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High-temperature Thermal Conductivity of Uranium Dioxide

by

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Introduction: One of the major disadvantages in the use of UO_2 as a reactor fuel is its low thermal conductivity at normal operating temperature. The thermal conductivity of most solids decreases with increasing temperature. Bates(1) made measurements of the high-temperature thermal conductivity of UO_2 and concluded that the conductivity increases with temperature above about 1500°C. He attributed this effect to "radiation conductivity."

The object here is to examine the high-temperature conductivity of UO_2 theoretically, and to decide whether radiation conductivity or some other mechanism could cause an effect like that observed by Bates.

Measurements of the Thermal Conductivity of UO_2: Most of the thermal conductivity measurements made on UO_2 have been made at temperatures under 1500°C. The measurements of Kingery(2), Hedge and Fieldhouse(3), and Scott(4) are shown in Figure 1.

Bates has made measurements of the thermal conductivity of UO_2 up to the melting point at about 2700°C. He deduced the thermal conductivity from observations made on irradiated fuel rods. Previous laboratory experiments indicated the temperatures at which various changes in the microstructure occur. By examining the microstructure of the irradiated rods, Bates was able to estimate the steady-state temperature profiles in the rods,

(1) J. L. Bates, Nucleonics 19 (6), 83 (1961).
(2) W. D. Kingery, J. Francl, R. L. Coble, and T. Vasilos, J. Am. Cer. Soc. 37, 107 (1954).
(3) J. C. Hedge and I. B. Fieldhouse, AECU-3381, (Sept. 20, 1956).
(4) R. Scott, AERE-M/R-2526, (March, 1958).

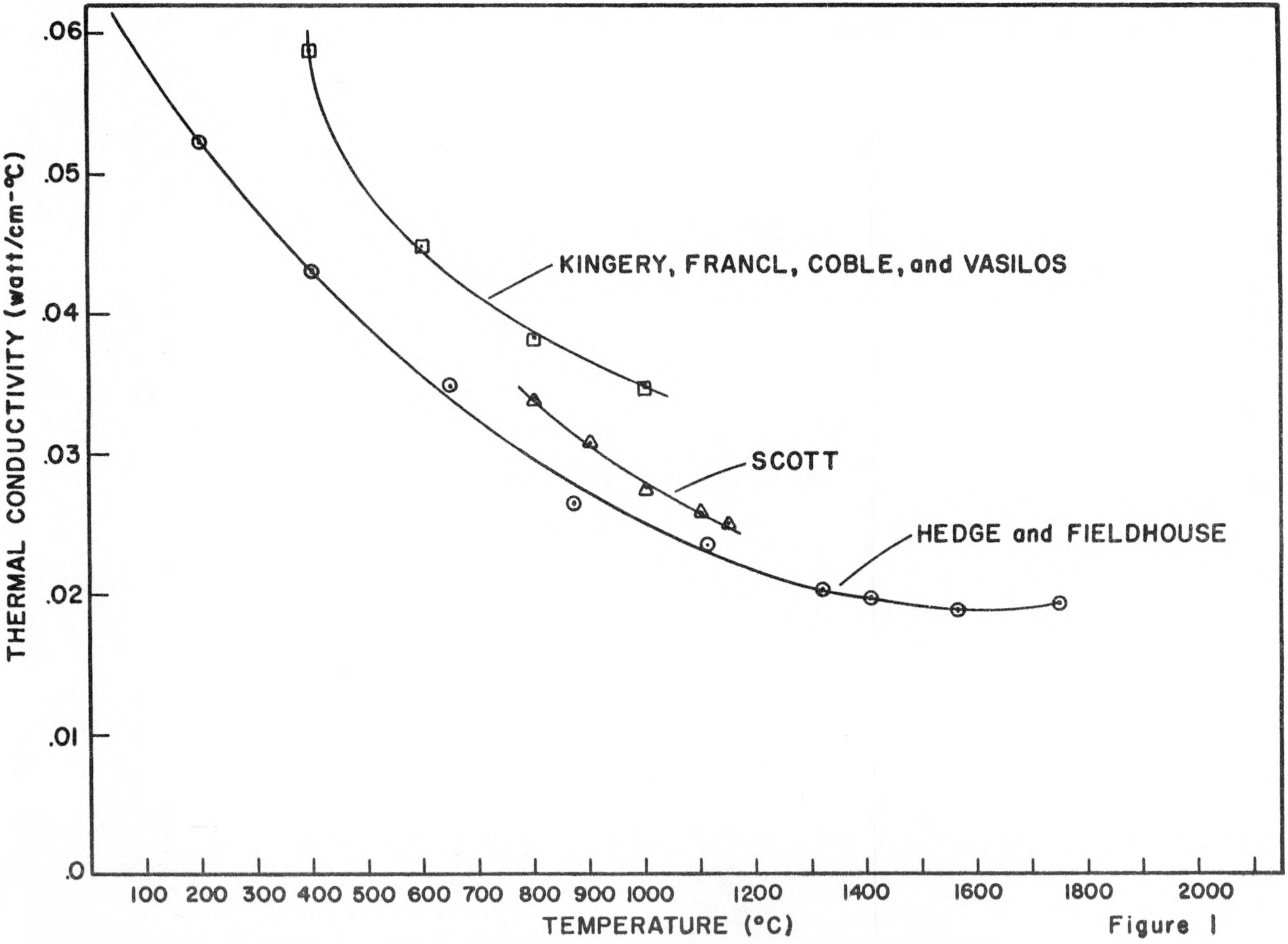

Figure 1

THERMAL CONDUCTIVITY MEASUREMENTS

and he was thus able to estimate the thermal conductivity. His estimates are shown in Figure 2. The boxes indicate the probable range of error in his conductivity estimates.

We note that the data of Hedge and Fieldhouse go up to about 1700°C, with practically no measured rise in the conductivity. (Actually the last measurement indicates a very slight increase.) Thus the measurements of Bates are somewhat in disagreement with those of Hedge and Fieldhouse.

<u>Mechanisms of Thermal Conductivity</u>: At reasonably low temperatures, the thermal conductivity is due mainly to lattice vibrations. Heat conduction involves the scattering of phonons. This scattering, due to anharmonicity in the lattice, increases with increased temperature, and the mean free path is proportional to 1/T. Consequently the conductivity should be proportional to 1/T until the phonon mean free path gets down to the same order of magnitude as the lattice constant. At higher temperatures, the conductivity should be roughly constant. This constant value of conductivity for UO_2 should be about .0173 watt/cm-°C.(5) Thus the conductivity would be expected to deviate from the 1/T law over 1500°C somewhat like the data of Hedge and Fieldhouse indicate.

A second mechanism which may have considerable influence on the thermal conductivity at high temperatures is "radiation conductivity", i.e. the direct transfer of radiation through a semi-transparent medium. The radiative flux through a transparent material is not in general propor-

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(5) W. D. Kingery, WAPD-183, (Oct. 1957).

