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## FOREWORD

This report was prepared by the Department of Materials Science, The Technological Institute, Northwestern University under USAF Contract No. AF 33(616)-6194. This contract was initiated under Project No. 7022, "Surface and Interface Phenomena of Matter," Task No. 73664, "Interaction of Surfaces with Extreme Environments." The work was administered under the direction of the Materials Central, Advanced Systems Technology, Wright Air Development Division, with Dr. R. J. Barton acting as project scientist.

This report covers work conducted from January 1960 to January 1961.

WADD TR 60-866

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## ABSTRACT

The problem of the anomalous increase in the observed thermal conductivity of single-phase ceramics at high temperatures has been considered. At temperatures above the onset of this anomalous rise, account has been taken of the possibility that phonon, electronic, and radiative heat transfer, as well as transport of thermal energy by electron-hole pairs, excitons and dissociated gas molecules, may operate simultaneously and individually contribute significantly to the total heat flow. On the basis of reliable conductivity data on monocrystals of single-phase ceramics, estimations have been made on the magnitudes of these high-temperature components which reveal that excited states of low excitation energy may occur in certain ceramics. In these instances, such excited energy-carrying states are able to diffuse down the temperature gradient in the specimen thereby producing a non-negligible contribution to its observed thermal conductivity.

This technical documentary report has been reviewed and is approved.

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## I. INTRODUCTION

A controversy has been waging among solid physicists for a number of years regarding the increase in thermal conductivity observed in a number of semiconductors at high temperatures. Since this increase is obviously not attributable to phonon transport which obeys a  $1/T$  law, attempts have been made to account for it on the basis of ambipolar transport of gap energy by electron hole pairs,<sup>1,2</sup> internal radiation<sup>3</sup> and various other excitation mechanisms.<sup>4</sup>

The existence of a similar, anomalous rise in the high-temperature, thermal conductivity of some single-phase ceramics has been clearly demonstrated by the careful measurements of Charvat and Kingery.<sup>5</sup> The present paper attempts to rationalize this behavior in ceramics by considering the observed conductivity as some linear combination of phonon and electronic components, a radiative heat transfer component, and components resulting from certain excitation processes. In particular, the contribution to the observed conductivity from radiative transfer is considered to be too small to fit the observed deviations from a  $1/T$  law in the case of single crystalline  $TiO_2$ ,  $CaF_2$  and  $Al_2O_3$ . Thus, in such cases, consideration must be given to components of the observed thermal conductivity arising from simple excitation processes occurring in the crystal at elevated temperatures.

## II. THE MODEL

At temperatures above the onset of its anomalous rise, it is assumed that the observed thermal conductivity,  $k_{obs}$ , of the ceramic may in general be written

$$k_{obs} = k_{ph} + k_{el} + k_r + k_{ex} \quad (1)$$

where  $k_{ph}$  is the phonon component,  $k_{el}$  is the electronic component,  $k_r$  is the component due to radiative heat transport,  $k_{ex}$  is the sum of components resulting from certain excitation processes.

It is further assumed that the phonon component obeys the usual  $1/T$  law for an ideal dielectric predicted by Peierls,<sup>6</sup> and that, below the onset of the anomalous increase in observed conductivity, this is the predominate mechanism. Thus, the phonon component at high temperatures may be evaluated by extrapolation of the low-temperature  $k_{obs}$  data according to a  $1/T$  law.

The electronic contribution,  $k_{el}$ , to the observed thermal conductivity is given by the well-known Wiedsmann-Franz law. Thus,

$$k_{el} = S \left( \frac{k}{e} \right)^2 T \sigma \quad (2)$$

Manuscript released for publication January 1961 as a WADD Technical Report.

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where  $k$  is the Boltzmann constant,  $e$  is the electronic charge,  $T$  is the absolute temperature,  $\sigma$  is the electrical conductivity and  $S$  is a factor which depends on the degree of degeneracy and the type of scattering of the carriers. For a Boltzmann distribution and thermal scattering  $S = 2$ , and for degeneracy  $S = \pi^{2/3}$ .

Assuming that the crystal is optically isotropic and that the absorption coefficient is independent of the wavelength, the radiation component may be computed from the expression<sup>7,8</sup>

$$k_r = \frac{16}{3} \frac{b T^3 n^2}{a} \quad (3)$$

where  $a$  is the optical absorption constant for the wavelength corresponding to the peak of blackbody radiation at temperature  $T$ ,  $n$  is the refractive index and  $b$  is Stefan's radiation constant.

