

Thermal Conductivity and Thermoelectric Power of Rutile (TiO_2)

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The thermal conductivity K and the thermoelectric power Q of single-crystal samples of rutile were measured from 2 to 300°K. Pure, niobium-doped, vacuum-reduced, and hydrogen-reduced specimens were investigated. The thermal conductivity of the pure crystals is similar to that usually found for insulators, with a maximum at about 15°K. Boundary scattering determines K below the maximum, and in the range 25 to 100°K the conductivity varies exponentially with temperature, which is characteristic of umklapp scattering. The Callaway expression for K was used to fit the data over the entire temperature range. From measurements in both the c and an a direction, it was found that the anisotropy ratio $K_c/K_a = 1.5 \pm 0.1$ above 25°K. The ratio decreases below 25°K to a limiting value of 1.05 ± 0.1 . A sample doped with 0.1% Nb has a thermal conductivity quite similar to the pure TiO_2 . The K of the reduced samples is quite depressed at low temperatures and a discussion of possible processes is included. On oxidation of a reduced sample it was discovered that the thermal conductivity did not recover completely to the original values measured on the same specimen before reduction. For one crystal a comparison of K in the reduced and reoxidized states yields values for the extra thermal resistance which are compatible with the number of point defects introduced by the reduction. The thermoelectric power of the semiconducting samples (Nb-doped and reduced) increases rapidly below 100°K, indicating a large phonon-drag contribution.

I. INTRODUCTION

IT has been known for some time that low-temperature thermal-conductivity measurements constitute a sensitive method for studying the scattering of phonons by lattice defects. In general, it can be said that isotopes and other defects involving only a mass difference are fairly well understood, but that other types of defects which involve a change in force constant or an associated strain field are still quite puzzling in many cases. In the last five to ten years, many pronounced low-temperature effects have been discovered and their explanation is still largely a mystery. We will not go into more detail since this has been done by several authors in recent papers.¹⁻³ A reader unfamiliar with the field can consult review articles by Klemens,⁴ Carruthers,⁵ and Grieg.⁶

It was thought that rutile (TiO_2) would provide a good lattice in which to study the nature of defects introduced as a consequence of nonstoichiometry. The oxygen-deficient (reduced) samples are n -type semiconductors with a blue-black color at room temperature. The question of whether reduction of rutile produces oxygen vacancies or Ti^{3+} interstitials is not yet completely solved, although the bulk of the evidence is on the side of the latter.⁷⁻¹¹ Some recent work seems to

indicate that the nature of the defect depends somewhat on the method of reduction.^{12,13}

An advantage of a defect crystal such as rutile for these studies is that a sample can be measured in the pure state, subjected to a reduction treatment, and then reoxidized and measured again. This approach has enabled us to subtract effects which we do not believe are related to scattering by "point" defects. The pure material was of interest in its own right since we wanted to know if the presence of isotopes would overshadow the phonon scattering by umklapp processes.^{14,15}

Section II of this paper is concerned with the preparation and properties of the samples; Sec. III includes a discussion of our apparatus and experimental techniques. In Sec. IV we analyze our thermal-conductivity data and discuss the results. Section V is devoted to the thermoelectric power and its relation to the thermal conductivity.

II. SAMPLES

The single-crystal samples of pure TiO_2 used for these measurements were cut from a boule grown by the Verneuil method.¹⁶ The major impurities as determined by a qualitative spectrochemical analysis were: barium, copper, and silicon in the concentration range from 0.0001 to 0.001%, and perhaps smaller quantities of aluminum, calcium, and iron. The boule axis was approximately in the c direction, so samples whose length was parallel to c were slightly longer than the a samples cut from a cross-section slice of the boule. It was our aim to measure the thermal conductivity of the two oriented samples in the stoichiometric state and

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¹ C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

² C. T. Walker, Phys. Rev. **132**, 1963 (1963).

³ M. G. Holland, Phys. Rev. **134**, A471 (1964).

⁴ P. G. Klemens, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 7, p. 1.

⁵ P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

⁶ D. Greig, *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon Press Inc., New York, 1964), Vol. 1, p. 175.

⁷ H. P. R. Frederikse, J. Appl. Phys. Suppl. **32**, 2211 (1961).

⁸ J. B. Wachtman, Jr., and L. R. Doyle, Phys. Rev. **135**, A276 (1964).

⁹ T. Hurlen, Acta Chem. Scand. **13**, 365 (1959).

¹⁰ J. H. Becker and W. R. Hosler, J. Phys. Soc. Japan **18** (Suppl. II), 152 (1963).

¹¹ J. Yahia, Phys. Rev. **130**, 1711 (1963).

¹² P. F. Chester, J. Appl. Phys. Suppl. **32**, 2233 (1961).

¹³ R. Shannon, J. Appl. Phys. **35**, 3414 (1964).

¹⁴ R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

¹⁵ J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), p. 310.

¹⁶ Boule supplied by the National Lead Company.

TABLE I. Characteristics of measured TiO₂ samples.

Sample	Preparation	Dimensions (mm)	ρ (Ω cm at 300°K)	N_d (cm ⁻³)
1cO	700°C oxidation in air for 2 days	1×4×24		} as grown 10 ¹⁷ to 10 ¹⁸ chemical impurities
1aO	same as 1cO	1×4×19		
1cOVR	1cO heated at 1175°C in vacuum (Vac-Ion pump, $\approx 10^{-5}$ mm Hg) for 27 h	1×4×17	1.05	1×10 ¹⁹
1aOVR	1aO reduced with 1cO (see 1cOVR)	1×4×19	3.5	1×10 ¹⁹
2aOHR	heated in flowing H ₂ gas for 2 h at 900°C	1×4×19	0.35	1×10 ²⁰
1aOVRO	1aOVR reoxidized at 600°C for 2 days in flowing O ₂	1×4×19		
1aOVROO	1aOVRO reoxidized at 700°C for 7 days and at 800°C for 10 days in flowing O ₂	1×4×19		
2aOHRO	2aOHR oxidized at 700°C in flowing O ₂ for 10 days	1×4×18		
3aNb	0.1% Nb ₂ O ₅ added to TiO ₂ powder before growth	1×3.5×14	3.1	1.6×10 ¹⁹ Nb atoms

then give them identical reduction treatments and re-measure K . Table I gives the approximate size of all samples as well as a summary of their preparation, electrical resistivity, and number of defects.

The pure specimens were oxidized together at 700°C in air for two days prior to any measurements. The sample surfaces were roughened with silicon carbide paper with No. 600 used for the final finish.

The two pure samples measured are designated as 1cO and 1aO, where 1 is the sample number (with members of a pair given the same number but differentiated by their orientation, a or c) and O refers to the oxidation treatment.

When the measurements on the pure samples were concluded, these same crystals were vacuum reduced (VR) together in the same quartz tube. The samples, while still in vacuum, were cooled to near room temperature in 1 or 2 min by pouring water over the quartz tube after sliding the furnace away.

