave number K, $\hbar\omega$ gives the energy while $\hbar K$ behaves rather like a momentum.

In the presence of a temperature gradient the phonon distribution differs from that corresponding to the equilibrium distribution at uniform temperature – the Planck distribution. Collisions between phonons tend to restore the equilibrium distribution and the rate of the restoring process determines the thermal conductivity. Collisions are possible if the three values of ω and K obey the equations:

$$\omega_1 + \omega_2 = \omega_3 \qquad (2) \text{ and}$$

$$K_1 + K_2 = K_3 \qquad (3)$$

Equation (2) states that after a collision the resulting wave or waves still carry the same energy as before and (3) implies that this energy is still flowing in the same direction. Such collisions do not in themselves give rise to a thermal resistance. Peierls also showed that, for a discrete lattice, collisions are possible in which equation (3) does not hold but is replaced by

$$K_1 + K_2 = K_3 + \frac{2\pi\epsilon}{a} \qquad (4)$$

where "a" is the lattice constant and ϵ is a unit vector, the possible directions of which depend on the crystal symmetry. Equation (4) implies that the direction of flow of the energy is changed after a collision and as ϵ can take up one of several directions (e.g., six directions parallel to the axes of a cubic crystal), the result of such collisions is much the same as if the waves were scattered at random. This type of collision, which Peierls called an "Umklapp", gives rise to thermal resistance.

It is convenient to use the concept of mean free path, as in Debye's theory, but since waves have been replaced by phonons, equation (1) is rewritten as,

$$k = 1/3\ cvl \qquad (5)$$

In the case just discussed "l" is the mean free path for U-processes.

As a result of the treatment developed by Peierls the theory predicts that the thermal conductivity varies as 1/T at high temperatures, i.e., $T > \Theta$ but at low temperatures it leads to a relation of the form $k = QT^{\upsilon} \exp(\Theta/2T)$, where Q is a constant, υ is of the order of unity and Θ is the Debye specific heat parameter. It is this law which in most cases is approximated by the thermal conductivity of the common ceramic oxides. As the processes responsible for the form of this law are not widely understood, it will be useful to discuss them in some detail.

In a large pure crystal free from impurities, cracks and strains in its structure, the scattering of thermal waves or phonons will only be caused by collisions between the waves themselves. In this case the conditions described by equations (2) and (4) exist. Peierls named the phonon collision an "Umklapp" process, which can best be translated as a "flap-over" process; at a collision the wave number vector "flaps over" and takes up a new position. These U-processes come about because of the possibility of interference effects between the phonons and the lattice by which the lattice can transfer momentum between itself and the phonons. It is as if the phonons can suffer Bragg reflections from the lattice. If a U-process is to take place at all, we see from (4) that

$$K_1 + K_2 \geq \frac{2\pi\epsilon}{a} \qquad (6)$$

This implies that phonons must have a certain minimum energy before they can "Umklapp", and Peierls shows that, as a rough criterion, this minimum energy may be taken as $K\Theta/2$, where k is Boltzmann's constant.

The mean free path noted in equation (5) can be approximated by the expression,

$$\lambda_U = A \exp(\Theta/bT) \qquad (7)$$

where A is a constant depending on the crystal and b has a value slightly greater than 2. Now the number of phonons with this energy is proportional to $1/(\exp(\frac{\Theta}{2T} - 1)$. From this it can be deduced that the temperature dependencies of ℓ or λ is $\frac{1}{T}$ and hence that of k is 1/T for $T > \Theta$ which is the temperature range involved in the proposed application of UO_2.

There are processes involved in heat conduction other than Umklapp collisions(4). The phonons may be scattered by the crystal or grain boundaries(24) and by impurities and lattice imperfections. Some years ago, de Haas and Biermasz(5) made measurements on crystals of quartz, potassium chloride and potassium bromide at low temperatures, and together with Casimir(6) demonstrated that in the region where conductivity falls with temperature the flow of thermal energy is limited by its being scattered at the walls of the crystal. This is the so called "size effect" which results in the measured thermal conductivity becoming proportional to the smallest dimension of the specimen and to the cube of the absolute temperature. These two processes, i.e., Umklapp scattering and boundary scattering, one predominant at low and the other predominant at high temperatures, lead to a maximum in the thermal conductivity in the temperature region where they both contribute least to the thermal resistivity, 1/k, i.e., at temperatures in the vicinity of $\Theta/20$(7). This maximum in the thermal conductivity exhibits values much higher than those possessed by any metals at room temperature. For example, a crystal of sapphire, Al_2O_3, has a maximum value of 15.5 cal.cm/cm^{2}sec°C at 40°K which is over 19 times that of copper at 25°C whose conductivity is approximately 0.8 cal.cm/cm^{2}sec°C. Diamond, the best thermal conductor of all materials at room temperature, has a maximum value of 7.17 cal cm/cm^{2}sec°C, which extends from about 40° to 100°K. However, the thermal conductivity does not drop as rapidly with increasing temperature as it does in other known insulators and has a value of about 2.2 cal cm/cm^{2}sec°C at 100°C. This is 10 times higher than the thermal conductivity of most irons and steels at this temperature, i.e. 100°C, and is over 3.5 times the thermal conductivity of polycrystalline BeO which is the best oxidic thermal conductor known(8). Unfortunately the position of this maximum of the conductivity in the absolute temperature scale is dictated by variables which cannot be controlled. Thus, there is essentially no possibility of displacing this maximum by some means to the temperature region in the vicinity of the Debye temperature, i.e., 870°K for UO_2. The low temperature conductivity of UO_2 hasn't been measured, hence the value at the maximum isn't known. However, it is safe to say that if such a displacement could be accomplished the thermal conductivity problem of UO_2 would be solved.