The component,  $k_{ex}$ , results from a major class of heat transporting mechanisms in which there is an excitation energy,  $E$ , between the ground state and the first excited states of the system. These include thermal energy transport by electron-hole pairs, excitons and dissociated gas molecules. Assuming that all energy-carrying states,  $g$  in number, are at energy level  $E$  above the ground state and that  $E / kT \gg 1$ , then according to Krumhansl<sup>9</sup>  $k_{ex}$  is given by

$$k_{ex} = k \ell v \left( \frac{E}{kT} \right)^2 g^2 \exp \frac{-E}{kT} \quad (4)$$

where  $\ell$  is a characteristic length for damping out temperature differences,  $v$  is the velocity of transport of these excited energy states, and  $k$  is the Boltzmann constant. A similar result has been rigorously derived by Pikus<sup>10</sup> for the case of an exciton mechanism and by Price<sup>2</sup> for an ambipolar mechanism. Depending upon the particular circumstance, the excitation energy,  $E$ , may be the gap, exciton, dissociation or ionization energy; the values of  $\ell$  and  $v$  must be appropriately chosen for the particular case considered.

It should be remarked that the present model of elevated-temperature, heat transfer mechanisms in ceramics bears a resemblance to an earlier one proposed by Jamieson and Lawson<sup>11</sup> to explain the deviations of the observed conductivity data for porous ceramics from a  $1/T$  law. However, their arguments are completely unconvincing for the case of porous ceramics because, if the sum  $(k_{ph} + k_r)$  is deducted from  $k_{obs}/(1 - P)$  the results will be  $k_{ex} + P \bar{k}/(1 - P)^*$  and not, as claimed, just  $k_{ex}$ . In point of fact, if thermal conductivity data for nonporous, monocrystalline  $Al_2O_3$ <sup>5</sup> is treated by the method discussed in the present paper,  $k_{ex}$  values are larger by a factor of about ten than corresponding

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\* Here  $\bar{k}$  is an effective thermal conductivity for a heterogeneous region containing both solid and pores. The magnitude of this conductivity term at high temperatures is such that it can seldom be neglected. See A. L. Loeb, J. Amer. Ceram. Soc. 37, 96 (1954) and J. Francl and W. D. Kingery, J. Amer. Ceram. Soc. 37, 99 (1954).



ones calculated by Jamieson and Lawson; moreover, the activation energy for the excitation contribution to the total heat flux in  $\text{Al}_2\text{O}_3$  predicted by the present analysis (0.25 ev) is very much smaller than theirs (1.52 ev).

As Herring<sup>12</sup> has suggested, unless exciton transport in a crystal has a very much lower activation energy than an ambipolar mechanism, it could not make a contribution of comparable magnitude to the ambipolar mechanism because of its less favorable statistical factor arising from the much smaller number of momentum states accessible to the exciton. Indeed, if the rather large activation energies predicted by Jamieson and Lawson<sup>11</sup> for  $\text{Al}_2\text{O}_3$  (1.42 ev) and  $\text{MgO}$  (1.35 ev) were correct, exciton transport would appear to be a remote possibility in these cases.

### III. COMPARISON WITH EXPERIMENT

The procedure employed in evaluating the  $\Delta k$  data listed in Table 1 for single crystalline  $\text{TiO}_2$ ,  $\text{CaF}_2$  and  $\text{Al}_2\text{O}_3$  is to extrapolate the low-temperature conductivity data of Charvat and Kingery<sup>5</sup> to temperatures above the onset of the anomalous rise by means of a  $1/T$  law and to take the difference between the observed conductivity and this extrapolated conductivity which represents the phonon component. Thus, according to Eq. (1),  $\Delta k$  represents the sum of  $k_{e1}$ ,  $k_r$  and  $k_{ex}$ .