The hydrogen-reduced (HR) sample was not water quenched, but the hydrogen gas was flushed out with argon and the furnace cooled to near room temperature in 2 or 3 h.

The hydrogen-reduced and one vacuum-reduced crystal were reoxidized in flowing oxygen to determine how well the thermal conductivity would recover following the severe treatments. For example, in Table I the sample 1aOVRO was originally 1aO and then vacuum-reduced and subsequently oxidized.

The niobium-doped sample was cut from a boule¹⁶ grown from rutile powder which contained 0.1% by weight of Nb₂O₅. From measurements of the Hall coefficient it was concluded that all the niobium had been

absorbed and that each niobium atom had donated one electron. The paramagnetic-resonance experiments of Chester¹² on niobium-doped rutile samples provide evidence that niobium substitutes for titanium in the lattice.

The electrical resistivity ρ of the semiconducting samples was determined by four terminal measurements using indium contacts. The approximate defect concentration N_d was determined from a relation based on that used by Becker and Hosler.¹⁰ We used $N_d = 1 \times 10^{19} / \rho_{11c}(300^\circ\text{K})$. To obtain ρ_{11c} for an a sample, the value $\rho_{11a}/\rho_{11c} = 3.5$ was used which is the ratio found by Bogomolov and Shavkunov¹⁷ and generally confirmed by Becker and Hosler¹⁸ for samples of low resistivity. One can estimate N_d from the carrier concentration n as given by $1/\rho = ne\mu$ since the electron mobility μ is known. The two methods are in good agreement.

III. EXPERIMENTAL ASPECTS

The sample chamber used for these measurements is shown in Fig. 1. Measurements up to 30°K were made with helium as the refrigerant, from 14 to 80°K with hydrogen, above 80°K with nitrogen, and at room temperature alcohol was used. The data were obtained with the sample chamber evacuated, usually to a pressure of about 10^{-5} mm of Hg.

The copper heat sink is supported by a stainless steel tube which also serves as a variable heat leak. When using liquid helium, it was possible to condense helium

¹⁷ V. N. Bogomolov and P. M. Shavkunov, Fiz. Tverd. Tela 5, 2027 (1963) [English transl.: Soviet Phys.—Solid State 5, 1481 (1963)].

¹⁸ J. H. Becker and W. R. Hosler, Phys. Rev. 137, A1872 (1965).

in the tube and thereby keep the sink near 4°K while maintaining a reasonable gradient in the sample (a few tenths of a degree). A little over-pressure was sometimes found to be necessary and the method proved very useful until the sample temperature was about 10 or 12°K. Then the condensed helium was removed by pumping and measurements continued with the tube evacuated or with a small amount of helium exchange gas in it. It was also possible to cool the sink below the outside bath temperature by pumping on the condensed helium, and thus make measurements below 4°K without pumping on the outside helium bath. Usually both methods were used since not enough helium could be condensed to last for very long with a sample heater on.

Differential thermocouples of silver normal versus gold-iron or gold-cobalt were used to measure the temperature gradient as well as the absolute temperature. The thermocouple wires and all other electrical leads were brought out of the sample chamber through hollow, Kovar-glass feedthroughs. The reference junction for the sample temperature was in the bath just above the feedthroughs.

The Au+0.03 at.%Fe wire¹⁹ has a thermoelectric power (TEP) which is greater than 10 $\mu\text{V}/^\circ\text{K}$ from helium temperatures to about 20°K. The suitability of this wire as a low-temperature thermocouple is discussed in a recent article by Berman, Brock, and Huntley.²⁰ We calibrated the wire many times against a four-lead germanium resistance thermometer and found it to be very reproducible, especially above 4°K. Owing to experimental difficulties, our calibration in the pumped-helium range was not so reproducible; however, our TEP was usually 1 to 2 $\mu\text{V}/^\circ\text{K}$ less than Berman obtained on wire of the same nominal composition.

The output of the gold-iron drops rapidly in the liquid-hydrogen range, and for the measurements in this range and above we replaced it with Au+2.1 at.% Co wire.²¹ By comparing the data in the overlap region between 20 and 30°K, we noticed an apparent decline in the TEP of our gold-cobalt wire in later runs. A calibration against our germanium thermometer showed the TEP to be less than we had thought. We attributed this to the known influence of strain and aging on the output of this wire. With the calibration correction applied, the data taken with the two wires are in good agreement.²²

The thermocouples were attached to the sample with the aid of the copper clamps shown in Fig. 1. The ridges of each clamp which pressed against the sample

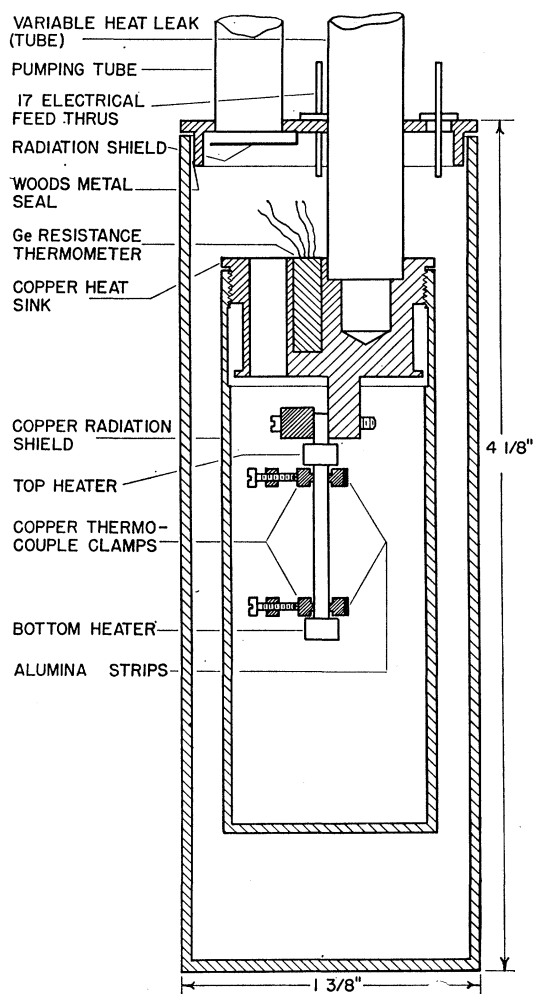


FIG. 1. The sample chamber used for the measurements.

were tinned with indium. The thermocouples were then soldered to the clamps. For conducting samples, thin alumina strips which were metallized on both sides were used to insulate electrically the differential thermocouples from the sample and still provide reasonable thermal contact.

A two-heater method, similar to that used by Berman and Huntley,²³ was employed for determining the net gradient along the sample. The two heaters of 40 Ω each of 0.003-in. resistance wire with a small temperature coefficient were wrapped around the sample and secured with GE-7031 cement.