Most of the common oxides do not obey Debye's or Peierls' equations implicitly but the general trend is for the thermal conductivity to decrease as a function of 1/T at high temperatures. Uranium dioxide exhibits this behavior between 600°C and 1400°C. From considerations of U-processes, impurity scattering and the isotopic scattering predicted by Klemens(9) in 1955 and found experimentally by Berman(10) in 1956 it is evident that anything disturbing the periodicity of the lattice will lower the thermal conductivity from the theoretical maximum which at present cannot be quantitatively calculated. From Klemen's work on isotopic scattering we might expect the enrichment of UO_2 with U^{235} to decrease the thermal conductivity from the values found by Kingery(28) and Hedge(21). This isotopic scattering might explain the anamolous behavior of enriched fuel pellets noted by Eichenberg(38), et al. It was found that fuel pellets of 19.5% enriched UO_2 had to have abnormally low thermal conductivities to explain the center melting which occurred in the pellets during in-pile operation. No detailed study has been made on the effect of enrichment of UO_2 on its thermal conductivity. This anomaly might also have been due in part to the greater rate of bond disruption and generation of lattice distortion caused by the higher population of U^{235} and its resulting fission products in the enriched specimens.

Therefore, treating UO_2 as an insulator it is evident there is apparently no possible way to improve the thermal conductivity of very dense UO_2 ceramics without introducing a considerable quantity of another phase which has a high thermal conductivity. This approach leads to the formulation of UO_2 cermets or the use of metal grids and the resulting problem of dilution. A great deal of work has already been done in this direction in the AEC program.

However, UO_2 is not what might be considered a good insulator, since less than 1 eV separates the conduction band from the valence band. The electrical conductivities of the oxides of uranium have been studied by many investigators and their work has been summarized by Meyer(11) and by Katz and Rabinowtich(12). The oxides UO_3 and U_3O_8 are reported to be metal-excess semiconductors. The conductivity of UO_3 at room temperature is very low; the reported values range from 10^{-7} to less than 10 $(\Omega\text{-cm})^{-1}$, hence this oxide might be thought of as an insulator. Part of the conductivity of U_3O_8 is ionic in nature. The reported values, which include both the ionic and electronic contributions to the conductivity, vary from 2×10^{-4} to 1×10^{-7} $(\Omega\text{-cm})^{-1}$. In UO_2 conductivity values ranging from 3×10^{-1} to 4×10^{-8} $(\Omega\text{-cm})^{-1}$ have been measured at 27°C. The variation of conductivities is, of course, caused by variations in the composition, purity, apparent density, and crystalline perfection of the specimens studied(13). Prigent(14) studied the electrical resistivity of UO_2 pellets and found they were unacceptable for thermistor applications due to the wide variations in resistance from sample to sample. However, he did find that the conductance was an exponential function of temperature. Even though polycrystalline UO_2 exhibits relatively high electrical resistivities it can properly be classed an oxidic semiconductor, an energy of about 0.4 eV being required to free a positive carrier from the interstitial oxygen in UO_{2+x}.

The theory of heat conduction in semiconductors has largely originated in the past six years. A semiconductor is unique in that in a thermal sense it is a combination of an insulator and a metal. In elemental metals the lattice conductivity is usually negligible compared to the thermal conductivity component due to the conduction electrons whereas the opposite is the case in insulators.

Most of the work in this area has been done on the elemental semiconductors germanium and silicon and recent work has been published on some intermetallic compounds. In nearly all these cases only intrinsic conduction mechanisms are considered, i.e. the charge carriers are raised from the valence band to the conduction band solely by thermal excitation and the forbidden band is devoid of occupied acceptor or donor levels. Price(15) derived an expression for the electronic thermal conductivity component in such a model. He proposed that a temperature gradient in a semiconductor leads to gradients of the carrier concentrations, and hence to carrier diffusion currents N,

$$N = -\frac{\sigma_1\sigma_2}{\sigma_1+\sigma_2}\left(\frac{k}{e^2}\right)\left[\frac{\Delta}{kT} + 3 + \gamma_1 + \gamma_2\right]\text{grad } T \qquad (8)$$

where Δ is the energy gap between the bands and the thermal diffusion factors γ_1, and γ_2 are each 1/2 for pure lattice scattering. Price assumed nondegeneracy in the electron and hole distributions and neglected any impurity band transport effects. Each electron-hole pair transports annihilation energy Δ, as well as band energy of order kT, and hence the carrier flow contributes to the thermal conduction,

$$k_{flow} = \frac{\sigma_1\sigma_2}{\sigma_1+\sigma_2}\left(\frac{k}{e^2}\right)\left[\frac{\Delta^2}{kT} + \alpha\Delta + \beta kT\right] \qquad (9)$$

where α and β depend on the scattering processes. For silicon and germanium the term Δ^2 in (9) could attain about 0.3 watt units at their melting points. Thus the possibility of a thermal conductivity minimum at high temperatures is demonstrated in this type of solid.