Values of the radiative heat transfer component given in Table 1 are computed with the aid of Eq. (3), using as a value of the absorption constant either  $100 \text{ cm}^{-1}$  ( $\text{Al}_2\text{O}_3$  and  $\text{CaF}_2$ ) or both 10 and  $100 \text{ cm}^{-1}$  ( $\text{TiO}_2$ ). There is obviously some arbitrariness in the choice of these values, but it is believed that they bracket the range<sup>13</sup> for this parameter over the temperature range involved.\*

The  $k_{e1}$  values for  $\text{TiO}_2$  may be evaluated by means of Eq. (2), the electrical conductivity data of Cronmeyer<sup>14</sup> for intrinsic rutile and assuming thermal scattering and non-degeneracy so that the parameter  $S$  in Eq. (2) takes on the value two. As expected, the magnitude of this component is so small for stoichiometric  $\text{TiO}_2$  ( $k_{e1} = 3.6 \times 10^{-8} \text{ cal sec}^{-1} \text{ }^\circ\text{C}^{-1} \text{ cm}^{-1}$  at  $1000^\circ\text{K}$ ) that it contributes negligibly to the observed thermal conductivity at all temperatures of interest. However, even though  $k_{e1}$  is negligibly small for intrinsic  $\text{TiO}_2$ , this will certainly not always be true; as a matter of fact, it is reasonable to expect that the electronic component might be significant in reduced rutile which is a degenerate semiconductor.

It is apparent from the foregoing discussion that deducting the radiative component from each  $\Delta k$  value listed in Table 1 results in  $k_{ex}$ . According to Eq. (4), the slope of a plot of  $\ln k_{ex}$  vs.  $1/T$  should be  $-E/k$  where  $E$  is the

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\* For instance, if one chooses  $\alpha = 1 \text{ cm}^{-1}$  as the lower limit for the range of the absorption coefficient in  $\text{TiO}_2$ , as has been suggested for well-annealed single crystals, the radiation component assumes values much larger than the corresponding  $\Delta k$  values.

activation energy of the excitation transport process operating. Figure 1 represents such a plot for  $TiO_2$  with the activation energy computed from the slopes being 0.20 eV for both  $a = 10$  and  $100 \text{ cm}^{-1}$ .

It is easy to demonstrate that the diffusion of electron-hole pairs in intrinsic  $TiO_2$  will result in contributions to  $k_{obs}$  of such small magnitude that this mechanism can be ruled out as being important in this case. This ambipolar contribution may be evaluated by an expression due to Price<sup>2</sup>

$$k_{amb} = \left(\frac{k}{e}\right)^2 T \frac{\sigma_n \sigma_p}{\sigma} \left\{ \frac{E_G}{kT} + 4 \right\}^2 \quad (5)$$

where  $E_G$  is the gap energy and  $\sigma_n$ ,  $\sigma_p$  are the electrical conductivities of electrons and holes, respectively. A detailed knowledge of the position of the Fermi level and the density of states is needed in order to calculate the dependence of  $k_{amb}$  on  $\sigma$ . Fortunately, however, in the present case where  $TiO_2$  is assumed to be intrinsic, Eq. (5) can be simplified to

$$k_{amb} = \left(\frac{k}{e}\right)^2 T \sigma \left\{ 2 + c + \frac{1}{c} \right\}^{-1} \left\{ \frac{E_G}{kT} + 4 \right\}^2 \quad (6)$$

where  $c$  is the ratio of the mobility of electrons to that of holes and  $\sigma$  is the electrical conductivity. A value of  $4.7 \times 10^{-6} \text{ cal sec}^{-1} \text{ deg}^{-1} \text{ cm}^{-1}$  was computed for  $k_{amb}$  at  $1000^\circ\text{K}$  by assuming  $c = 2$  and utilizing Cronmeyer's data for  $E_G$  and  $\sigma$ . Thus, it is clear, not only from the small magnitude of  $k_{amb}$  but also from the excitation energy of about 3 eV required for this ambipolar mechanism, that this process is unimportant in the present instance where an energy of about 0.2 eV has been predicted for the excitation process from thermal conductivity data.

It is probably fortuitous that a 0.2 eV activation energy for the ionization of singly ionized oxygen ion vacancies was likewise observed by Breckenridge and Hosler<sup>13</sup> on reduced rutile. It is unlikely that this mechanism would be significant in intrinsic  $TiO_2$ , but it might become important in reduced material. Since it must be assumed, from the manner in which they conducted their experiments, that Charvat and Kingery<sup>5</sup> measured the thermal conductivity of intrinsic  $TiO_2$ , the enhanced conductivity,  $k_{ex}$ , cannot be ascribed to such an ionization process. Moreover, it is not possible, on the basis of our present understanding of excitation processes in rutile, to designate unambiguously the predominant operating excitation mechanism; although, on the basis of the predicted low activation energy, it is attractive to postulate that exciton diffusion may occur. It is noteworthy that the enhanced conductivity of PbTe at elevated temperatures has been attributed by Joffe<sup>4</sup> to the diffusion of unidentified, energy-carrying states of comparably low excitation energy.