It was concluded that this assembly operated satisfactorily when no overshoot was observed on switching between heaters and when the reading obtained with the top heater on was fairly constant during a series of measurements. If this value tended to vary systematically, it was concluded that one of the clamps was probably making poor contact with the sample. The

¹⁹ Wire obtained from the Johnson-Matthey Company of London.

²⁰ R. Berman, J. C. F. Brock, and D. J. Huntley, *Cryogenics* 4, 233 (1964).

²¹ Wire obtained from Sigmund Cohn.

²² The recent article by Berman and co-workers (Ref. 18) points out that a thermocouple of gold-iron versus chromel is probably the best choice for the 1 to 300°K temperature range.

²³ R. Berman and D. J. Huntley, *Cryogenics* 3, 70 (1963).

current for the sample heaters was supplied by wet cells and the power was determined by making current and voltage measurements with a potentiometer. A heater wrapped around the sink could be used to obtain temperatures in the range somewhat above the bath while keeping the gradient within a few degrees.

The thermocouple voltages were measured with a thermofree potentiometer (smallest division, $0.01 \mu\text{V}$) using a galvanometer with an auxiliary mirror attached to obtain multiple reflections and thus greatly increased sensitivity.²⁴ Our final scale sensitivity was about $0.25 \mu\text{V}/\text{cm}$.

The electrical resistivity of the semiconducting TiO_2 samples becomes quite large at low temperatures, so the measurement of the Seebeck effect required a well-shielded circuit and electrical leads which were well insulated from ground and each other. (The sample holder was grounded.) An electrometer (10 mV full scale on lowest range), placed in a special copper shield, was used during the low temperature runs and data could be obtained until the sample resistance was about $10^8 \Omega$. A good indication of reliable data was a thermoelectric power voltage of zero when the top heater was on.

IV. THERMAL CONDUCTIVITY

A. Pure and Niobium-Doped Rutile

Figure 2 shows the results of our thermal-conductivity measurements of samples 1aO and 1cO together with some measurements by other authors, which were obtained from Ref. 25. Some of the measurements on

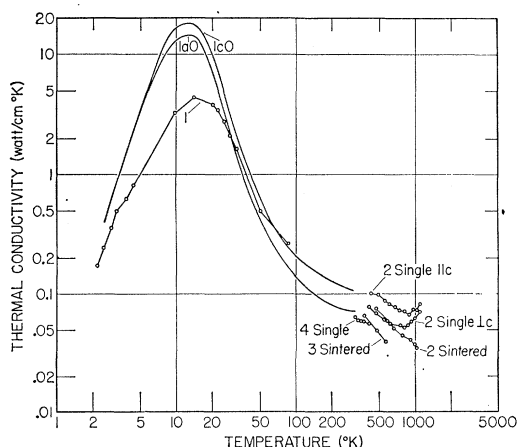


FIG. 2. The thermal conductivity of TiO_2 from 2 to 1000°K showing the present work and some results of other authors. The numbers on the graph refer as follows to the respective observers: 1. Berman, *et al.* (Ref. 14), 2. Kingery *et al.* (Ref. 26), 3. Yoshida (Ref. 27), 4. Koenig (Ref. 28).

²⁴ T. M. Dauphinee, *Rev. Sci. Instr.* **26**, 873 (1955).

²⁵ The Thermophysical Properties Research Center, Purdue University, Lafayette, Indiana, Data Book, Vol. 3 (unpublished).

polycrystalline TiO_2 samples are not included in our graph.

A comparison of the low-temperature measurements by Berman, Foster, and Ziman (curve 1)¹⁴ with ours indicates that their sample was less pure or less perfect than the samples we measured. Above the maximum their results are in general agreement with ours.

Our measurements indicate an exponential decrease of the conductivity above the maximum, a strong indication of umklapp scattering. The effect is more apparent in our measurements than in those by Berman, Foster, and Ziman because our samples have a higher conductivity in the region of the maximum. We believe that umklapp scattering is easily observable in TiO_2 since the isotope scattering by the Ti isotopes is sufficiently decreased by the oxygen molecules which dilute the titanium. The high temperature measurements by Kingery,²⁶ Yoshida,²⁷ and Koenig²⁸ agree with the present measurements. A $1/T$ dependence at the Debye temperature—as umklapp scattering is expected to give—has only been observed in two measurements on ceramic samples. It is possible that radiation affects all the measurements on single crystals of rutile above 100°K . A room-temperature measurement on specimen 1aOVRO, in which the sample chamber was filled with perlite powder and evacuated, yielded a lower value for the thermal conductivity than did a similar experiment without the powder. The geometry of our apparatus did not allow us to make an accurate estimate of the heat loss through the powder. Valuable data could not be obtained, but the experiment proved that radiation influences the room-temperature measurements.

In the temperature range below 100°K we can interpret our measurements on the pure and niobium-doped samples by using a simplified version of Callaway's formalism.²⁹ In the following paragraphs we will discuss the Callaway approach and apply it to sample 1aO. A Debye model is assumed and the phonon heat current is limited by the following scattering mechanisms: (a) boundaries, (b) impurities, including isotopes, and (c) phonon-phonon (umklapp). The effect of phonon-phonon normal processes will be neglected. The thermal conductivity can be expressed as

$$K = \frac{k}{2\pi^2v} \left(\frac{kT}{\hbar} \right)^3 \int_0^{\Theta/T} \tau_c(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where k = Boltzmann's constant, v = average sound velocity, T = absolute temperature, \hbar = Planck's constant, Θ = Debye temperature, $x = \hbar\omega/kT$ (ω = phonon fre-

²⁶ F. R. Charvat and W. D. Kingery, *J. Am. Ceram. Soc.* **40**, 306 (1957).

²⁷ I. Yoshida, *J. Phys. Soc. Japan* **15**, 2211 (1960).

²⁸ J. H. Koenig, Ceramic Research Station Progress Report 5, Rutgers University, New Jersey, 1954 (unpublished).

²⁹ J. Callaway, *Phys. Rev.* **113**, 1046 (1959); *Phys. Rev.* **122**, 787 (1961); and J. Callaway and H. C. von Baeyer, *Phys. Rev.* **120**, 1149 (1960).

quency), and τ_c = combined relaxation time as given by

$$\tau_c^{-1} = \tau_b^{-1} + \tau_i^{-1} + \tau_u^{-1}. \quad (2)$$

(a) The relaxation time τ_b for boundary scattering can be written as follows:

$$\tau_b^{-1} = v/L. \quad (3)$$

The length parameter L depends on the sample dimensions.