In general one can say that the thermal conductivity k of a semiconductor may be written as the sum of two components: k_g the lattice conduction and k_e the electronic conduction, thus

$$k = k_g + k_e \qquad (10)$$

For sufficiently high temperatures k_g decreases as 1/T as noted in the discussion on insulators. At the same time k_e is expected to increase very rapidly with temperature owing to the increasing number of free charge carriers in the semiconductor. The total heat conductivity would therefore be expected to show a minimum at intermediate temperatures. A calculation of k_e based on the assumptions currently made in calculating thermoelectric forces leads to the well known Wiedemann-Franz law,

$$k_e = 2\left(\frac{k}{e}\right)^2 T \sigma \qquad (11)$$

k = Boltzmann constant

e = electronic charge

σ = electrical conductivity

The introduction of experimental values of into equation (11) for a given semiconductor gives values of k_e far too small to be observed. Measurements of the thermal conductivity of the intermetallic compound Mg_2Sn show that there is no indication of a minimum and that the total heat conductivity decreases as 1/T approximately. Busch and Schneider(16) reported an anomalous behavior in the thermal conductivity of InSb. Accurate measurements revealed a pronounced minimum in k at 100°C and just below the melting point of the compound k attained a value of one fourth that of copper, i.e. at 400°C. A plot of k as a function of 1/T yielded a straight line at low temperatures which permitted an extrapolation of k_g for higher values of T. It was found that the electronic conduction k_e determined in this manner could be represented by the expression,

$$k_e = \text{const. exp. } (-\Delta E_k/2kT) \qquad (12)$$

From this data it was concluded that the experimentally determined k_e of InSb was larger than what one would expect according to equation (11) by approximately a factor of 100.

Fröhlich and Kittel(17) point out that in the theory of the electronic part of the thermal conductivity of semiconductors in the intrinsic range it is important to take into account the transport of ionization energy, E. In the case where the electron and hole mobilities are equal the electronic contribution can be understood in terms of the expression,

$$k_e \cong C_e \mu l \qquad (13)$$

where k_e is the electronic thermal conductivity, C_e is the carrier heat capacity per unit volume, μ is the carrier velocity and l is the mean free path. The number of carriers, N, excited for $E >> kT$ is proportional to $\exp(-E/2kT)$ so that very roughly

$$C_e \cong Nk(E/kT)^2 \qquad (14)$$

which is larger than the usual translational heat capacity by a factor of the order of $(E/kT)^2$. This factor at room temperature may be of the order of 100 or more in representative semiconductors, so that it is important to take it into account. However, since equal electron and hole mobilities in a semiconductor are unusual, a more general theory is still required.

J. M. Thullier(18) presented a comprehensive theory for thermal conduction in intrinsic semiconductors in 1955 and specifically attempted to explain the anomaly observed in InSb. Thullier's calculations involve an attempted modification of the Wiedemann-Franz ratio by taking into account both the kinetic and ionization energies transported by the charge carriers. However, his results differ markedly from equation (11) only when $n\mu_n = p\mu_p$ where n and p are the electron and hole concentrations and μ_x their respective mobilities. This condition would be very unique and would not be expected to exist in an oxide and certainly would not apply in the extrinsic case of a doped oxide.

Joffe(19) has summarized certain rules on thermal conductivity:

(1) For substances with similar structures k_{phonon} decreases as $\bar{A}$ increases, where $\bar{A}$ is the mean atomic weight of the elements comprising the sample.

(2) The phonon conductivity decreases with increase in the proportion of the ionic part of the chemical bond; in fact k_{phonon} decreases along the following sequence: the elements of Group IV, compounds of elements of Groups III and V, then II with VI, and finally I with VII.

(3) Ionic crystals with ions of equal masses have higher conductivities than crystals with ions of different masses. This rule was stated by Eucken some years ago.

From (2) we see that UO_2 would be expected to possess a low thermal conductivity since its cation is of Group VI and its cation and anion differ greatly in mass.

Joffe also investigated the effect of impurity additions on the thermal conductivity of a semiconductor. All of the impurities investigated had the same coordination number as the host they were replacing so the data illustrates the effect on the lattice conductivity only; the number of charge carriers remaining essentially the same. The considerations here are the same as those enumerated for impurity scattering in insulators. The effect of substituting Se for Te in PbTe is illustrated in Figure 1.

Denoting by λ_o the free path of phonons in a non-disturbed lattice and by "a" the lattice constant, the ratio of the undisturbed lattice's conductivity to that of the disturbed lattice is:

$$\frac{k_o}{k} = 1 + \frac{N}{N_o} S \frac{\lambda_o}{a} \qquad (15)$$

where $S = So/a^2$ stands for the cross section of an atom expressed in lattice units. This expression takes into account both the quantity of impurities and the kind of distortion they produce. Experiments on various semiconductors revealed some cases of interstitial impurities with $S > 1$ up to $S = 10$. The introduction of Te atoms in the lattice of GaSb lead to $S = 7$; while in the same substance Se gave $S = 3$. Apparently in some cases S must be taken at $S < 1$. For instance, a clustering in groups of n atoms leads to $S = n^{-1/3}$. For $n \cong 10$, $S = 0.46$. For most of the semiconductors investigated equation (15) holds good on the condition that $S = 1$ for substitutional impurities; for instance Si in Ge, Sn in Si, Se in PbTe.