Thermal conductivity data<sup>5</sup> on  $CaF_2$  and  $Al_2O_3$  have also been analyzed on the same basis as the  $TiO_2$  data and the results are shown in Figs. 2 and 3. The calculated activation energy for the excitation mechanism operating in the case

of  $\text{CaF}_2$  is only 0.34 ev by comparison with a gap energy of about 1 ev.<sup>16</sup> As mentioned earlier, the activation energy calculated for the excitation mechanism in  $\text{Al}_2\text{O}_3$  is only 0.25 ev, a considerably smaller value than that predicted by Jamieson and Lawson (1.42 ev) for the same material.<sup>11</sup>

#### IV. SUMMARY

A reanalysis of thermal conductivity data for some single-phase, monocrystalline ceramics, particularly rutile, has indicated that the anomalous increase in the observed thermal conductivity at elevated temperatures may not be explained solely on the basis of radiative heat transfer alone. Departures from the usual  $1/T$  law for phonon conductivity may, in general, be ascribed to some combination of electronic and radiative heat transfer and transport by such excitation mechanisms as diffusion of electron-hole pairs, excitons and dissociated gas molecules. In the case of rutile, the flow of excited states of low excitation energy, possibly excitons, makes a significant contribution to the total heat flux through the crystal at temperatures above its anomalous rise in thermal conductivity.

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## V. LIST OF REFERENCES

1. H. Frohlich and C. Kittel, *Physica* 20, 1086 (1954).
2. P. J. Price, *Phil. Mag.* 46, 1252 (1955); *Phys. Rev.* 95, 596A (1954).
3. E. D. Devyatkova, B. Ya. Moizhes and I. A. Smirnov, *Soviet Physics - Solid State* 1, 555 (1959).
4. A. F. Joffe, *Canad. J. Phys.* 34, 1342 (1956); *J. Phys. Chem. Solids* 8, 6 (1959).
5. F. R. Charvat and W. D. Kingery, *J. Amer. Ceram. Soc.* 40, 306 (1957).
6. R. Peierls, *Ann. Physik* 3, 1055 (1929).
7. M. Czerny and L. Genzel, *Glastech, Ber.* 25, 387 (1952).
8. L. Genzel, *Z. Physik* 135, 177 (1953).
9. J. A. Krumhansl, *J. Phys. Chem. Solids* 8, 343 (1959).
10. G. E. Pikus, *Zhur. Tekh. Fiz.* 26, 36 (1959); *Soviet Phys. - Tech. Phys.* 1, 32 (1957).
11. J. C. Jamieson and A. W. Lawson, *J. Appl. Phys.* 29, 1313 (1958).
12. C. Herring, *J. Phys. Chem. Solids* 8, 543 (1959).
13. S. P. Clark, *Trans. Am. Geophys. Union* 38, 931 (1957).
14. D. C. Cronmeyer, *Phys. Rev.* 87, 876 (1952).
15. R. C. Breckenridge and W. R. Hosler, *Phys. Rev.* 91, 793 (1953).
16. R. W. Ure, *J. Chem. Phys.* 26, 1363 (1957).

TABLE 1. Calculated values of the radiation and excitation components of the total thermal conductivity of TiO<sub>2</sub>, CaF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Temperature (°K)	TiO <sub>2</sub>					
	k x 10 <sup>3</sup> (cal sec <sup>-1</sup> deg <sup>-1</sup> cm <sup>-1</sup> )	k <sub>r</sub> x 10 <sup>3</sup> (cal sec <sup>-1</sup> deg <sup>-1</sup> cm <sup>-1</sup> )		k <sub>ex</sub> x 10 <sup>-3</sup> (cal sec <sup>-1</sup> deg <sup>-1</sup> cm <sup>-1</sup> )		
		α = 10cm <sup>-1</sup>	α = 100cm <sup>-1</sup>	α = 10cm <sup>-1</sup>	α = 100cm <sup>-1</sup>	
573	1.14	0.79	0.08	0.35	1.06	
673	2.00	1.29	0.13	0.71	1.87	
773	3.14	1.94	0.19	1.20	2.95	
873	4.38	2.80	0.28	1.58	4.10	
973	5.65	3.88	0.39	1.77	5.26	
1073	7.15	5.67	0.57	1.95	6.95	
CaF <sub>2</sub>						
573	0.11	0.28	0.03		0.08	
673	0.40	0.46	0.05		0.35	
773	0.68	0.69	0.07		0.61	
873	1.02	0.99	0.10		0.92	
973	1.65	1.38	0.14		1.51	
Al <sub>2</sub> O <sub>3</sub>						
773	1.10	1.04	0.10		1.00	
873	1.73	1.47	0.15		1.58	
973	2.31	2.04	0.20		2.21	
1073	2.60	2.72	0.27		2.33	
1173	3.18	3.56	0.36		2.82	
1273	4.05	4.55	0.46		3.59	
1373	5.32	5.70	0.57		4.75	
1473	7.11	7.05	0.71		6.40	