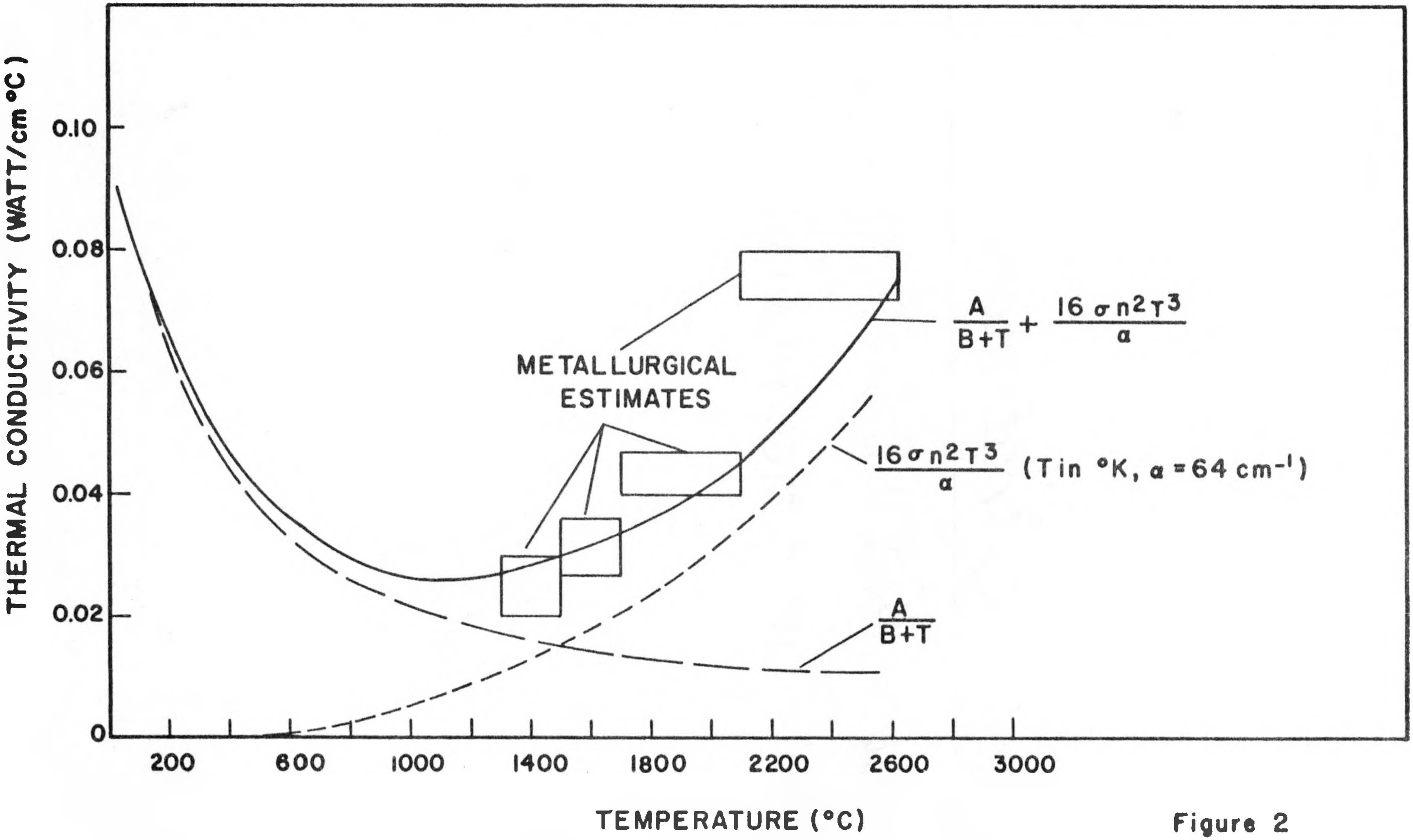

Figure 2

THERMAL CONDUCTIVITY of UO_2
(BATES)

tional to the temperature gradient, but looks like:

$$\Phi_x = \frac{16\sigma n^2 T^3}{3}\left(\frac{dT}{dx}\Lambda + \alpha\frac{d^2T}{dx^2}\Lambda^2 + \beta\frac{d^3T}{dx^3}\Lambda^3 + \dots\right)$$

where $\alpha, \beta, \dots$ are all of order of magnitude one, and Λ is the mean free path of radiation in the material.

σ = Stefan - Boltzmann constant
n = index of refraction

If the critical dimensions of the system are all much larger than Λ, then we can drop all but the first order term and hence the "radiation conductivity" is$^{(6)}$:

$$k_{rad} = \frac{16\sigma n^2 T^3}{3\alpha}$$

where $\alpha = \frac{1}{\Lambda}$ = absorption coefficient. This assumes that the absorption coefficient is independent of wavelength, which is not usually true. In general,

$$k_{rad} = \frac{2\pi n^2 c^3 h^2}{3KT^2}\int_0^\infty \frac{e^{hc\nu/KT}\nu^4 d\nu}{\alpha(\nu)\left(e^{hc\nu/KT}-1\right)^2} = \frac{16\sigma n^2 T^3}{3}\overline{\left(\frac{1}{\alpha}\right)}$$

where

$$\overline{\left(\frac{1}{\alpha}\right)} = \frac{\displaystyle\int_0^\infty \frac{e^{hc\nu/KT}\nu^4 d\nu}{\alpha(\nu)\left(e^{hc\nu/KT}-1\right)^2}}{\displaystyle\int_0^\infty \frac{e^{hc\nu/KT}\nu^4 d\nu}{\left(e^{hc\nu/KT}-1\right)^2}}$$

and ν = wave number; h = Planck's constant; c = speed of light.

The line A drawn in Figure 2 corresponds to $\frac{16\sigma n^2 T^3}{3}\overline{\left(\frac{1}{\alpha}\right)}$ when $\overline{\left(\frac{1}{\alpha}\right)} = \frac{1}{64\ cm^{-1}}$. It is clear that this corresponds roughly to the data of Bates. The object here will be to examine the question of whether

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(6) L. Genzel, Z. Physik 135, 177 (1953).

this value of $\overline{(1/\alpha)}$ can reasonably be expected for UO_2.

There have only been a few measurements of the optical absorption of UO_2. The best measurements were those made by Ackermann et al.(7) Some of their results are shown in Figure 3. Note that, over most of the range, $\alpha >> 64\ cm^{-1}$. The problem is that no such measurements are available for $\lambda = \frac{1}{\nu} > .8\mu$ and it will be possible to obtain only very rough indications of the spectrum between $.8\mu$ and 3.0μ.

<u>Absorption between $.2\mu$ and 3μ</u> ($5 \times 10^4 cm^{-1} > \nu > .33 \times 10^4 cm^{-1}$)

The Planck function, describing the frequency distribution of radiation as a function of temperature has its maximum between 1μ and 2μ, for temperatures between 1500°C and 2200°C. Thus, this short-wavelength region is the most important part of the spectrum for our purpose.

The theoretical problems will be to:

(1) Find the locations of spectral lines in this region ($.2\mu$ to 3μ).
(2) Estimate the intensities of these lines as functions of temperature.
(3) Estimate the widths of the lines as functions of temperature.
(4) Try to estimate the intensity of the background absorption.

Knowing the locations, widths, and intensities of the lines and the background level, we should be able to decide whether $\overline{(1/\alpha)}$ could get as large as $1/64\ cm^{-1}$.

By far the most important contribution to the absorption spectrum between

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(7) R. J. Ackermann, R. J. Thorn, and G. H. Winslow, <u>J. Opt. Soc. Am.</u> <u>49</u>, 1107 (1959).

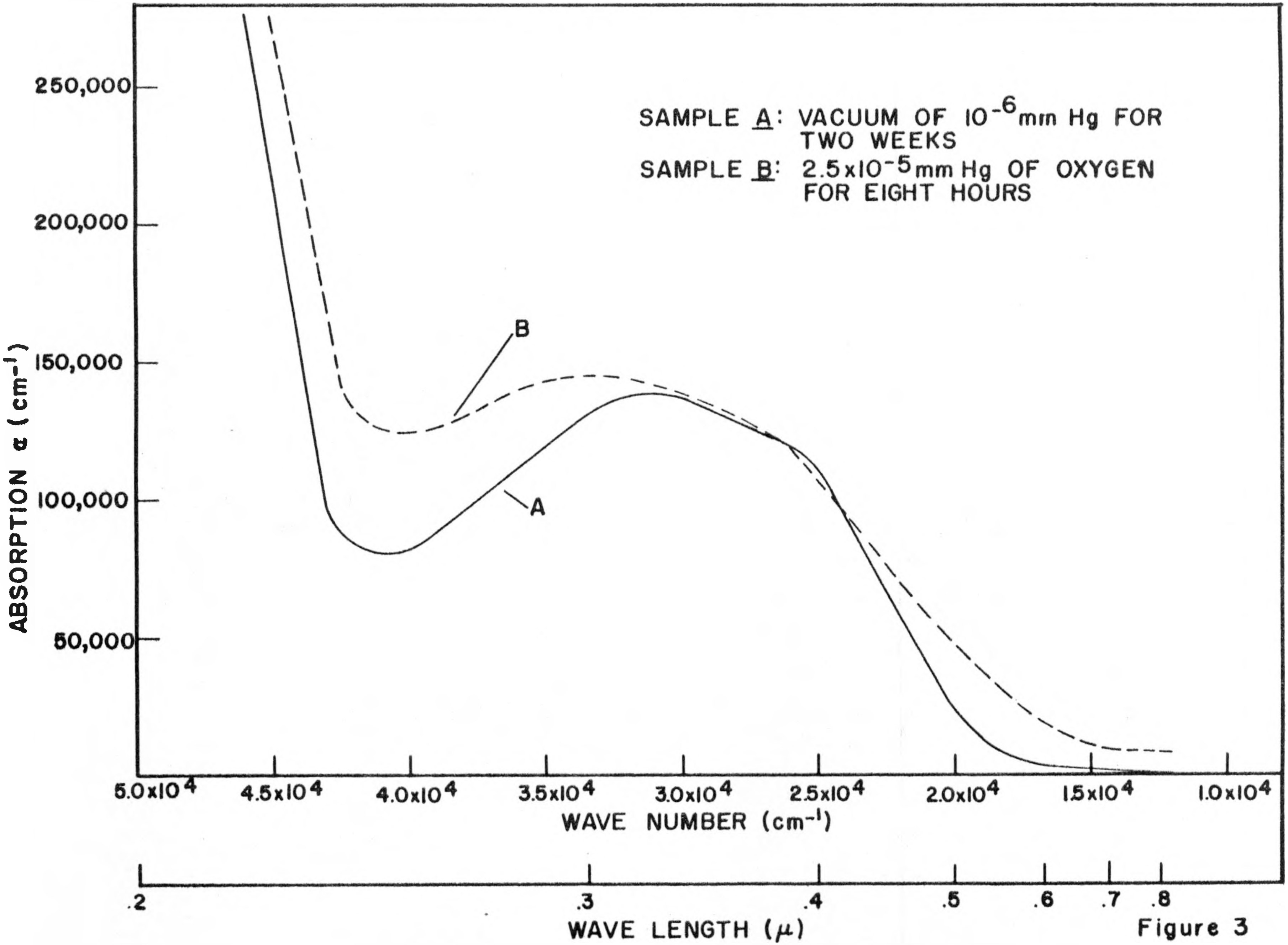

Figure 3

OPTICAL ABSORPTION OF UO2

(ACKERMANN ET AL)

.2 μ and 3 μ should be that caused by transitions within the 5f shells of the uranium ions in the crystal. The neutral uranium atom has an electronic configuration $(5f)^3$ $(6d)$ $(7s)^2$.