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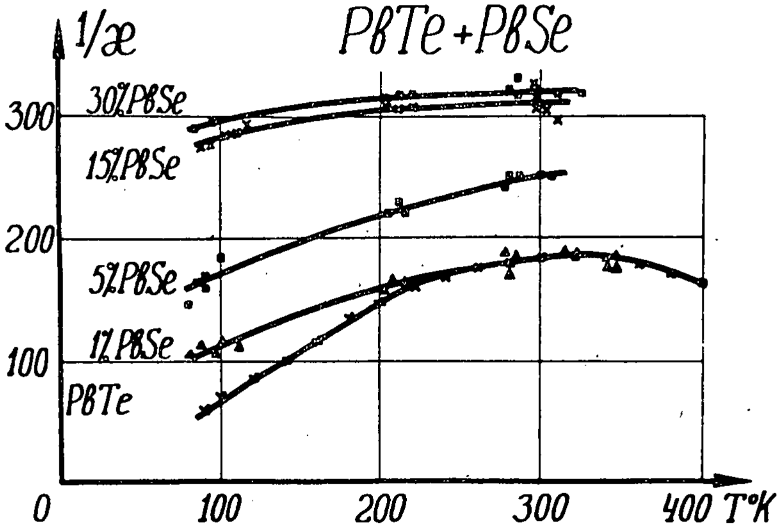

FIGURE 1

Thermal resistivity, 1/k vs. Temperature
for Se additions in PbTe.

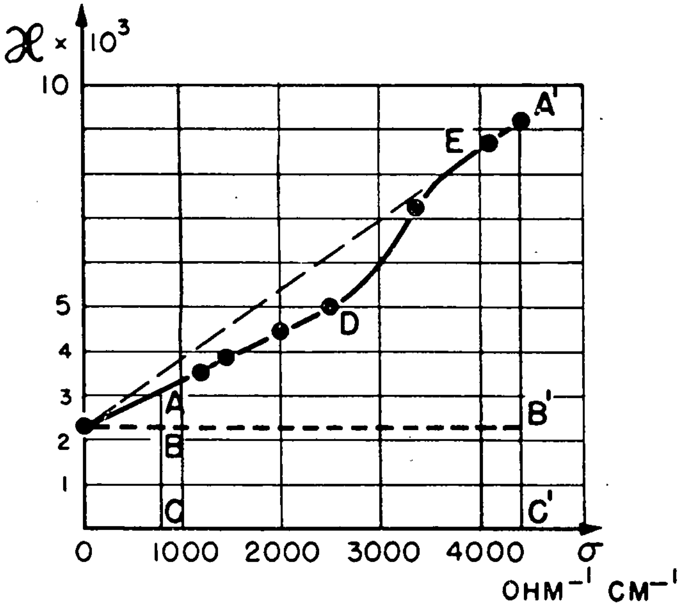

FIGURE 2

Dependence of Thermal Conductivity, k,
of PbTe on the Electrical Conductivity, σ
AB and A'B' = k_e
D, Beginning of Degeneracy

In accordance with (15) the influence of impurities is more pronounced the larger is the free path $\frac{\lambda_0}{a}$. A contamination of Si (with $\frac{\lambda_0}{a} = 40$) or Ge (with $\lambda_0/a = 30$) is already noticeable at $N/N_0 = 10^{-2}$ (1% of impurities), while in PbTe (with $\lambda_0/a = 3$) only 10% of impurities produce an equal effect.

For semiconductors with a large phonon free path, $1/k$ rises quickly with the introduction of impurities. For Ge with $\lambda_0/a \cong 35$, 1% of impurities increases the thermal resistivity by 35%, while for PbTe with $\frac{\lambda_0}{a} \cong 3$ the resistivity would increase by only 3%. Unfortunately, the phonon free path as a function of temperature isn't known for UO_2.

Another important consideration in semiconductors is the way phonons and electrons combine in the heat transport. The assumption is made that they act independently, and this is reasonable up to a concentration of electrons of $10^{20}/cm^{+3}$. A check was made by Joffe on this assumption by introducing impurity atoms and in this way changing to a large degree the electrical conductivity without affecting the phonon conductivity markedly.

Figure 2 illustrates the dependence of the thermal conductivity on σ, the electrical conductivity in PbTe. Between $\sigma = 1000$ and $\sigma = 2500$ $(\text{ohm-cm})^{-1}$ the electrons must be considered as nondegenerate, i.e. they obey the ideal gas law. From Figure 2 we see that in this case an increase in the electrical conductivity definitely increases the thermal conductivity of PbTe.

Another important mechanism of thermal transfer is that of radiation through the solid. This additional mechanism of energy transport would attain significance only at high temperatures. Genzel has computed the corresponding Δk:

$$\Delta k = \frac{16}{3}\,\frac{a\epsilon}{k}\,T^3 \tag{16}$$

where ϵ is the electronic part of the dielectric constant and "a" is the factor in Stefan's law. This effect has been observed by McQuarrie(20) in MgO, BeO and Al_2O_3. Apparently an oxide must be translucent before this effect is appreciable. Hence it was not observed by Kingery in UO_2 up to 1500°C or by Hedge and Fieldhouse(21) at 1680°C.

From this discussion we can draw some conclusions about the feasibility of improving the thermal conductivity of UO_2.