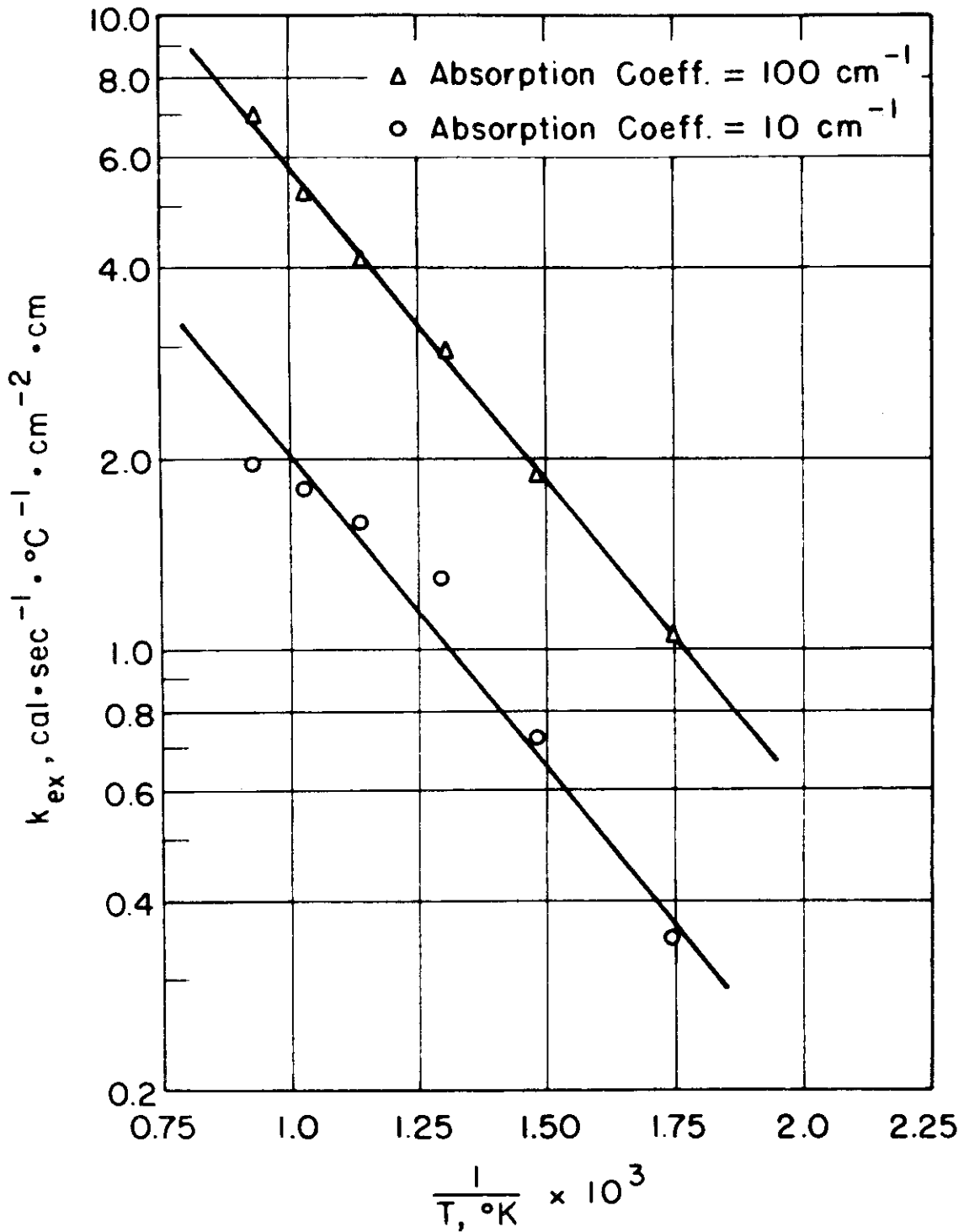


Figure 1. Variation of the excitation component of the total heat flux in  $\text{TiO}_2$  with temperature. (Experimental data from Charvat and Kingery.<sup>5</sup>)