The approximation usually made for the uranium ions in UO_2 is that they are U^{4+}.(8) The configuration then becomes $(5f)^2$. It will be assumed that the remaining bond-electrons do not affect transitions of the ordinary 5f electrons.

There are a number of effects which cause splitting of the energy levels in a $(5f)^2$ configuration, mainly:

(1) Coulomb repulsion between the 5f electrons;
(2) Spin-orbit coupling;
(3) Interactions with surrounding atoms.

The Coulomb repulsion results in the separation of levels for different values of the total electronic orbital angular momentum L.
The allowed levels are: ^1S, ^3P, ^1D, ^3F, ^1G, ^3H, and ^1I, where the left superscript indicates the spin degeneracy 2S+1 and the letter indicates the orbital angular momentum of the two-electron system. The degeneracy of each level is (2S+1)(2L+1), and there are 91 states altogether. The eigenfunctions are linear combinations of products of ordinary 5f single-electron wave functions. The energy splittings due to the Coulomb repulsion are calculated using first order perturbation theory.

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(8) S. Aronson, J. E. Rulli, and B. E. Schaner, J. Chem. Phys. 35, 1382 (1961).

For the $(5f)^2$ configuration, these values have been computed in terms of four parameters: F_0, F_2, F_4, and F_6, where

$$F_K(n\ell) = e^2 \int_0^\infty \int_0^\infty \frac{r_<^K}{r_>^{K+1}} R_1^2(n\ell) R_2^2(n\ell) r_1^2 r_2^2 \, dr_1 dr_2$$

The R's are radial wave functions and are very difficult to estimate. Usually the F's are obtained by fitting the observed spectral data.

The Hamiltonian representing spin-orbit coupling is $\mathcal{H}_s = \xi(r_1) \underline{l}_1 \cdot \underline{s}_1 + \xi(r_2) \underline{l}_2 \cdot \underline{s}_2$. This operator commutes with the total electronic angular momentum $\underline{J}$, but not with $\underline{L}$ or $\underline{S}$. The usual way to label a group of states split by both Coulomb repulsion and spin-orbit coupling is by the numbers $LSJM_J$, where J and M_J are the total electronic angular momentum and its Z component. If the spin-orbit splitting is very small compared to the Coulomb splitting, it is legitimate to neglect matrix elements like $\langle L'S J M_J | \mathcal{H}_s | L S J M_J \rangle$ where $L \neq L'$. Then the splittings are given by $\Delta E(SLJM_J) = \frac{1}{2} \zeta(SL) [J(J+1) - L(L+1) - S(S+1)]$. This is called the Russell-Saunders coupling scheme.

In the case of uranium, this is not a good assumption and the whole spin-orbit matrix (all L and S) must be diagonalized to obtain the splitting values, again in terms of the parameter ζ, which must be determined experimentally. This is called the intermediate coupling scheme.

Few spectral absorption measurements have been performed on UO_2 in this wavelength region. Assuming, however, that a uranium atom in UO_2 is roughly the same as a U^{4+} ion, approximate values of the F_0, F_2, F_4, F_6 and ζ can be obtained using measurements on U^{4+} ions in other configurations.

A number of sets of measurements have been taken on U^{4+} spectra.$^{(9)-(12)}$

The data of McLaughlin, Cohen and Carnall, and Conway are in reasonable agreement and they agree in their assignments of terms. The energy levels calculated by Conway are given below, and the absorption spectrum obtained by Cohen and Carnall is shown in Figure 4.

LEVEL	WAVE NUMBER
$^1S_0$	39,482 cm^{-1}
$^3P_2$	23,330
$^1I_6$	19,480
$^3P_1$	18,503
$^3P_0$	15,672
$^1D_2$	15,413
$^1G_4$	15,664
$^3H_6$	10,992
$^3F_4$	8,619
$^3F_3$	8,574
$^3H_5$	5,875
$^3F_2$	4,031
$^3H_4$	0 (assumed ground state)

But these calculations neglect completely the effects of the ions surrounding the U^{4+} (the "ligand field"). The data of McLaughlin, Cohen and Carnall, and Conway are in reasonable agreement, although the ligand fields must differ considerably for the different compounds considered. Hence these investigators conclude that the effect of the ligand field is probably small compared to the spin-orbit and Coulomb splittings. Using more highly complexed U^{4+}, Satten et al interpreted the ligand field as being

(9) On UCl_4, R. McLaughlin, J. Chem. Phys. 36, 2699 (1962).

(10) On organic complexes, R. A. Satten, D. Young, and D. M. Gruen, J. Chem. Phys. 33, 1140 (1960).

(11) On U^{4+} in $DClO_4$ solution, D. Cohen and W. T. Carnall, J. Phys. Chem. 64, 1933 (1960).

(12) On UF_4, J. C. Conway, J. Chem. Phys. 31, 1002 (1959).

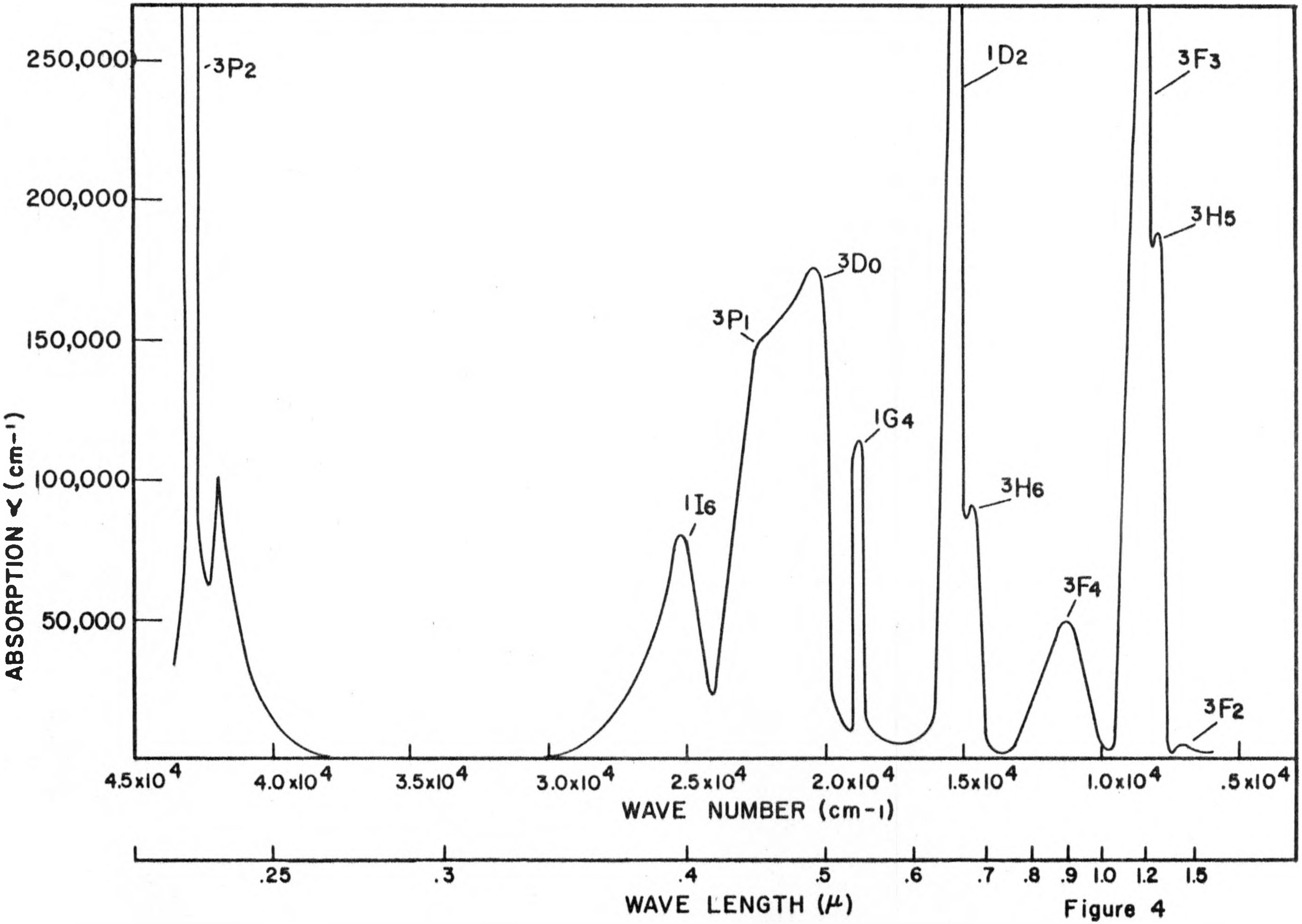


Figure 4

ABSORPTION SPECTRUM of U(IV) IN SOLUTION

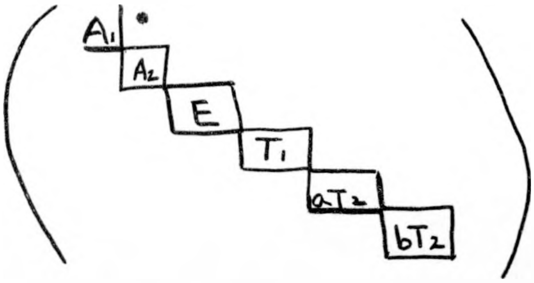
(COHEN and CARNALL)