(1) The oxide must be as close to theoretical density as possible as gas filled voids in the solid act as thermal insulators.

(2) As noted previously, the effect of the introduction of any foreign ions into the UO_2 lattice will be to decrease the phonon conductivity. The magnitude of this depression cannot be computed as the phonon free path as a function of temperature isn't known for UO_2. W. D. Kingery$^{(35)}$ has pointed out that in single-phase ceramics, lattice thermal conductivity may, under suitable conditions of elevated temperature or lattice disturbance by irradiation, be reduced to a minimum value set by phonon scattering at mean free paths of the order of the lattice spacing: in the case of UO_2, such a minimum value would be approximately 0.0173 watt cm/cm^2 °C. Using this value for the phonon free path at elevated temperatures the value S in (15) could be determined by experimentally measuring k and k_o at high temperatures for samples with controlled impurity concentrations.

In conjunction with the theoretical considerations just discussed there is a possibility of increasing the thermal conductivity of polycrystalline UO_2. This might be accomplished by introducing an ion into the lattice whose size would permit it to isomorphously replace U^{+4} and whose valence was preferably either +5 or +3. In the case of a +3 ion the lattice would gain one-half a positive hole per substituted ion whereas a +5 ion would result in the release of a free electron to the lattice. These charge carriers may then be able to transport enough heat in the presence of a thermal gradient to result in a sizeable electronic conduction component. Since U^{+4} is easily oxidized to U^{+6} (this occurs in UO_2 at room temperature with the absorption of oxygen) the advantage of adding a +5 ion may be counterbalanced by the ability of its uranium near neighbors to alter their valence so as to reduce the lattice strain. The substitution of a +3 ion for U^{+4} on the other hand has been found to stabilize the oxidizing tendency of UO_2 at high concentrations. The atomic species selected for substitution into the UO_2 must be chosen such that its size will not drastically distort the lattice. Ions whose masses differ markedly from that of U^{+4} will act as scattering centers and may reduce the already low phonon conductivity. The Goldschmidt rule which states that an ion whose radius is $\pm$ 15% of that of the host ion can be substituted into a lattice without severe lattice distortion would limit the ionic radius selection to the range 0.8245 to 1.1155 Å using 0.9700 Å as the radius of the U^{+4} ion. The species chosen should also have only one stable valence state. The +3 ions of the rare earths all fall within this range. Unfortunately the high neutron cross sections of some would prohibit their use in a fuel element. If the required impurity concentration was low then some of the higher cross section members of the family may be acceptable. The rare earths having the lowest cross sections and their ionic radii are listed:

Ion	Cross Section in Barns	Ionic Radius in Angstroms
La^{+3}	8.8	1.061
Ce^{+3}	0.7	1.034
Pr^{+3}	11.0	1.013
Pb^{+3}	44.0	0.923
Ho^{+3}	64.0	0.894
Er^{+3}	166.0	0.881
Tm^{+3}	120.0	0.869
Yb^{+3}	36.0	0.858
Lu^{+3}	108.0	0.848

Samarium has an ionic radius very close to that of U^{+4} but its cross section of 10,000 barns excludes its consideration as a possibility.

Other ions which should fit into the UO_2 lattice are:

Ion	Cross Section in Barns	Ionic Radius in Angstroms
Ca^{+2}	0.42	0.99
Y^{+3}	1.4	0.93

Surprisingly Sylvania Corning reports that Nb^{+5}, 1.1, 0.70 Å increases the thermal conductivity of UO_2 even though its radius is below the 0.8245 Å limit.

The substitution of a +3 ion into the lattice would markedly alter the electronic structure of the solid since the substitution of a X^{+3} ion for U^{+4} would result in the following:

$$U^{+4} + 2O^{-2} \text{ by } X^{+3} + 1.5O^{-2} + 0.5\,\square \qquad (17)$$

We see that the addition of the X^{+3} results in the creation of one-half a hole per substituted ion which in turn can act as a charge carrier(22).

Since all the theories discussed have been concerned primarily with elemental and intermetallic semiconductors we cannot extend them directly to oxides. However, the principles cited should certainly be valid. If the number of charge carriers in the UO_2 could be increased sufficiently and if their mobility was great enough then the thermal conductivity of the oxide would be expected to increase as a function of temperature. The effect of an in-pile environment on these properties may be drastic and would have to be measured.

Hartmann(23) pointed out that the increase of electrical conductivity with the addition of oxygen makes UO_2 a positive hole conductor. He made Hall-coefficient measurements and obtained a mobility value of 10 cm^2 per V-sec for the charge carriers which is a rather low mobility. No data was found on measurements of these properties of UO_2 which contained +3 impurities. The addition of +3 ions to the UO_2 lattice will result in unsatisfied oxygen bonds and p-type conduction. The effect on the thermal conductivity of non-stoichiometry in the oxide is unknown. Since the excess oxygen fits into interstices in the fluorite lattice of the UO_2 and subsequently oxidizes some of the U^{+4} to U^{+6} the oxygen may suppress the conductivity by two processes. By occupying a non-permitted lattice site the oxygen acts as an impurity scattering center. The U^{+6} resulting from the oxidation distorts the crystalline electric field and hence also acts as an impurity scattering center. This suppression of the phonon conductivity would probably mask any increase in the electronic thermal conductivity component due to the decreased resistivity which accompanies oxidation.