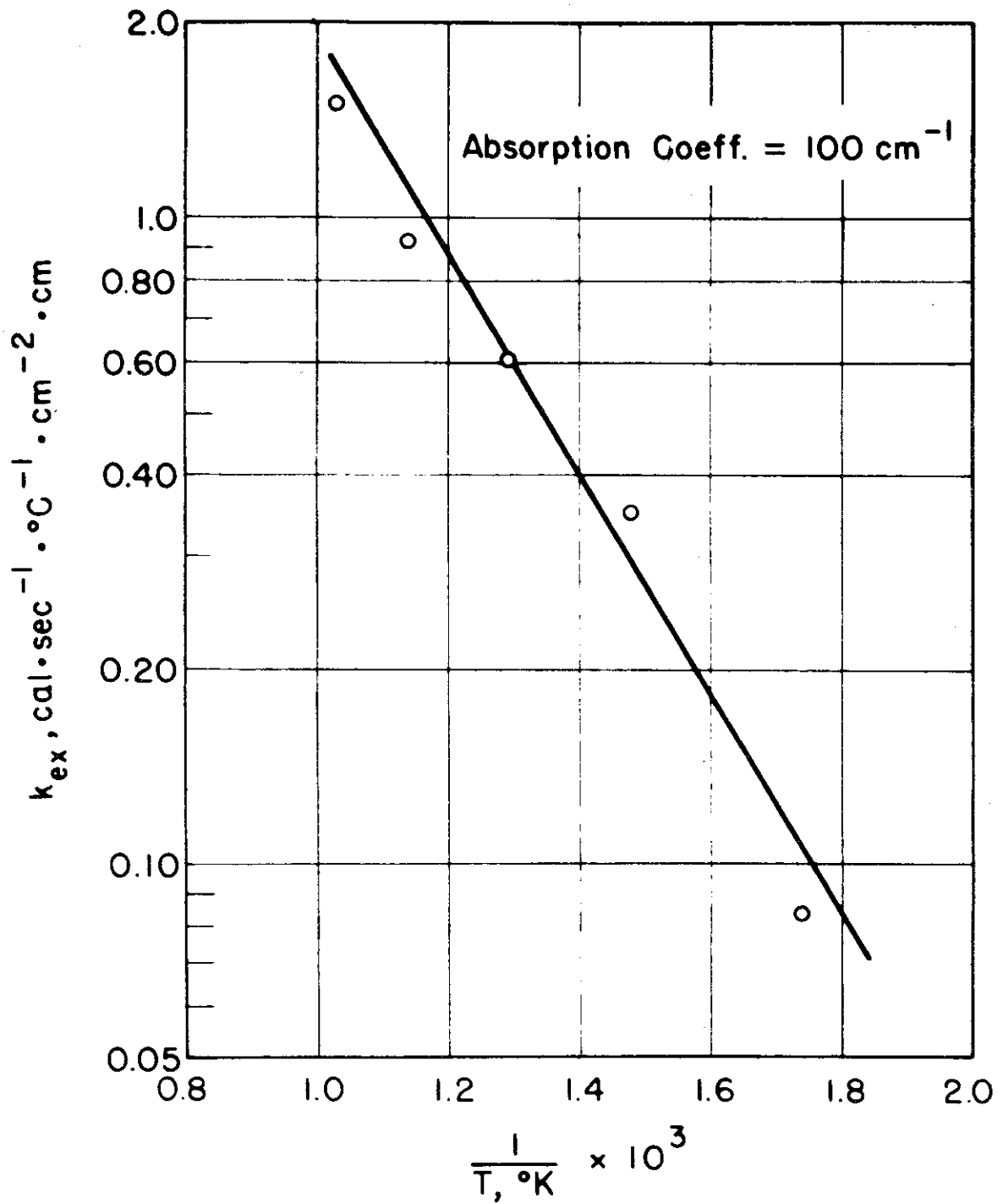


Figure 2. Temperature dependence of the excitation component of the total heat flux in  $\text{CaF}_2$ . (Data taken from Charvat and Kingery<sup>5</sup>)