rather large. We shall assume, however, that UO_2 exhibits a relatively small ligand field. (We shall eventually estimate its magnitude.) On this assumption, we shall be justified in considering the effects of the ligand field within each $LSJM_J$ level individually. That is, in calculating the splitting due to V, the ligand field, we consider matrix elements like $\langle LSJM_J|V|LSJM_J'\rangle$ but neglect elements like $\langle L'SJM_J'|V|LSJM_J\rangle$ or $\langle LSJ'M_J'|V|LSJM_J\rangle$.

For example, suppose we try to find the splitting of the 13-fold degenerate $^1I_6$ level. If we use the usual $LSJM_J$ eigenfunctions, we get a 13 x 13 matrix for V which we would have to diagonalize (if we knew the ligand field V). We can, however, simplify this matrix representation considerably.

The ligand field the uranium atom feels is due mainly to the oxygen atoms arranged at eight octahedral positions around the uranium. The ligand field thus has octahedral symmetry. Suppose we consider some operation g (a combination of rotations) which is equivalent to interchanging equivalent points on an octahedron. The ligand field V thus is not changed under the operation g.

Our V matrix has as its basis the thirteen (L=6, S=0, J=6) functions. The matrix can be greatly simplified if we find a set of basis functions which reflects the octahedral symmetry. In particular, according to group theory, there exists a set of basis functions, linear combinations of thirteen $^1I_6$ functions, such that the matrix representing any member g of the group G looks like:



There are no matrix elements of any operator g outside the six boxes. Furthermore, A_1 and A_2 have dimension one; E, dimension two; T_1, aT_2, and bT_2 dimension three. Also since V is invariant under any operation g, it follows from group theory that the matrix for V is of the same form. It also follows from group theory that all of the eigenvalues of any small matrix are equal. Furthermore, the eigenvalues of the aT_2 and bT_2 matrices are equal. The proper basis functions, consisting of linear combinations of the ${}^1I_6$ functions are tabulated in Griffith.(13) All of this has been deduced from the octahedral symmetry and general group theoretical considerations.

Furthermore, group theory can tell us something about the form of the function V. Any general V can be expressed in the form

$$V = \sum_{K=0}^{\infty} \sum_{\alpha=-K}^{K} \gamma_{K\alpha} \{ r_1{}^K Z_{K\alpha}(\theta_1, \phi_1) + r_2{}^K Z_{K\alpha}(\theta_2, \phi_2) \}$$

where $Z_{K\alpha}$ is a linear combination of $Z_{K\alpha}^{(c)} = \frac{1}{\sqrt{2}}(Y_{K\alpha} + Y_{K-\alpha})$ and $Z_{K\alpha}^{(s)} = \frac{1}{\sqrt{2}}(Y_{K\alpha} - Y_{K-\alpha})$.

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(13) J. S. Griffith, The Theory of Transition Metal Ions, Cambridge, 1961 p. 394.

But since V in invariant under any octahedral operation, it must be a basis for a representation of G of degree 1, and these bases are known. Furthermore, we only want to calculate the matrix elements of V using basis elements containing f electron functions. Neglecting those parts of V which would not contribute to these matrix elements,

$$\begin{aligned} V(\text{electron } 1) = {} & \gamma_{00} + \gamma_{40} r^4 \left(\sqrt{\tfrac{7}{12}}\, Z_{40} + \sqrt{\tfrac{5}{12}}\, Z_{44}^{(c)} \right) \\ & + \gamma_{60} r^6 \left(\tfrac{1}{\sqrt{8}}\, Z_{60} - \tfrac{1}{2}\sqrt{\tfrac{7}{2}}\, Z_{64}^{(c)} \right) \\ & + \gamma_{62} r^6 \left(\tfrac{\sqrt{11}}{4}\, Z_{62}^{(c)} - \tfrac{\sqrt{5}}{4}\, Z_{66}^{(c)} \right). \end{aligned}$$

Since we know the basis functions and V we can calculate the expectation values of V in terms of the γ's.

In the spirit of pure ligand field theory, all four γ's must be determined experimentally, since the "ligand field" V is due not only to the static electric fields of the ligand ions, but also to the various effects of bonding orbitals and the motion of the ligand ions.

Crystal field theory neglects all the effects of the uranium ion's environment except for the static electric field due to the neighboring ions. Under this assumption,

$$\gamma_{K\alpha} = -\frac{4\pi e}{2K+1} \int \frac{\rho(\underline{R})\, Z_{K\alpha}(\Theta, \Phi)}{R^{K+1}}\, d\tau$$

where ρ = charge density.

We could approximate the oxygen atoms as point charges -2e and compute the field splitting in the crystal field approximation. This would be a extremely tedious calculation and was not done. Rough calculations indicate however, that the ligand-field splitting is probably about 2000 cm^{-1}. Thus the crystal field effects are probably somewhat smaller than those of spin-orbit and Coulomb effects.

The resulting energy levels are:

$^1S_0$
$^3P_2$: E, T_2
$^1I_6$: A_1, A_2, E, T_1, T_2^2
$^3P_1$: T_1
$^3P_0$:
$^1D_2$: E, T_2
$^1G_4$: A_1, E, T_1, T_2
$^3H_6$: A_1, A_2, E, T_1, T_2^2
$^3F_4$: A_1, E, T_1, T_2
$^3F_3$: A_1, T_1, T_2
$^3H_5$: E, T_1^2, T_2
$^3F_2$: E, T_2
$^3H_4$: A_1, E, T_1, T_2

The energy level spectrum is thus expected to look very much like that of U^{4+} except for small splittings of each line due to ligand fields. But the plot of $\alpha(\nu)$ for UO_2 need not be similar to those of other U^{4+} compounds because the intensities and line widths need not be the same in the different compounds.

The most important mechanism for electronic transitions is dipole radiation. The transition probability is:

$$P_{qe} = \frac{4\pi^2 e^2}{\hbar^2 c^2} I(\omega_{qe}) |\underline{r}_{qe}|^2$$

where I (Wge) is the intensity of incident radiation near the transition frequency and $r_{ge} = \langle X_g | r | X_e \rangle$.   Xe, Xg = wave functions in excited state and ground state.

If the X's are purely combinations of 5f orbitals, then both wave functions have odd-parity, their product has even-parity, and $r_{ge} = 0$. If all of the perturbation Hamiltonians have even-parity, then there is no mixing with any even-parity orbitals. Since the uranium ion is at a site of inversion symmetry, the static crystal field has even-parity. But due to lattice vibrations the oxygen atoms may not be at their equilibrium positions, causing an even-parity component in the perturbed wave function. We assume that the even states mixed in are 6d orbitals. We shall see that the dipole transitions correspond to the absorption of a photon, a change in electronic level, and a change in vibrational level. These transitions are called "vibronic". Following Griffith$^{(14)}$, we calculate the matrix element between Xe, the wave function of the excited state, and Xg, the wave function of the ground state.

$$\langle X_e | r | X_g \rangle = -\sum_{Y} \langle X', n_o \pm 1 | r | Y, n_o \pm 1 \rangle \langle Y\, n_o \pm 1 | \mathcal{H}_v | X, n_o \rangle \left(\frac{1}{E}\right)_Y$$

$$- \sum_{Y} \langle X', n_o \pm 1 | \mathcal{H}_v | Y, n_o \rangle \langle Y, n_o | r | X, n_o \rangle \left(\frac{1}{E}\right)_Y$$

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(14) J. S. Griffith, loc. cit., p. 297

when X' = unperturbed excited state
X = unperturbed ground state
Hv = Hamiltonian coupling electronic and vibrational levels.
n_o represents all the quantum numbers of the vibrational modes in the ground state.
$n_o \pm 1$ represents the same numbers as n_o, except that just one mode has its quantum number increased or decreased by 1. This is the vibrational state of the excited level.
Y represents a general 6d orbital.