(b) The impurity-scattering relaxation time τ_i is given by³⁰

$$\tau_i^{-1} = (3V_0/\pi v^3)(S^2/G)\omega^4, \quad (4)$$

where V_0 is the volume of the unit cell, G^{-1} is the concentration of impurities per unit cell, and S^2 is a scattering parameter of the order unity. Specifically,

$$S^2 = S_1^2 + (S_2 + S_3)^2, \quad (5)$$

where $S_1^2 = (\Delta M/M)^2/12$, $S_2 = \Delta f/6^{1/2}f$, and $S_3 = -6(\frac{2}{3})^{1/2}(\Delta R/R)$. Here M is the mass of the unit cell, f is the force constant of a linkage, R is the distance between nearest neighbors, and ΔM , Δf , ΔR are the changes in the given parameters. If only isotope scattering is being considered, it is convenient to write $S^2/G = f_i(\Delta M_i/M)^2/12$, where f_i is the natural abundance of the isotope and ΔM_i is the change in the mass of the unit cell due to this isotope. (One can find about three different methods in the literature for computing the isotope term in compounds, but we believe that the above approach leads to the correct result.)

(c) The umklapp-scattering relaxation time τ_u is of the form

$$\tau_u^{-1} = A\omega^2 T e^{-B/T}. \quad (6)$$

The same expression was used by Slack and Galginaitis.³¹ A and B are adjustable parameters. This expression will give a $1/T$ temperature dependence for the conductivity at the Debye temperature and an exponential dependence in the region just above the maximum.

At 2–7°K, where boundary scattering is the only important mechanism, the Callaway formula goes over into Casimir's formula for the thermal conductivity $K = \frac{1}{3}Cv\bar{l}$.³² Using a value for the specific heat C as determined by Keesom and Pearlman,³³ we calculate that the phonon mean free path \bar{l} for the $1aO$ sample is 1.7 mm. The average sound velocity v used in this formula was computed from the longitudinal and transverse sound velocities v_l and $v_{l1,2}$ using the following expression:

$$v = \frac{(1/v_{l1}^2) + (1/v_{l2}^2) + (1/v_l^2)}{(1/v_{l1}^3) + (1/v_{l2}^3) + (1/v_l^3)}. \quad (7)$$

This is equivalent to the one used by Casimir.³² The values for v_l and $v_{l1,2}$ were derived from elastic constant data³⁴ giving $v_a = 6.16 \times 10^5$ cm/sec.

The formula $L = 1.21(L_1L_2)^{1/2}$,³⁵ where L_1L_2 is the cross section of the sample, was used to determine the length parameter from the physical sample size resulting in $L = 2.16$ mm. The length correction as used by Berman, Foster, and Ziman³⁶ decreases L to 1.84 mm in good agreement with the value from the thermal-conductivity data. In Callaway's formula a different derivation for the average sound velocities is called for³⁷ as given by

$$1/v = \frac{1}{3}[(1/v_{l1}) + (1/v_{l2}) + (1/v_l)], \quad (8)$$

resulting in $v_c = 6.65 \times 10^5$ cm/sec, and $v_a = 6.5 \times 10^5$ cm/sec. The value for τ_b was determined by making the Callaway formula fit at 4°K assuming $\tau_c = \tau_b$.

There are some difficulties in selecting a value for the Debye temperature. The specific heat measurements^{33,38–40} yield $\Theta = 760^\circ\text{K}$ at 0°K, indicate a minimum value of 440°K at 25°K, and then show that Θ increases to about 760° at room temperature. A calculation of Θ from the room temperature elastic constants gives 770°K.^{34,41} A mean value of Θ in the umklapp scattering range from 25 to 100°K is 530°K. In the Callaway integral, Eq. (1), the upper limit (Θ/T) has little effect on the result at temperatures below about 20°K, and is only moderately important at 100°K.

Above 30°K, umklapp scattering is the only important scattering mechanism. The constants A and B in the expression for τ_u were obtained by fitting the data at 30 and 90°K assuming that $\tau_c = \tau_u$. The best fit was obtained by using $A = 15.8 \times 10^4$ and $B = 109$. Berman⁴² determined the exponent Θ/aT for umklapp scattering of several materials from a plot of the log of the mean free path \bar{l} versus $1/T$, where \bar{l} was calculated from the relation $K = \frac{1}{3}Cv\bar{l}$. A value for a of 2.3 was found for solid helium, 2.7 for diamond, and 2.1 for sapphire. From this type of plot we find for rutile $a = 2.6$ using $\Theta = 530^\circ\text{K}$.

Near the maximum in the thermal conductivity all three scattering mechanisms are effective.

Substituting the various parameters into the Calla-

³⁴ J. B. Wachtman, Jr., W. F. Tefft, and D. G. Lam, J. Res. Natl. Bur. Std. (U. S.) **66A**, 465 (1962).

³⁵ M. G. Holland, Phys. Rev. **139**, A471 (1964).

³⁶ R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A231**, 130 (1955).

³⁷ M. G. Holland, Phys. Rev. **132**, 2461 (1963).

³⁸ H. J. M. McDonald and H. Seltz, J. Am. Chem. Soc. **61**, 2405 (1939).

³⁹ C. H. Shomate, J. Am. Chem. Soc. **69**, 218 (1947).

⁴⁰ J. S. Dugdale, J. A. Morrison, and D. Patterson, Proc. Roy. Soc. (London) **A224**, 228 (1954).

⁴¹ O. L. Anderson, J. Phys. Chem. Solids **24**, 909 (1963).

⁴² R. Berman, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1953), Vol. 2, p. 103.

³⁰ P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

³¹ G. Slack and S. Galginaitis, Phys. Rev. **133**, A253 (1964).

³² H. B. Casimir, Physica **5**, 495 (1938).

³³ P. H. Keesom and N. Pearlman, Phys. Rev. **112**, 800 (1958).

way expression, one obtains

$$K(T) = 2.402 \times 10^3 T^3 \int_0^{530/T} \frac{x^4 [e^x / (e^x - 1)^2] dx}{2.71 \times 10^6 + 0.3T^4 x^4 + 15.8 \times 10^4 T^3 x^2 \exp - (109/T)} \quad (9)$$

An IBM 7094 computer was used to generate a curve from this expression. This curve is plotted in Fig. 3 through the experimental data points of sample 1aO. The fit is very good except just at the maximum. If, in addition to the isotope contribution to τ_i , a small amount of chemical impurity scattering were included, then the fit would be improved at the maximum.

The thermal conductivity of the niobium-doped sample can very well be compared with that of the pure sample (Fig. 4). At the maximum the conductivity of the niobium-doped sample is higher, which is somewhat

surprising, but otherwise the two are quite similar. A computer fit to the data of sample 3aNb can be obtained by using a value of τ_i that is only slightly less than the value computed for isotope scattering. Although the concentration of the niobium atoms is 10 to 100 times the concentration of the chemical impurities in the 1aO sample, they do not seem to contribute to phonon scattering.