From theoretical considerations it follows that the logarithm of the density of carriers plotted versus the reciprocal temperature should yield a straight line of slope $-\Delta E/2k$ where ΔE is the donor ionization energy. As the temperature is increased to such values that the intrinsic excitation becomes important, the slope changes gradually to $-E$ gap$/2_k$. The heat carried by the intrinisically excited carriers is apparently small in UO_2 as is evidenced by the horizontal nature of the curves in the high temperature region of Figure 3. Therefore, if the impurity carriers are able to transmit a significant amount of thermal energy in this case, one would expect that at high temperatures the electronic component of the thermal conductivity would approach a constant value as the condition of complete ionization of the impurity centers is approached. Since the phonon conductivity would continue to decrease with temperature until the mean free path approached the lattice constant the thermal conductivity may again decrease at extremely high temperatures provided no significant radiation component appeared.

Review of Thermal Conductivity Measurements on UO_2

Snyder and Kamm at Princeton(25) determined the thermal conductivity of uranium dioxide powders, but these values are low because of the low densities of the samples that were tested. Weeks at Argonne(26) reported a thermal conductivity of 0.023 cal cm/cm^{2}sec°C at 70°C for a sample with a density of 10.23 gm/cc as compared to 0.00034 cal cm/cm^{2}sec°C at 100°C for the Princeton value. Week's value is approximately 68 times larger than the Princeton value, clearly illustrating the importance of high density for good thermal conduction. Englander(27) in France reports an average value of 0.01 cal cm/cm^{2}sec°C for material at approximately 70°C having a density of 9.2 g/cm^3. Kingery at MIT has made more recent measurements on UO_2. Kingery and Vasilos(28) reported data on UO_2 having 73% of theoretical density. The measurement was made utilizing a linear flow comparison method. Kingery(28) has also measured the thermal conductivity of UO_2 having 95% theoretical density by this method and this is the only measurement that has been made on high density material over an extended temperature range. He gives an empirical equation for the thermal conductivity as a function of temperature:

$$K = 0.143\ e^{-1.207T \times 10^{-3}} \qquad \text{watt cm/cm}^2\,{}^\circ\text{C}$$

$$\text{where } T = {}^\circ\text{K} \qquad T \quad 1473^\circ\text{K}$$

Calculation of conductivities at various temperatures gives the following values:

T °C	K watt cm/cm^2°C	K cal cm/cm^{2}sec°C
100	.0912	.0218
300	.0715	.0171
500	.0563	.0135
600	.0500	.0120
800	.0392	.0094
1000	.0307	.0073

McCreight(29) reported thermal conductivity values for several compositions including UO_2-MgO, UO_2-BeO, and UO_2-Zr. He found that a 29 wt % addition of BeO to UO_2 increased the thermal conductivity by nearly a factor of four over that of UO_2 at 450°C. This large addition probably resulted in the presence of two phases and the BeO phase conducted the additional heat.

Bowers, et al(30) reported that BeO additions of up to 15 wt % to UO_2 improved the thermal shock resistance of the body whereas ZrO_2 and CeO_2 did not affect this property.

A recent measurement of the thermal conductivity of UO_2 was made by Hedge and Fieldhouse at Armour. Using a stacked disk method which will be described in some detail later they obtained values of the thermal conductivity to 1670°C. Unfortunately their UO_2 samples had a density of 8.17 g/cc, 75% theoretical density. This probably explains why their values are considerably lower than Kingery's. Due to severe cracking of the samples the measurements were not extended to higher temperatures. A comparison of Hedge and Fieldhouse's values with those of Kingery for material with 95% theoretical density is shown in Figure 3. The dashed section of the curve is extrapolated data.

The only measurements on UO_2 with small impurity additions that were encountered are those presently being made by Sylvania-Corning. Their equipment is a modification of the linear flow comparison method of Kingery. The maximum temperature limit of the apparatus is 550°C. Yttrium and other +3 ions are being substituted for U^{+4} in UO_2 and the additions examined thus far appear to improve the thermal conductivity of the oxide although only a small amount of data has been obtained thus far. If these measurements are accurate then the data is conclusive proof that an electronic thermal conduction component can be induced in polycrystalline UO_2 with a subsequent increase in the thermal conductivity.