Actual evaluation of this matrix element would require knowledge both of the radial wave functions and of the normal modes of the lattice. The exact calculation of all the modes is extremely tedious and has never been done except for very simple crystal lattices. The normal modes were calculated, however, for the special case of a wave vector $\underline{K}$ parallel to one of the principle axes, and the resulting w (k) relations are plotted in Figure 7. Twenty-four of the 36 modes are roughly what they would be if the uranium atoms were infinitely heavy; i.e. they correspond to motion mainly by the oxygen atoms. For simplicity, let us use the approximation that the uranium ions are infinitely heavy, so the normal modes correspond to simple harmonic motion of the oxygen atoms. This accounts for the 24 high-frequency modes. The twelve low-frequency modes correspond to motion of the uraniums and oxygens with roughly the same velocities. It can be shown that the effects of these modes are about the same as the effects of the high-frequency modes.

Assume also that the interaction Hamiltonian is due entirely to the Coulomb interaction between the 5f electrons and the oxygen ions. In that case, the largest part of the interaction Hamiltonian which gives non-zero matrix elements is $\frac{3}{2}\frac{e^2}{r_{ou}^5}(\underline{r}_e\cdot\underline{r}_{ou})(\underline{r}_0\cdot\underline{r}_{ou})$ where

$\underline{r}_{ou}$ = vector between equilibrium positions of our oxygen and uranium.
$\underline{r}_0$ = position of electron relative to uranium nucleus.
$\underline{r}_e$ = position of oxygen atom relative to equilibrium position.

Inserting this into the equation for $\langle X_e|\underline{r}_e|X_g\rangle$ and assuming

$$|\langle\psi_{5f}|\underline{r}_e|\psi_{6d}\rangle|^2 \simeq \frac{\overline{r_e^2}}{3},$$

$$|\langle X_e|\underline{r}_e|X_g\rangle|^2 \approx \frac{18}{E^2}\left(\frac{e^4}{r_{ou}^6}\right)\frac{\hbar}{m\omega_0}\,\frac{\overline{r_e^4}}{9}\,\bar{n}.$$

where E = splitting between 5f and 6d levels
w_0 = restrahlen frequency of lattice
$\bar{n}$ = average number of vibrational quanta per mode.

Using the formula for the transition probability, the area under a peak in the absorption curve is

$$\int\alpha(\nu)d\nu = \frac{\nu}{\hbar c}\,\frac{4\pi e^2|r_{kn}|^2}{v} \approx \frac{512\pi e^6 \nu\,\overline{r_e^4}\,\bar{n}}{27a^9 m E^2 \nu_0 c^2}$$

where v = $\frac{\text{volume of lattice}}{\text{number of uranium atoms}}$ and ν_0 = restrahlen wave number = 400 cm^{-1}

a = ½ lattice constant
m = mass of oxygen atom.

$$\int\alpha(\nu)d\nu = (39.3\,\bar{n}\ cm^{-1})\,\nu_m$$

$$\bar{n} = \frac{e^{-\hbar\omega_0/KT}}{1-e^{-\hbar\omega_0/KT}} = 3.5 \text{ at } 2000°C.$$

ν_m= wave number of maximum of peak

$$\therefore \int\alpha(\nu)\,d\nu \approx (140\,cm^{-1})\,\nu_m.$$

It must also be noted that most of the lines correspond to transitions to degenerate states. This area should be multiplied by the degeneracy of the excited state.

This answer is of the same order of magnitude as the areas under the peaks observed by Ackermann. The different peak areas will vary, in actual practice, since the matrix element $\langle \psi_{5f} | r_e | \psi_{6d} \rangle$ varies with the choice of 5f orbitals.

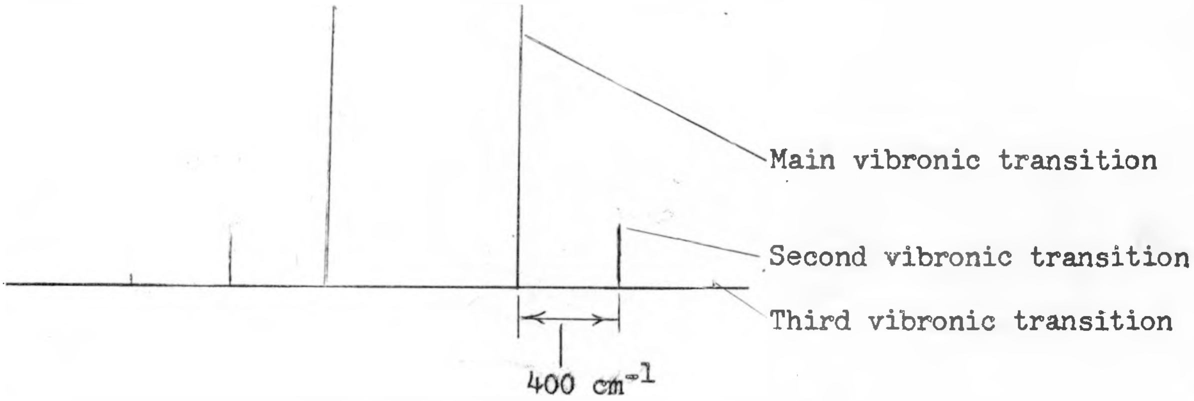
The widths of the peaks are also important. These widths must increase with increasing temperature. If the peak widths could get as large as, say, 10,000 cm^{-1}, then the whole spectrum would be very blurred, and there would be no chance of getting α near 64 cm^{-1}.

It is generally assumed that lattice vibrations cause most of the broadening of peaks in solids but little quantitative work seems to have been done.

The transitions have all been assumed vibronic. It was noted earlier that there is a change of one vibrational level in such an interaction. If a single vibrational frequency is assumed, the photons absorbed must have energies $\hbar(\omega_{elect} \pm \omega_o)$. Thus there is a minimum line width of about 800 cm^{-1} associated with the vibronic transition mechanism. It is also possible to have transitions in which two or more changes are made in the vibrational levels. We assume again that the interaction between the 5f electrons and the vibrational levels is due entirely to the electrostatic interaction between the nearest-neighbor oxygen atom and the 5f electrons. Furthermore, we neglect the effects of the low-frequency modes, since it may easily be shown that they have little effect on the peak width. The actual high-frequency modes are approximated by simple harmonic vibrations of the oxygen atom and a 5f electron is expanded in powers of Δr_0, the displacement of the oxygen atom. Only terms of first order in Δr_e are kept. The result is:

$$\mathcal{H}_V = \left[\frac{e^2}{r_{OU}^3} - \frac{3}{2}\frac{e^2(\underline{r}_{OU}\cdot\Delta\underline{r}_0)}{r_{OU}^5} + \frac{15}{8}\frac{e^2}{r_{OU}^7}(\underline{r}_{OU}\cdot\Delta\underline{r}_0)^2 - \frac{35}{16}\frac{e^2}{r_{OU}^9}(\underline{r}_{OU}\cdot\Delta\underline{r}_0)^3 + \dots\right]$$
$$\times(\underline{r}_{OU}\cdot\Delta\underline{r}_e).$$

We use the same procedure as above, calculating the matrix elements of the various terms of Hv. Terms in $(\Delta r_o)^2$ have matrix elements corresponding to the emission or absorption of 2 phonons, $(\Delta r_o)^3$ to the emission or absorption of 3 phonons, etc. Each of these terms causes two subsidiary peaks as shown below:



The real peaks are rounded instead of showing groups of lines because the vibrational states are not all at frequency w_o, but spread over a range of frequencies. But the transitions with wave numbers about 800 cm^{-1} away from the peak are probably mainly due to transitions involving the gain or loss of two phonons with frequencies near w_o The ratio of intensities at 400 cm^{-1} and 800 cm^{-1} from the peak should be roughly .003.

For our purposes, the "peak width" can be defined as the range in wave numbers over which the absorption is more than 64 cm^{-1}. If an average peak height is about 10,000 cm^{-1}, then the absorption 800 cm^{-1} to either side of the peak will be 300 cm^{-1}; 1200 cm^{-1} from the peak it will be about 1 cm^{-1}. Thus a typical peak width should be about 2000 cm^{-1}. Referring back to the energy levels calculated by Conway and to the spectral measurements of Cohen and Carnall, we see that some of the level separations are considerably larger than 2000 cm^{-1}. Hence this large a peak width does not preclude the existence of points in the spectrum with $\alpha \ll 64$ cm^{-1}.

The final effect which must be considered is background absorption, i.e. that absorption which is independent of transitions in U^{4+} ions. Probably the most important cause of background absorption is imperfections in the lattice. The spectrum has been calculated for U^{4+} in sites of octahedral symmetry. But uranium dioxide fuel materials will, in general, contain uranium atoms in other valence states. For example, if the compound is not quite stoichiometic, and, in particular, contains excess oxygen atoms, there will be U^{5+} ions present. It is usually assumed that all the oxygen atoms, even those in interstitial positions, are doubly ionized. Thus in the vicinity of each interstitial oxygen, there will be two U^{5+} ions. The U^{5+} ion is presumably $(5f)^1$ and has an energy level structure completely different from U^{4+}. Absorption spectra of U^{4+} ions in the disturbed regions are disturbed by the different crystal fields.