B. Reduced Rutile

The two vacuum-reduced samples, 1aOVR and 1cOVR, showed quite similar thermal conductivities; hence only the points for sample 1aOVR are shown in Fig. 3, with a smooth curve drawn through the points. The most striking feature of the data is a conductivity still following a T^3 dependence in the boundary scattering region but with a mean free path l about five times smaller than in the pure samples. As a consequence of this, the maximum is shifted slightly to higher temperatures and is much lower than in the pure material.

Sample 1aOVR was reoxidized and the result is shown in Fig. 3. The thermal conductivity did not change significantly at temperatures below 10°K, whereas, at higher temperatures, it almost approached that of the pure material. The specimen showed blue stripes parallel to the c direction, and it was thought that perhaps this was why the conductivity did not recover. M. I. Cohen, of this laboratory, concluded

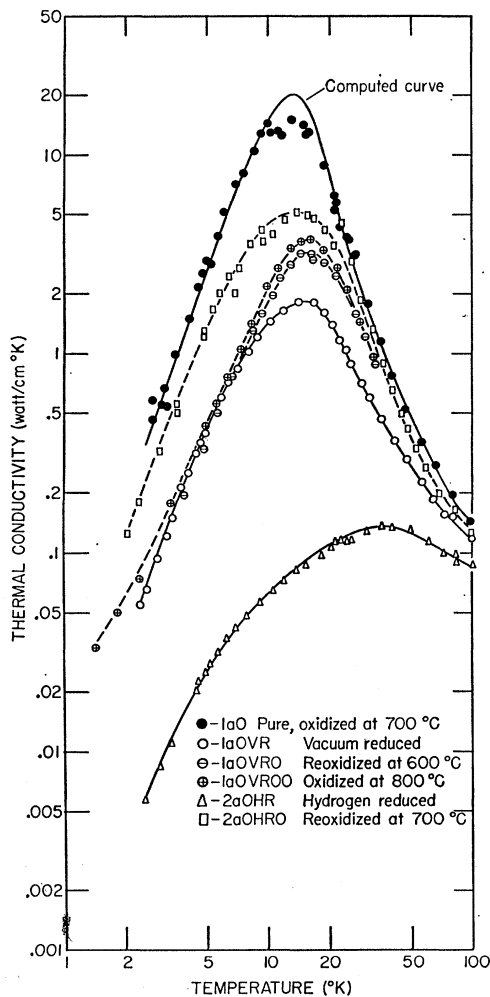


FIG. 3. The thermal conductivity from 2 to 100°K of pure, reduced, and reoxidized rutile samples. Smooth solid lines connect the data points of the reduced samples and dashed lines join the data points of the reoxidized samples. The fit to the pure sample was computed using the Callaway integral with isotopes as the only impurities.

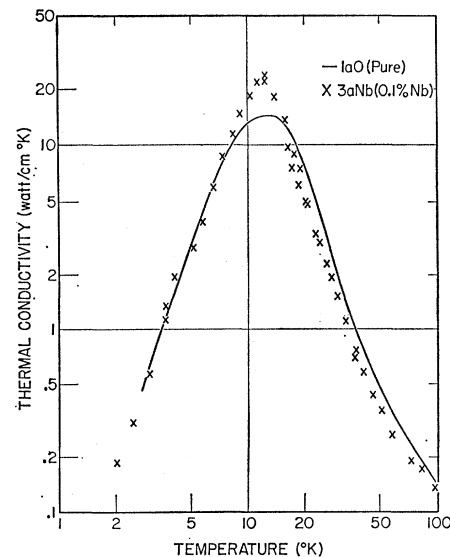


FIG. 4. The thermal conductivity from 2 to 100°K of the niobium-doped rutile sample with the smooth curve of the pure sample shown for comparison.

from x-ray data that the stripes were not correlated with grain boundaries. His x-ray photographs of sample 1cOVR indicated low-angle (1 or 2°) grain boundaries which were 1 or 2 mm apart, but this is similar to what he has found in pure material. The calculated scattering due to the observed grain boundaries is several orders of magnitude too low to account for our results.

The blue stripes referred to above disappeared when the sample was reoxidized for the second time, but the thermal conductivity showed little change. The temperature dependence of the reduced sample near 4°K was $T^{2.8}$, whereas lower powers were found after the reoxidations. There is a possibility that dislocations were introduced or shifted during the quenching of the reduced specimen and that this is the reason for the low conductivity in the boundary region.

At temperatures near the maximum and above, the thermal conductivity of sample 1aOVR increases significantly when the crystal is reoxidized, and it is logical to attribute the difference to point defects present only in the reduced specimen. The thermal resistance due to point defects has been shown by Klemens⁴ to be proportional to T as indicated by Eq. (4). The extra thermal resistance of sample 1aOVR in comparison to sample 1aOVRO can be obtained by subtracting $1/K$ for 1aOVRO from $1/K$ for 1aOVR. The extra resistance is proportional to T over the temperature range of the data (5° to 35°K). Since the concentration of point defects is known (see Table I), it is possible to obtain a value for S^2 in the Klemens formula from the data. We find $S^2=1.0$. For an interstitial atom, the calculated mass term is 0.08 and it is very reasonable that a change in force constant and nearest-neighbor distance accounts for the larger experimental S^2 .

The thermal conductivity of the hydrogen-reduced sample (Fig. 3) is considerably lower than that of the pure and vacuum-reduced samples, especially in the range below 20°K. It is evident that K is not $\propto T^3$ even at 2–3°K; hence a scattering of the phonons by internal boundaries such as defect clusters or defect planes (as reported by Magnéli⁴³ from x-ray work) does not provide an obvious explanation. The temperature dependence of the thermal conductivity is about what one would expect for scattering by dislocations. However, the fact that this crystal, when reoxidized, has a thermal conductivity almost equal to a pure specimen, is an indication that dislocations are not responsible for the low conductivity.

An attempt was made to analyze the heat conductivity of this sample using Klemens's method of additive resistances. Over and above scattering by the crystal boundaries, point impurities, and phonon-phonon processes, it appears that other resistance mechanisms are

required: below 7°K a scattering characterized by a mean free path l proportional to T^{-1} , and between 7 and 35°K a process giving rise to an $l \approx \propto T^{-2}$.

Phonon mean free paths with temperature dependence similar to our results have been reported in the literature and have generated considerable discussion. Scattering by free or bound electrons is the subject of papers by Makinson,⁴⁴ Keyes,⁴⁵ Griffin and Carruthers,⁴⁶ Pyle,⁴⁷ and Ziman.⁴⁸ Resonance scattering associated with impurity modes has been considered by Wagner.⁴⁹ We have examined our data in the light of these suggestions. However, it appeared that none of these approaches was exactly applicable in the case of heavily reduced rutile. Many parameters (e.g., the Debye Θ) are changing rapidly in the temperature interval 10–20°K. Hence a further search for additional scattering mechanisms in this sample does not seem to be meaningful at this time.