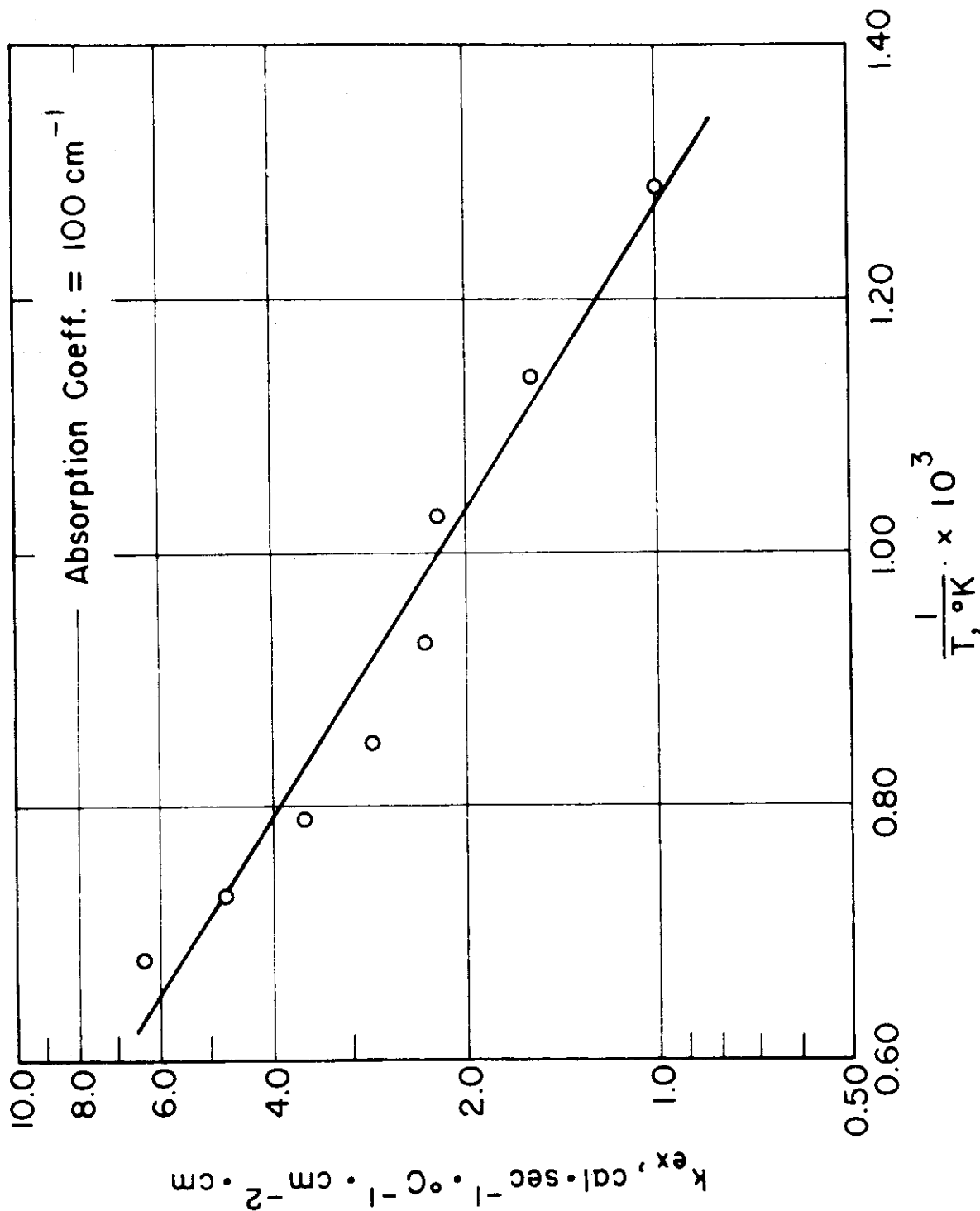


Figure 3. Variation of the excitation component of the total heat flux in Al<sub>2</sub>O<sub>3</sub> with temperature. (Data from Charvat and Kingery.<sup>5</sup>)