Even in stoichiometric UO_2 there will be an equilibrium concentration of oxygen vacancy-interstitial pairs. In the region near the interstitial oxygen, we would expect to find U^{5+} ions, just as in non-stoichiometric UO_2. If we assume the region around the oxygen vacancy to be electrically neutral, we would expect uranium ions of smaller valence to be present, perhaps U^{2+} or U^{3+}. In any case, the region around a vacancy or interstitial will certainly be disrupted sufficiently to cause uranium ions in states other than +4. If the energy required to create a vacancy-interstitial pair is E, then the ratio of the concentration of uranium atoms in states other than +4 to the concentration of U^{4+} is $ne^{-E/2kt}$, where n is the number of uranium atoms "disturbed" by one vacancy-interstitial pair. It is very difficult to obtain any estimate of E, but if E=2.5 ev, the ratio of the concentration of "disturbed" oxygen atoms (not in +4 state) to the concentration of U^{4+} is about .008. Also, when UO_2 is used as a reactor fuel, radiation damage would be expected to increase the number of crystal imperfections above the value for thermal equilibrium.

We can make a rough estimate of the effect of these defects on the background. In thermal equilibrium, there will be uranium atoms in a number of states other than U^{4+}. The intensities of their characteristic peaks should be about the same as U^{4+}, but the locations will be different. Hence, let us assume the background due to the various species of uranium atoms in different ligand fields has a constant magnitude equal to the average absorption of a U^{4+} ion multiplied by the number of uranium atoms in states other than U^{4+}. The average intensity of the lines is 280 x $10^4 cm^{-2}$. There are 90 excited states over a range in wave numbers of

$4 \times 10^4 \text{cm}^{-1}$. The average background should be 6300 cm^{-1} times the ratio of uraniums in valence states other than +4 to the total number of uranium atoms. Thus a compound UO_{2+x} would have an average background of 64 cm^{-1} for x = .0025. Also, if the energy of formation of a uranium Frenkel defect is about 2.5ev, the equilibrium number of defects at 2000°C would be enough to cause an average background of about 64 cm^{-1}.

Incidentally, in the plot of Ackermann's data for pure UO_2 in Figure 3, there is a very low minimum at about $\nu = 1.6 \times 10^{+4} \text{cm}^{-1}$. He also tested specimens which had been heated in oxygen atmospheres. These specimens had much higher minima, and their absorption coefficients never got below about 10,000 cm^{-1} between .2 μ and .8 μ.

Absorption for $\lambda > 3 \mu$

The only infrared absorption data available for UO_2 are those of Tsuboi et al (15). These data are shown in Figure 5. The scale indicated was not supplied by Tsuboi et al, but was calculated as will be explained below.

The two main absorption effects in the infrared region are: (1) lattice absorption, and (2) free carrier absorption.

The primary mechanism of lattice absorption occurs when a photon is transformed directly into a phonon. This occurs mainly in ionic crystals, in

(15) M. Tsuboi, M. Terada, T. Shimanouchi, J. Chem. Phys. 36, 1301 (1962).

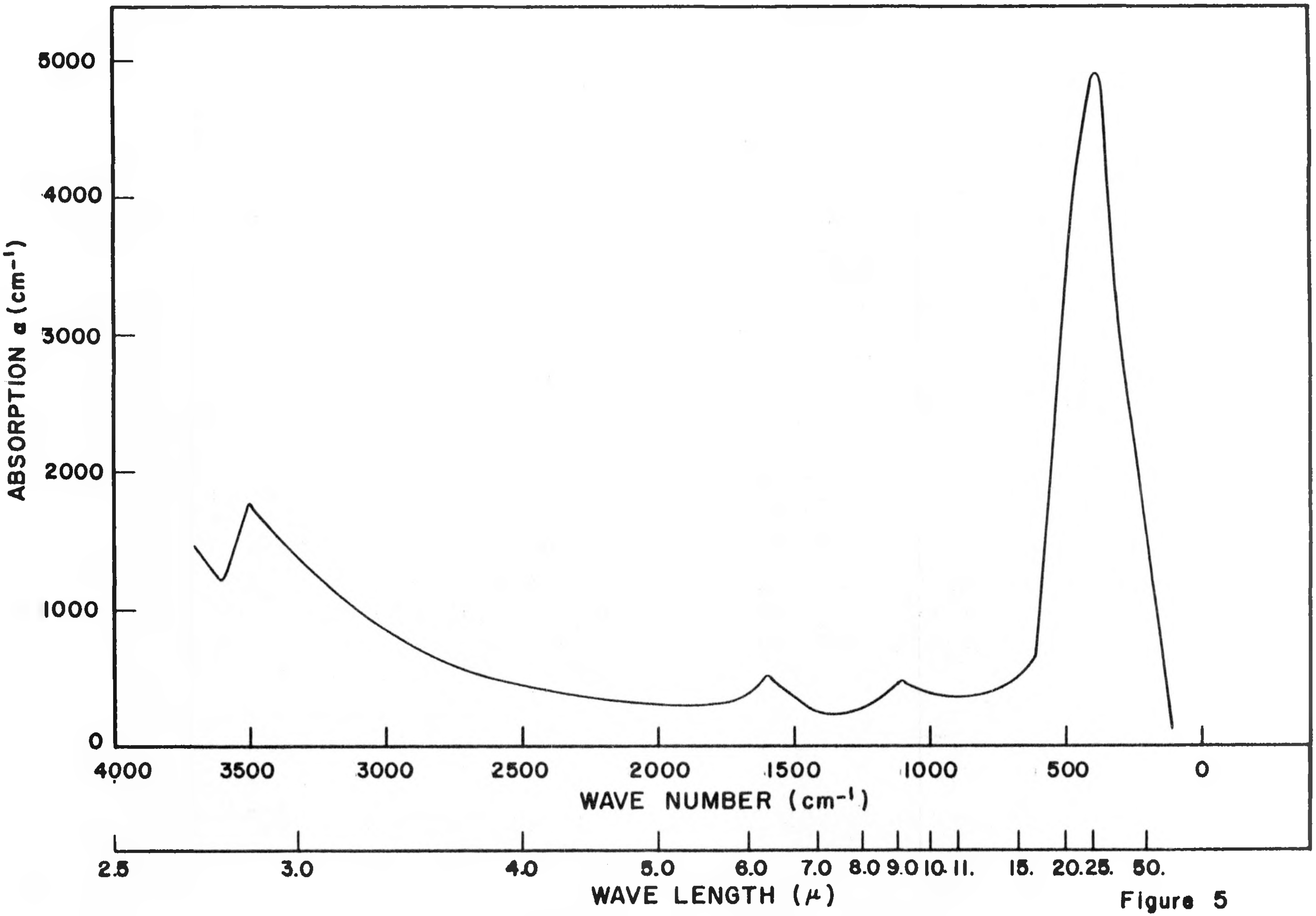


Figure 5

FAR INFRARED ABSORPTION of UO_2

(TSUBOI ET AL)

which ionic displacements cause dipole moments. These dipole moments then interact with incident photons. This interaction can only take place if the wave vectors of the photon and phonon are the same, and conservation of energy requires that the frequencies be the same. The allowed frequencies of absorption can then be found if the w ($\underline{k}$) relations of the lattice are known. These are, in general, difficult to calculate, and complete results have only been published for a few monatomic crystals. The normal modes of a UO_2 lattice have been calculated, however, for the specific case of $\underline{k}$ along one the primary crystal axes. These are shown in Figure 6.

Assuming that the dipole moment is exactly proportional to the lattice displacements, and the lattice potentials are exactly harmonic, the only possible means by which the lattice can absorb photons is by this direct photon-phonon method.

Since the speed of light $\frac{w}{k}$ is much larger than the acoustical velocity in UO_2, direct photon-phonon interaction can only occur near the points indicated in the w ($\underline{k}$) diagram. Only at these points can w and $\underline{k}$ both be conserved. If the corresponding frequencies are denoted by w_o, then the transition probability for the photon-phonon absorption is roughly(16)

$$P \simeq \frac{\delta(\omega-\omega_0)\pi\rho e^2}{M_1 M_2} \qquad (*)$$

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(16) R. E. Peirls, *The Quantum Theory of Solids*, Oxford (1955).