C. Anisotropy

Because of the tetragonal structure of rutile, the heat flow along the c axis differs from that along an a axis. From the thermal-conductivity measurements made on the two pure samples, 1cO and 1aO, one can determine the anisotropy ratio K_c/K_a , where K_c is the conductivity parallel to the c axis and K_a is the value perpendicular to c along an a axis. The smooth curves in Fig. 2 were used to determine the anisotropy ratio as a function of temperature and the result is shown in Fig. 5. A correction of 4% in the boundary-scattering region was applied to compensate for the difference in sample lengths.

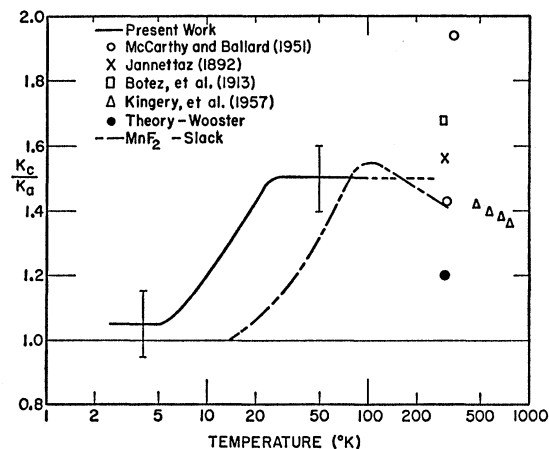


FIG. 5. The thermal-conductivity anisotropy of TiO_2 as a function of temperature showing present results and the measurements of other observers. Slack's result for MnF_2 is plotted for comparison.

⁴⁴ R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 471 (1938).

⁴⁵ R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

⁴⁶ A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

⁴⁷ I. C. Pyle, Phil. Mag. **6**, 609 (1961).

⁴⁸ J. M. Ziman, Phil. Mag. **1**, 191 (1956).

⁴⁹ M. Wagner, Phys. Rev. **131**, 1443 (1963).

⁴³ A. Magnéli, in *Transition Metal Compounds, Informal Proceedings of the Buhl International Conference on Materials, Pittsburgh, Pennsylvania, 1963*, edited by E. R. Schatz (Gordon and Breach Publishers Inc., New York, 1964).

Above 100°K we feel that radiation is affecting our data, so the anisotropy above 100°K is shown by the dashed line to be constant and was determined by extrapolating each curve to $K \propto 1/T$ at the point where each curve shows this temperature dependence. This pair of samples also showed the same general anisotropy behavior when reduced. The data of other observers are also plotted on the same graph. The smoothed high-temperature values of Kingery *et al.*²⁶ are the most extensive, and an extrapolation of their results to 300°K indicates good agreement with our value of $K_c/K_a = 1.5 \pm 0.1$. The other points⁵⁰⁻⁵² are just room-temperature values and it is difficult to assess their reliability.

At very low temperatures $K_c/K_a = 1.05 \pm 0.1$, with the major error being a possible $\pm 5\%$ uncertainty in the measurement of the clamp spacing for each sample.

As mentioned in the prior section, the Casimir expression for the thermal conductivity is $K = \frac{1}{3}Cvl$. Boundary scattering determines K at very low temperatures so the mean free path l should be the same (except for a small length correction) for the two samples since both had the same cross section. In a simple first approximation, the anisotropy ratio reduces to $K_c/K_a = v_c/v_a$ as discussed by Slack,⁵³ where the velocity in each direction is some average over the longitudinal and transverse sound velocities. The weighting used by Casimir⁵² favors the transverse velocities and leads to $v_c/v_a = 0.94$. The average sound velocities computed using Eq. (8) have the ratio 1.02. It is also quite common to give equal weight to the one longitudinal and two transverse velocities ($3v = v_l + v_{t1} + v_{t2}$).⁵⁴ This method yields $v_c/v_a = 1.07$. The latter two ratios are in good agreement with the experimental data.

An anisotropy ratio of 1.5 at 300°K is about what Slack⁵⁵ obtained for MnF_2 which also has rutile structure. A significant difference is that the ratio for MnF_2 shows a gradual decrease to 1.0 below 100°K whereas the ratio for TiO_2 begins to decrease only below 25°K. However, MnF_2 is antiferromagnetic below 67°K, and this may influence the phonon scattering and consequently the anisotropy at low temperatures.

The decrease in the anisotropy of TiO_2 is attributed to the onset of point-defect and boundary scattering which are beginning to compete with the intrinsic phonon-phonon scattering below 25°K. The thermal conductivity for point-defect scattering involves the sound velocity squared, and when such processes are important, the anisotropy ratio could reasonably be expected to decrease, since the sound-velocity factor is

less than 1.5. The ratio in the boundary-scattering region seems to be fairly well explained by assuming that the only anisotropy present is that due to the sound velocities.

There has been very little work either theoretically or experimentally on the thermal-conductivity anisotropy in crystals. A paper by Wooster⁵⁶ is of some interest in the intrinsic region where he attempts to correlate the anisotropy with the crystal structure. He determines the number of bonds between the atoms and their angle with the respective axes and assumes that the thermal conductivity is greatest in the direction of strongest bonding. For rutile this leads to a calculated $K_c/K_a = 1.2$, which is somewhat less than the experimental value but at least indicates a greater conductivity along the c axis.

V. THERMOELECTRIC POWER

The thermoelectric powers of the four semiconducting samples discussed in the previous sections are shown in Fig. 6. Some of the data from 30 to 300°K shown for sample $3a\text{Nb}$ were taken more than a year ago in another apparatus and these fit nicely on the curve for the present points.

It is quite apparent from the magnitude of the thermoelectric power Q at low temperatures that the usual electron-diffusion model is not adequate to explain the results. It seems certain that phonon drag is the cause of the large value of Q . In this effect the electrons are preferentially scattered in the direction of the temperature gradient by the phonons which comprise the heat current. This interaction has been observed in many semiconductors; discussions of theory and experiment are available in the articles by Herring.^{57,58}

The total thermoelectric power can be expressed as the sum of an electronic component Q_e and a phonon drag component Q_p . The electronic component is given by

$$Q_e = -k/e(A_n + E_F/kT),$$

where A_n is the energy transport term, and E_F is the Fermi energy which can be expressed in terms of the density of states and carrier concentration.

It is possible to obtain the density-of-states effective mass m^* from measurements of Q_e and R_H (Hall coefficient). However, at low temperatures Q_p is very large, but no expression predicts its magnitude exactly and hence Q_e is uncertain too. At higher temperatures ($\approx 300^\circ\text{K}$) Q_p is negligible; unfortunately Q_e is complicated by the fact that the electrons are distributed over two slightly separated conduction bands.¹⁸ The complexity of the two-band analysis plus a lack of knowledge of some of the parameters precludes obtaining the density of states for each band at this time.