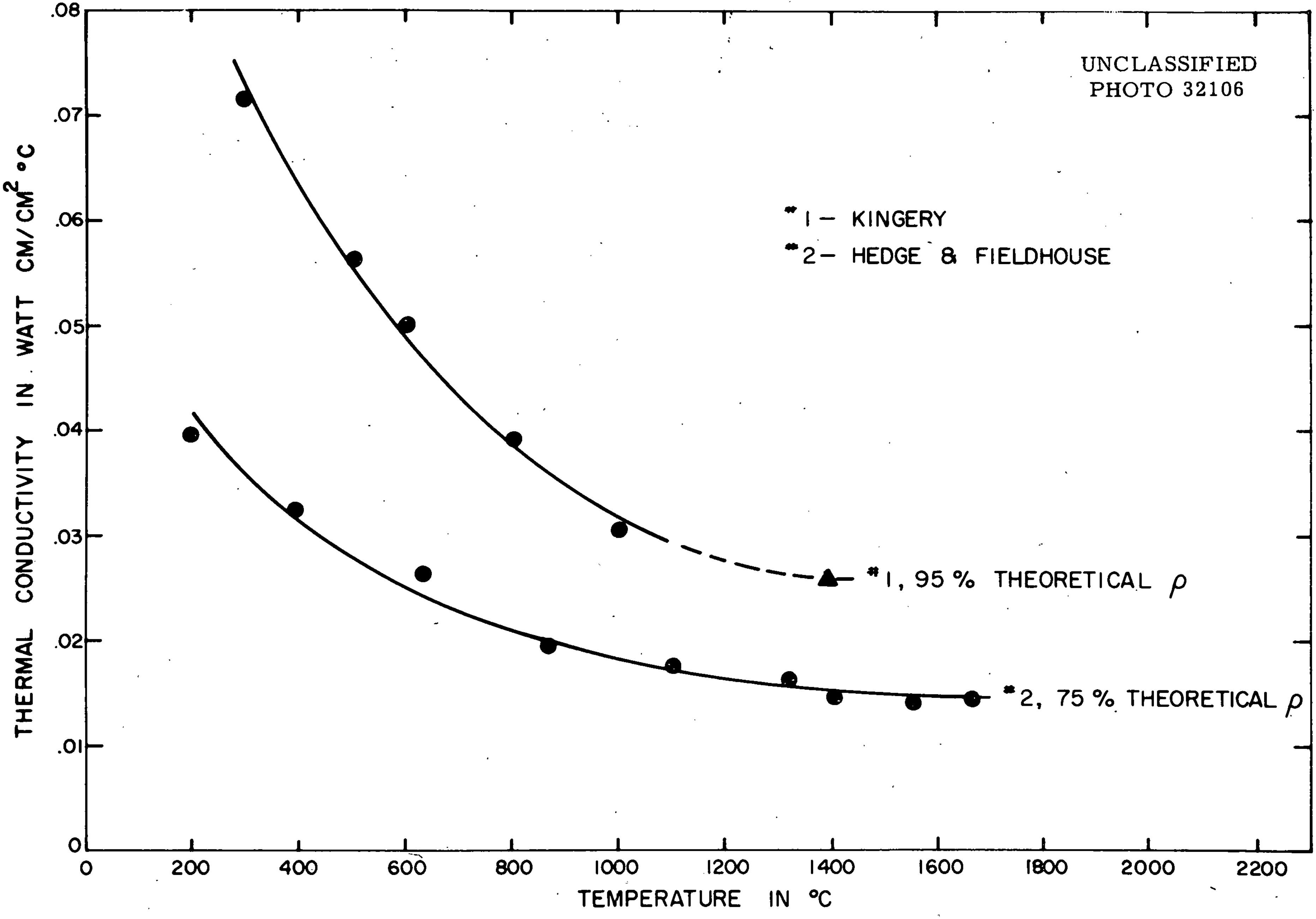

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FIGURE 3. THERMAL CONDUCTIVITY VERSUS TEMPERATURE OF UO_2

Since the theory of heat transfer in semiconductors will not presently permit the quantitative calculation of the magnitude of the electronic component, k_e, its presence and magnitude can only be deduced by physical measurements.

Flinta(36) has recently reported the effect of relatively low fluxes (1.8×10^{12} neutrons/cm^2) on the in-pile thermal conductivity of UO_2. The measurements, which were made in Sweden, were performed on annular UO_2 pellets having 91% theoretical density. The thermal conductivity was determined with data obtained from a thermocouple near the center of the UO_2 together with a thermocouple located near the O.D. of the pellets. The method was essentially a stacked disk method, the samples being 15 mm in diameter and 20 mm in length. Five disks were stacked together with a tungsten rod passing through the central hole and serving as a heat source in addition to that caused by the fissioning. With the outer surface of the pellets cooled to 50°C by water, thermal cycling of the center to 1800°C, out of pile, resulted in a marked decrease in the measured K, presumably due to shock failure of the pellets. The thermal conductivity was found to be erratic with neutron irradiation, and dropped to 0.007 watt cm/cm^2°C after three heating cycles. At about 350°C and high neutron fluxes (10^{18} n/cm^2) k increased from a minimum of 0.005 to 0.007 watt cm/cm^2°C. This behavior could not be explained.

The latest measurement of k for UO_2 was made by Eichenberg(37) in the Materials Testing Reactor. The samples consisted of PWR pellets 0.3535-in. in diameter and they were stacked in a stainless steel capsule. The central temperature of the UO_2 was measured with a thermocouple in the central hole of the pellets. Thermocouples located in the interior of the capsule wall provided data from which the heat generation in the UO_2 was calculated. The pellets had an estimated exposure of 0.7×10^{20} nvt thermal. The thermal conductivity was determined up to 480°C and the values were about 50% of the Armour data shown in Figure 3.

Methods of Measuring Thermal Conductivity of Insulators and Semiconductors

In general the methods employed for measuring the thermal conductivity of semiconductors and insulators are the same. Some methods which utilize certain unique properties of metals, i.e. high electrical conductivity, are applicable only to good conductors while others can be used for metals or non-metals.

Thermal conductivity may be measured by either static or dynamic methods. In dynamic methods the temperature is varied suddenly or periodically for one portion of the sample and the temperature change with time is measured to determine the thermal diffusivity, $k/c\rho$. In static methods, the sample is allowed to come to a steady state and the temperature distribution measured to determine the thermal conductivity k, by an integrated form of

$$Q = kA \frac{dT}{dx} \qquad (18)$$

where Q = amount of heat flowing per unit time through an area A and the temperature gradient in a direction perpendicular to A is dt/dx. This expression also serves to define k, the thermal conductivity.