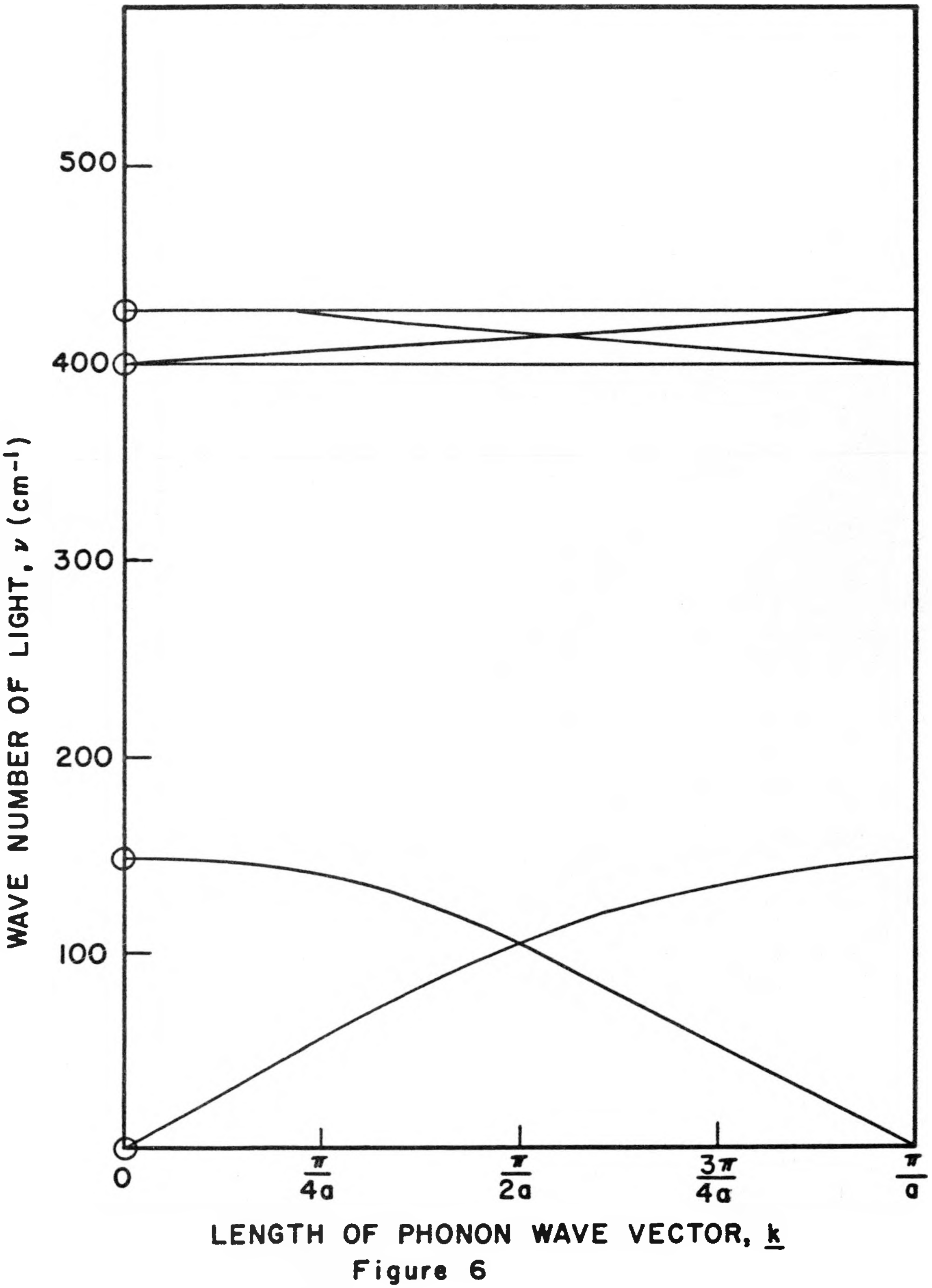

Figure 6

NORMAL MODES OF LATTIC FOR k ALONG A PRINCIPAL AXIS

The peaks actually observed have been broadened because of a number of factors. We can, however, obtain an estimate of the area of the infrared peaks from the above expression. This was, in fact, the way in which the scale was determined in Figure 5, since data on the absolute magnitudes of the absorption peaks were not published by Tsuboi et al.

The general formula for the transition probability between two lattice states n and p is(17)

$$P_{np} = \left(\frac{\pi^2}{\hbar^2}\right) E_o^2(\omega_{np}) \left|\langle \psi_n | M | \psi_p \rangle\right|^2$$

where E_o is the amplitude of the incident field, M is the dipole moment of the solid, and ψ_n and ψ_p represent the initial and final lattice wave functions. If $M = \alpha_o Q_o$ where Q_o is a normal mode corresponding to k=0 and the ψ_n and ψ_p are the lattice functions characteristic of harmonic potentials only, this reduces to equation (*). Following Szigeti, if the lattice vibrations are not exactly simple harmonic or M contains higher order terms, additional effects are brought in. In particular, if $M = \alpha_o Q_o + \sum \beta_{ij} Q_i Q_j$ where the Q's are normal mode coordinates,

$$\alpha \approx \frac{\pi^2 KT}{v \cdot 2nc} \frac{1}{\delta\omega} \sum_{\substack{i,j \\ (\omega_i + \omega_j \text{ between } \omega \text{ and } \omega + \delta\omega)}} \frac{1}{\omega_i^2 \omega_j^2} \beta_{ij}^2$$

(This is a simplified form which should only give the correct order of magnitude. It actually only applies to $\omega \ll \omega_0$ or $\omega \approx 2\omega_0$).

Making a conservative estimate on β_{ij}, $\alpha \approx 2500 \text{ cm}^{-1}$ at $\omega = 2\omega_0$. This

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(17) B. Szigeti, Proc. Roy. Soc. London, 252 217 (1959) and 258, 377 (1960).

type of absorption corresponds to the creation of two phonons from one photon. The total energy of the two phonons cannot exceed about $2\hbar\omega_0$. For higher frequencies (and $\nu \geq 800\ \text{cm}^{-1}$), higher order effects must be brought in, corresponding to the creation of three or more photons. In this way the lattice absorption reaches to shorter wavelengths, but it probably gets quite small below $\lambda \approx 10\mu$.

No calculations have been performed on the third and fourth order effects, but it seems reasonable to assume that each higher order effect is smaller than the preceding one by a factor of the ratio of the lattice vibrational displacement to the distance between atoms. For UO_2 at 2000°C, this ratio is about 1/10. Thus we might make an extremely rough estimate.

$$
\begin{aligned}
(800\ \text{cm}^{-1}) &= 2500\ \text{cm}^{-1} \\
(1200\ \text{cm}^{-1}) &= 250\ \text{cm}^{-1} \\
(1600\ \text{cm}^{-1}) &= 25\ \text{cm}^{-1} \\
(2000\ \text{cm}^{-1}) &= 2.5\ \text{cm}^{-1}
\end{aligned}
$$

The other mechanism to be considered in attempting to estimate the infrared absorption properties of UO_2 is free carrier absorption. Free electrons and holes in UO_2 absorb energy from the alternating electromagnetic field. The classical formula for the rate of absorption is given by Moss (18)

$$\alpha_{\text{free carrier}} \approx \frac{\lambda^2 e^2}{4\pi^2 \varepsilon_0 c^3 n} \left[\frac{\sigma_n}{m_n^2 \mu_n^2} + \frac{\sigma_p}{m_p^2 \mu_p^2} \right].$$

(18) T. S. Moss, Optical Properties of Semiconductors, Academic Press, 1959.

where ε_o = permittivity of free space;
σ_n, σ_p = conductivities of electrons and holes;
μ_n, μ_p = mobilities of electrons and holes;
Mn, Mp = effective masses of electrons and holes.

There is considerable difficulty involved in evaluating α, however, because several of the parameters in the equation for α can only be estimated very loosely. Since we shall need to know the values of some of these quantities, it is worthwhile to consider some of the relevant experiments:

(a) Intrinsic Conductivity:

(1) Willardson, Moody, and Goering(19) took data on conductivity of almost stoichiometric specimens. The slopes of the conductivity curves correspond to an extrinsic gap of .4ev. At higher temperatures the slope becomes larger, corresponding to about 3ev gap between the valence and conduction bands. But Willardson et al assume that this is not the actual energy gap. Estimates of the energy gap between the valence and conduction bands range from .8ev to 2.0ev.

Taking the highest-temperature point in the Willardson-Moody-Goering data as a basis and extrapolating the data using various slopes, the values of the predicted conductivities at 2000°C are the following:

Energy gap	(2000°C)
.8ev	2.8 (ohm-cm)$^{-1}$
1.0	6.5
1.2	15
1.5	50
1.7	120
1.9	270
2.1	647

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(19) R. K. Willardson, J. W. Moody, and H. L. Goering, BMI - 1135, 1956.

(2) Data taken by R. Scott (20) on intrinsic UO_2 between 800°C and 1300°C correspond to an energy gap separation of .69ev. Extrapolation to 2000°C gives 1.8 $(\text{ohm-cm})^{-1}$.