⁵⁰ K. A. McCarthy and S. S. Ballard, *J. Opt. Soc. Am.* **41**, 1062 (1951).

⁵¹ E. Jannettaz, *Compt. Rend.* **114**, 1352 (1892).

⁵² N. Botez and H. Hertenstein, *Physik Z.* **14**, 332 (1913).

⁵³ G. A. Slack, *Phys. Rev.* **127**, 694 (1962).

⁵⁴ G. A. Slack, *J. Appl. Phys.* **35**, 3460 (1964).

⁵⁵ G. A. Slack, *Phys. Rev.* **122**, 1451 (1961).

⁵⁶ W. A. Wooster, *Z. Krist.* **95**, 138 (1936).

⁵⁷ C. Herring, *Phys. Rev.* **96**, 1163 (1954).

⁵⁸ C. Herring, *Halbleiter und Phosphore*, edited by M. Schön and H. Welker (Vieweg und Sohn, Braunschweig, 1958), Vol. 5, p. 184.

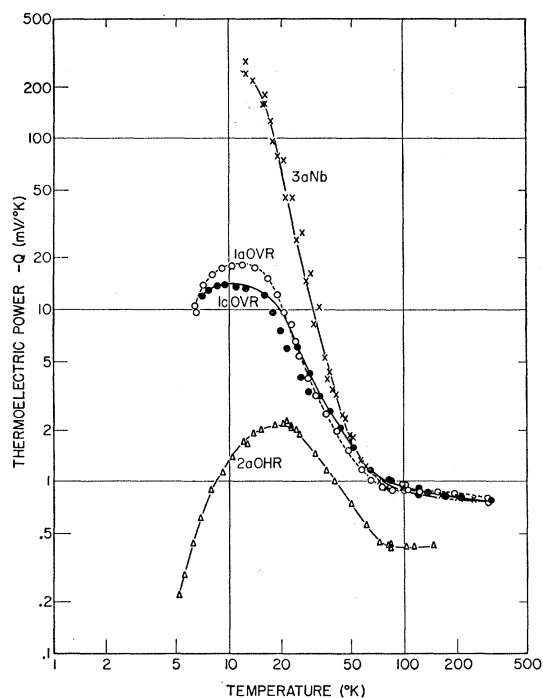


FIG. 6. The thermoelectric power of the semiconducting rutile samples from 5 to 300°K.

Other observers have quoted values based on the one-band model so we will briefly mention our results. The value of m^* is quite dependent on the choice of A_n . For intravalley scattering $A_n = 2.0$, whereas for other forms of scattering one should use a larger value with the exception of intervalley scattering which decreases A_n .⁵⁹ The mobility data indicate that this latter type of scattering is important in rutile. The results for several vacuum-reduced samples parallel to c with room temperature resistivities of 1 to 10 Ω cm yield an average m^* of 30 to 35 electron masses (m_0) at 300°K for $A_n = 2.0$; if $A_n = 2.5$, then m^* is about 20 m_0 . These values are in good agreement with those found by Frederikse on similar samples.⁷

The values quoted for m^* are probably not very accurate because a small fraction of the electrons are in the higher band. However, the order of magnitude of m^* indicates that we are dealing with a $3d$ conduction band whose character is not much different from the $3d$ band of titanium in SrTiO_3 .⁶⁰

The thermoelectric powers of samples measured along the a and c directions were approximately the same ($\pm 5\%$) at room temperature. When the electron current is in an a direction, there are two Hall coefficients ($H_{||c}$ and $H_{\perp c}$) whose ratio varies with temperature; consequently the calculated m^* is quite dependent on which one is chosen. When the temperature gradient

is in an a direction, the use of $R_{H_{||c}}$ yields an m^* in agreement with the c sample data and m^* is temperature-independent down to about 150°K where phonon drag becomes important. Such is not the case if $R_{H_{\perp c}}$ is chosen.

For the phonon-drag component Herring⁵⁷ obtained the result

$$Q_p = - (fv^2\bar{\tau}/\mu T),$$

where f is the fraction of the momentum lost by the electrons which is delivered to the lattice, v is an average velocity of sound, $\bar{\tau}$ is an average relaxation time for the long-wavelength phonons which are the only ones with the correct energy to interact with the electrons, and μ is the electron mobility. To obtain the temperature dependence, Herring assumed lattice scattering with $\mu \propto T^{-1.5}$ and an expression for τ valid for long wavelengths and $T \ll \Theta$. For longitudinal modes $\tau^{-1} = T^3 q^2$, whereas for transverse modes $\tau^{-1} = T^4 q$. After the necessary computations, Herring found for longitudinal modes $Q_p \propto T^{-3.5}$, and for transverse modes $Q_p \propto T^{-4.0}$. In the boundary-scattering region $\bar{\tau} = \tau_b$ and then $Q_p \propto T^{0.5}$.

If many electrons are present, they constitute an important source of phonon scattering, which leads to a reduction in $\bar{\tau}$ and consequently Q_p . Herring has called this the saturation effect. The change of carrier concentration with temperature is evident from Fig. 7 which gives the Hall coefficient and electrical resistivity for sample 3aNb as well as for vacuum- and hydrogen-reduced samples which should approximate quite closely the electrical properties of our other crystals. Rough calculations indicate that the saturation effect should not be a major factor in determining the magnitude and temperature dependence of Q_p for our samples.

The phonon component of the thermoelectric power was obtained by subtracting the estimated electronic component from the total Q . Figure 8 shows Q_p as a function of temperature on a log-log plot. It is quite apparent that Q_p increases as a high negative power of T at temperatures above the boundary scattering region. The low-temperature points are quite insensitive to the choice of the electronic component, whereas above 100°K Q_p is the difference of two almost equal numbers. From an extrapolation of the low temperature data it seems fairly certain that Q_p is negligible at room temperature.

The most unusual feature of the data is the rapid increase of Q_p as T decreases ($\propto T^{-4.5}$) for the niobium-doped sample. An infinite specimen would have a slightly larger negative exponent, but even 4.5 is considerably greater than predicted by theory. The largest exponent the authors are aware of is the 3.6 reported for semiconducting diamond.⁶¹ The absolute value of Q_p at 12°K is 250 mV/°K which is much larger than the values normally obtained for semiconductors.

⁵⁹ C. Herring, Bell System Tech. J. 34, 237 (1955).

⁶⁰ A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).

⁶¹ H. J. Goldsmid, C. C. Jenks, and D. A. Wright, Proc. Phys. Soc. (London) 73, 393 (1954).