Present experimental evidence indicates that the conductivity is not a function of the heat flowing, and (18) may be said to be verified by experimental evidence.

The dynamic or non-steady state methods are usually not utilized for the determination of the thermal conductivity at high temperatures since they require a periodic heat source and knowledge of the heat capacity at the temperature of measurement.

A steady state method often utilized for ceramics is one using a long bar specimen. One end is heated while the other is connected thermally to a heat sink. Thermocouples are inserted at selected distances along the bar and these temperatures plus the known amount of heat flowing along the bar permit the calculation of k. Theoretically this is a good method but practically it has serious disadvantages. One of the main disadvantages, which is the one which plagues all thermal conductivity determinations, is that the radial heat flow from the bar must either be neglected or decreased by means of thermal guard rings. Any radial heat flow is a violation of the boundary conditions assumed in (18) and the accuracy of the measurement is seriously affected.

This loss can be reduced by decreasing the length of the bar so that the longitudinal surface area is small with respect to the cross sectional area. These conditions require the sample to assume the shape of a thin plate. When dealing with samples of low conductivity the plate thickness can be quite small and reliable values of $\frac{dT}{dx}$ still be obtained. However, where ceramics are concerned the forming of large flat plate samples is often not possible. Guard rings are still required and they are inevitably imperfect.

A method of insuring correct heat flow without the use of heat guards is to employ a specimen which completely surrounds the heat source. This may consist of an infinite cylinder or slab, surrounding an infinite heat source, or it may consist of a hollow sphere or spheroid. Shapes approximating an infinite cylinder or slab are satisfactory, if only the center section is employed (this is equivalent to using heat guards), but they are difficult to formulate from ceramic materials, particularly dense oxides. A spherical shape is satisfactory, but the highly curved isothermals present a difficulty in temperature measurement.

Loeb(31) has developed an expression for the case of a hollow ellipsoid (prolate spheroid). The expression makes possible the use of an envelope sample of relatively small size which can be formed from pure materials and which has nearly flat isothermals in the central section. Kingery(32) et al, describes this method and the other envelope methods in considerable detail. The ellipsoids are approximately 11 cm long, i.e. 2a = 11 cm and 4.2 cm thick, 2b = 4.2 cm. They are heated internally either by a conductor wound on a shaped core or by a susceptor shaped to fit the internal cavity of the ellipsoid.

The ellipsoids were cast of selected refractory oxides, hence any oxide whose structure is susceptible to change in the presence of the casting environment could not easily be formed to a suitable shape. In the case of MgO and CaO special casting procedures were necessary. These envelope methods can be used at high temperatures, in the range of interest here and could be utilized if ellipsoids of dense UO_2 can be formed.

Another method improved upon by Kingery is the comparative flow method wherein samples of known conductivity are placed in series with the unknown samples. This method is the one presently being used by Sylvania-Corning for UO_2 and they are encountering great difficulty eliminating lateral heat flow. The maximum temperature attained by Kingery in this measurement has been 900°C and it is not likely that guards would be satisfactory at higher temperatures.

As noted previously, one of the latest measurements of the thermal conductivity of UO_2 was made by Hedge and Fieldhouse at Armour. Rather than utilizing the linear flow method of Kingery the radial heat flow method of Powell(33) was used. This method consists of measuring, under steady state conditions, the radial heat flow and radial temperature drop in a vertical stack of disks composed of the material whose conductivity is to be measured. The disks were in the form of annular rings and the heat which flowed through the disks was supplied by an electric heater centered in the axial hole of the stacked disks. In order to attain high temperatures the entire column of disks was placed in an electrically heated furnace in which a helium atmosphere was maintained.

This method has some decided advantages over the prolate spheroid or other envelope methods and the linear flow methods which deserve some enumeration. First, the problem of guarding is lessened since the direction in which flow is desired to be decreased is now the longitudinal rather than radial. The interfaces between the disks act as natural thermal barriers and hence reduce this longitudinal flow. The interfacial thermal resistance is one of the most serious disadvantages of the comparative method described previously. Thermal guards placed on the top and bottom of the column reduced the longitudinal flow to the point where it was negligible. Secondly, the disk samples which had an inside diameter of 0.50 inches and an outside diameter of 3.0 inches could be formed by dry process techniques rather than by casting. Hydrostatic pressing of the green samples may permit the formulation of high density samples.

If high density UO_2 samples of this shape could be formed this method appears to be the simplest for giving reliable data. It was checked using Armco iron as a standard by Hedge and the results agreed with Powell's within experimental error to 790°C, the maximum temperature of the test.

A recent report by Paine and Stonehouse(34) involves the measurement of the thermal conductivity of intermetallic compounds. Their measurement resembles that of Hedge and Fieldhouse, the main difference being that the radial heat flow is inward rather than outward. Also all of the heat is supplied by a molybdenum winding around the outside of the cylindrical specimen. The heat is conducted away by water flowing through a tube in the center of the column of disks. For high temperatures this type of heat sink would create severe thermal stresses in a sample and would probably lead to cracking in a brittle material having a low conductivity such as UO_2.

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