(b) In the extrinsic region, the data are considerably more reliable. Aronson et al (21) give data on several non-stoichiometric samples. Extrapolating these data to 2000°C yields the following conductivity estimates:

$UO_{2.028}$ ------------------------------ 19.2 $(\text{ohm-cm})^{-1}$
$UO_{2.143}$ ------------------------------ 81.3 "
$UO_{2.212}$ ------------------------------ 100 "

The mobilities are even harder to estimate than the conductivities. The only measurements made on the Hall coefficient of UO_2 were made by Hartmann (22) in 1936. His measurements indicate that, at room temperature, UO_2 is a p-type semiconductor with mobility 10 $\text{cm}^2/\text{volt-sec}$. μ should go as $T^{-3/4}$ so $\mu (2000^\circ) \doteq 2\ \text{cm}^2/\text{volt-sec}$. Given the compositions of the specimens of Aronson et al, and the gap between the acceptors and the valence band, it is possible to estimate the number of free carriers. Dividing the conductivity by the number of carriers and extrapolating to 2000°C gives $\mu (2000^\circ) = .8\ \text{cm}^2/\text{volts-sec}$.

These values apply only to hole mobilities. It is usually assumed that the electron mobility is larger than the hole mobility, but no estimates

(20) R. Scott, AERE MIR 2526.
(21) S. Aronson, J. E. Rulli, and B. E. Schaner, loc. cit.
(22) W. Hartmann, *Zeits. Physik* *102*, 709 (1936)

of the electron mobility seem to have been made in the literature.

We shall assume $\mu_n > \mu_p$ and neglect the electron term in the expression for the free carrier absorption.

Using these values for μ and σ and assuming $M_p = 10^{-27}$ gm,

α(most probable) = $45\ \text{cm}^{-1}\ \lambda^2$ for intrinsic UO_2.
α(minimum estimate) = $7\ \text{cm}^{-1}\lambda^2$ (λ in microns).

The corresponding values for $UO_{2.14}$ would be about eight times as large. There is another matter to be considered in calculating the absorption of bulk UO_2, namely the effect of porosity. Small pores in the solid act as scattering centers for radiation. Each pore scatters a large fraction of the radiation hitting it because the index of refraction is about 2.2, and there is total internal reflection for light incident at any angle greater than about 26°.

The pores range in size from about .1 μ to .1 mm. Assume that the maximum volume density is for pores of size 3×10^{-3} cm and the number of pores per unit volume with diameters between D and D+dD is $Ce^{-\beta D}dD$.
Then $\beta = 10^{+3}\ \text{cm}^{-1}$. For 3% porosity,

$$\frac{dn}{dD} = 5 \times 10^9\ \text{cm}^{-4}\ e^{-10^3 D}.$$

The scattering cross-section per particle is roughly D^2. Hence,

$$\alpha_{sc} = \int_0^\infty D^2 \frac{dn}{dD}\, dD = 5 \times 10^9\ \text{cm}^{-4} \int_0^\infty D^2 e^{-10^3 D}\, dD$$

$$\alpha_{sc} \approx 10\ \text{cm}^{-1}$$

Since the light is assumed to be scattered, not absorbed in this process, and the light is scattered roughly isotropically,

$$\alpha_{\text{effective}} \doteq \sqrt{\alpha_{\text{scatt.}}\,\alpha_{\text{pure absorption}}}$$

if $\alpha_{\text{scatt.}} >> \alpha_{\text{pure absorption}}$.

The effect of porosity, then, is to reduce the "mean free path" of light rays in the solid. It could only be important in those wavelength regions where $\alpha_{\text{pure abs.}} < 10\ \text{cm}^{-1}$; i.e. those regions in which most of the radiation is transmitted. This tends further to reduce the probability that the radiation conductivity could be as large as that required to explain the observation of Bates. If the radiation conductivity could get that large, it would be due to narrow transmission bands between peaks, probably just one or two of them. To have an average $(\overline{1/\alpha}) = (1/64\ \text{cm}^{-1})$, the absorption coefficient would have to get down near 1 cm^{-1} at the minima. If it did get down this low, this scattering effect would increase it by about a factor of 3.

Conduction by free carriers

There are two obvious ways in which the free carriers in a semiconductor like UO_2 can conduct energy. First, their average kinetic energy will be higher in the warmer regions. When carriers from the warm regions drift into the cooler ones, energy is transferred. The contribution to the thermal conductivity due to the free carrier transfer of kinetic energy is given by the Wiedemann-Franz law, $K_T = 2\left(\frac{k}{e}\right)^2 \sigma T$.

Also, it would be expected that more electrons and holes should be produced in the warmer regions. On entering the cooler regions, these electron-hole pairs should recombine, yielding recombination energy. Price (23) has considered this process in detail. He predicts this contribution to the thermal conductivity will be:

$$K_{recomb.} \approx 2\left(\frac{k}{e}\right)^2 \sigma T \left(\frac{\sigma_1\sigma_2}{\sigma^2}\right)\left(\frac{E_{gap}}{kT}\right)^2$$

For UO_2, $\frac{E_g^{\ 2}}{(KT)^2} = 58$ at 2000°C.

$\frac{\sigma_1\sigma_2}{\sigma^2}$ is between 1/4 and 1/100 for intrinsic specimens.

Assuming $\sigma_{elect.} \approx \frac{1}{10}\sigma_{holes} = 1\ (\text{ohm cm})^{-1}$

$K_{recomb} + K_T = .002$ watts/cm°C.

The observed deviation from the 1/T law is about ten times this large.

Conclusions

From the spectral analysis, we can conclude that it is improbable that an average transmission value $\overline{(1/\alpha)} = 1/64\ \text{cm}^{-1}$ could be achieved in UO_2 in the neighborhood of 2000°C. This follows from a number of considerations:

(1) In the vicinity of the electronic peaks or the restrahlen peak in the infrared, the absorption is usually hundreds of times 64 cm^{-1}.

(2) There are thirteen electronic energy levels in the free ion, spread roughly uniformly over the range from $4 \times 10^4\ \text{cm}^{-1}$ to $.4 \times 10^4\ \text{cm}^{-1}$. These are split up by the crystal field into 37 different levels. Each peak should have a width of

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(23) P. J. Price, Philosophical Magazine 46, 1252 (1955).

about 2000 cm^{-1}. Hence, there should only be a few places in the spectrum for $\nu > .4 \times 10^4$ cm^{-1} where the absorption by the U^{4+} should be smaller than 64 cm^{-1}.

(3) In non-stoichiometric oxides of uranium UO_2 x UO_{2+x} other valence states of U are present, primarily U^{5+}. It is unlikely that the few low points in the U^{4+} spectrum should also correspond to low points in the U^{5+} spectrum. Concentrations of a few tenths of a per cent of U^{5+} should be capable of causing significant background. If the activation energy of a Frenkel defect involving an oxygen vacancy and interstitial is less than about 2.5 ev, there should be enough of these defects in stoichiometric UO_2 at 2000°C to cause an average background greater than 64 cm^{-1}.

(4) In the range of $\nu < .4 \times 10^4$ cm^{-1}, the absorption by free carriers would probably amount to more than $\lambda = 200$ cm^{-1} although the uncertainty in this calculation is very large.

(5) For $\nu < .4 \times 10^4$ cm^{-1}, α due to lattice absorption should at least be a few cm^{-1}.

(6) If α ever does get significantly lower than 64 cm^{-1}, it would probably only be that low for a small fraction of the spectrum. For $\frac{1}{\lambda}$ to average (1/64 cm^{-1}), α would probably have to get down to a few cm^{-1} at the low points. For this small absorption, scattering by the pores would become important, and the effective λ would be roughly

$\sqrt{\alpha \text{ scattering } \alpha \text{ pure absorption}}$, further reducing the probability of averaging 1/64 cm^{-1}.

The conclusion that radiation conductivity could not cause the effect observed by Bates is extremely tentative, however, due to the lack of spectral measurements. The field splitting, intensity, and peak width estimates are of orders of magnitude only and could easily be off by factors of 2 or 3. A complete lack of knowledge of the defects in UO_2 makes the background estimate very indefinite. We can only state that it is improbable that radiation conductivity could be large enough to account for the data of Bates.

It is possible that free carrier conductivity might be large enough to account for the data of Bates. The knowledge of the electrical resistance and the mobilities could be off by a factor of 100 in either direction.

Suggestions for experimental work

(1) Spectral absorption measurements should be made on UO_2 in the range from .2 μ to 12 μ. The aim should be to see if there are any points in the spectrum where the absorption gets small compared to $\alpha = 64$ cm^{-1}. Instead of using thin films like those of Ackermann, it would be advisable to use crystal thicknesses of about 1 millimeter.

(2) Thermal conductivity measurements should, of course, be made.

One effect should be noted, however. If it does turn out that the absorption spectrum does have a few points at which α gets very small (a few cm^{-1}) the dimensions of the test sample must be kept much larger than the maximum value of $1/\alpha$. Otherwise, the mean free path of the photons is comparable with the dimensions of the sample, and the concept of "radiation conductivity" does not apply. Very complicated analysis would be required to deduce any general material properties from the experimental results.