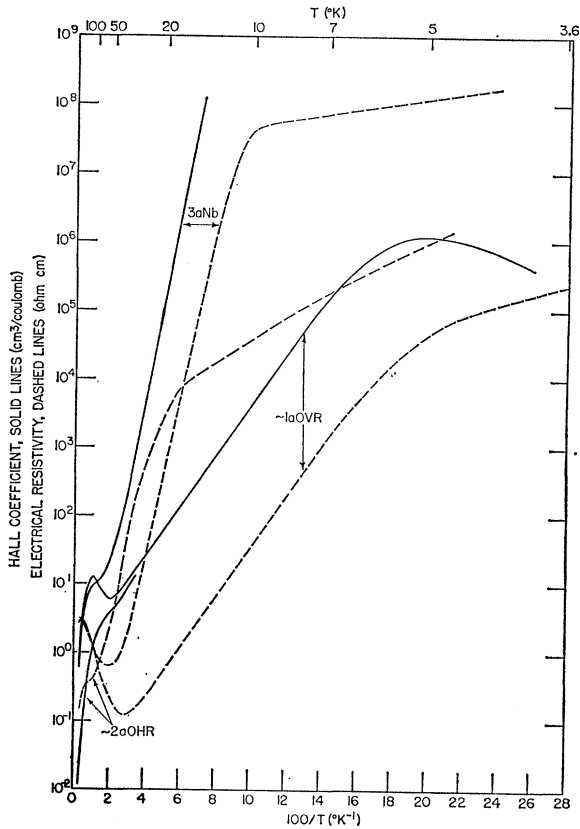


FIG. 7. The Hall coefficient and electrical resistivity as a function of reciprocal temperature for our niobium-doped rutile sample and for samples which are comparable with our vacuum- and hydrogen-reduced specimens.

Turning to the data obtained on the vacuum-reduced sample (1aOVR), one notes that the slope of Q_p versus T is considerably smaller (≈ 2.8), and that the absolute

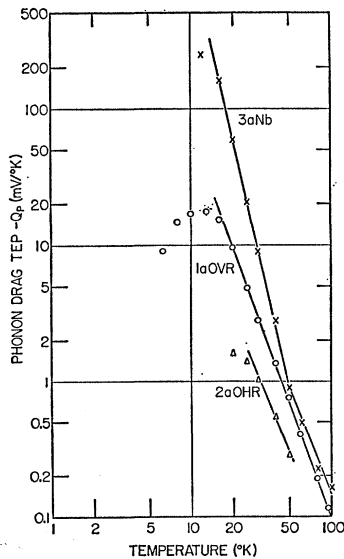


FIG. 8. The phonon-drag component of the thermoelectric power versus temperature for three of the semiconducting rutile samples.

value of Q_p is much less than for sample 3aNb. These facts can be at least partially accounted for by observing that the heat conductivity of this sample in the boundary-scattering region is about a factor 5 smaller than that of sample 3aNb. The smaller τ_b limits Q_p accordingly at the lower temperatures.

Analysis of the thermoelectric powers of the vacuum-reduced pair of samples (1aOVR and 1cOVR) indicates some dependence of the phonon component on direction. This is in accord with the work of Gurevich and Firsov⁶² who predicted a slight anisotropy in Q_p in order to eliminate the divergence in the expression for the thermoelectric power. In an extension of their work to tetragonal crystals, Gashimzade⁶³ obtained for the c direction $Q_p \propto T^{-3.5} \ln T$, and for an a direction $Q_p \propto T^{-3.5}$. Our results are in good agreement with an anisotropy of this magnitude.

The total Q for the hydrogen-reduced sample decreases very rapidly below 20°K, and it is not clear what fraction of the decrease should be attributed to a changing Q_e . Reliable Hall-coefficient data could not be obtained below 30°K, so Q_e is uncertain at lower temperatures, but it seems reasonable that the variation in Q is largely due to the change in Q_p . The decrease is much faster than boundary scattering would predict and resembles that found by Geballe and Hull⁶⁴ in silicon samples with about 10^{18} impurities per cc. They attributed the effect to impurity-band conduction in silicon at low temperatures and this could be the explanation for our data as well.

As the temperature drops, the effect of boundary scattering should become apparent sooner in the thermoelectric power than in the thermal conductivity. Thus the maximum of Q_p should be at a higher temperature than that of K . However, the maximum of the phonon-drag component seems to occur a few degrees lower in temperature for the vacuum-reduced and Nb-doped samples and about 15° lower for the hydrogen-reduced sample. Similar experiments on tellurium have shown that the K and Q_p maxima occur at about the same temperature.⁶⁵

In this connection it is interesting to compare the temperature dependence of the phonon mean free path from the thermal-conductivity data with that computed from the phonon drag component of the thermoelectric power. The values of l_K were calculated using the Casimir expression for K , and the values for l_Q were obtained from the equation $l_Q = Q_p \mu T / f v$. The factor f has been arbitrarily set equal to 0.1 because we are interested only in the temperature dependence and not in the magnitude. The experimental electron mobility was

⁶² V. L. Gurevich and Yu. A. Firsov, *Fiz. Tverd. Tela* 4, 530 (1962) [English transl.: *Soviet Phys.—Solid State* 4, 385 (1962)].

⁶³ F. M. Gashimzade, *Fiz. Tverd. Tela* 5, 883 (1963) [English transl.: *Soviet Phys.—Solid State* 5, 650 (1963)].

⁶⁴ T. H. Geballe and G. W. Hull, *Phys. Rev.* 98, 940 (1955).

⁶⁵ L. N. Timchenko and S. S. Shalyt, *Fiz. Tverd. Tela* 4, 934 (1962) [English transl.: *Soviet Phys.—Solid State* 4, 685 (1962)].

used and the power-law variation of μ with temperature, observed at temperatures above the impurity-scattering region, was extrapolated to 20°K (e.g., $\mu \propto T^{-3.4}$ above 30°K in 3aNb; $\mu \propto T^{-2.9}$ above 30°K in 1aOVR; and $\mu \propto T^{-2.4}$ above 80°K in 2aOHR). The computed l_K and l_Q for the three samples are plotted in Fig. 9. It is interesting that the two mean free paths show qualitatively the same behavior. For the niobium-doped sample, l_Q is increasing somewhat faster than l_K , especially below 30°K, but for the reduced samples the two l 's follow each other very closely as the temperature changes.

The fact that l_K and l_Q as a function of temperature behave quite similarly, and that the maxima of K and Q_p occur at about the same temperature, suggests that approximately the same group of phonons is prominent in both phenomena. This is very reasonable if $T \ll \Theta$. When impurity scattering is important, the short-wavelength phonons are strongly scattered by these imperfections; thus only long-wavelength phonons contribute to K as well as to Q_p . Impurity scattering is somewhat important in samples 1aOVR and 2aOHR, but not in sample 3aNb, so this fact may explain why l_K and l_Q diverge more in the latter specimen.

VI. CONCLUSIONS

(1) The thermal conductivity of pure rutile is that expected for an ideal insulator. Below about 7°K the conductivity varies almost as T^3 with a phonon mean free path nearly equal to the average sample diameter. In the temperature range 25 to 100°K, the conductivity varies exponentially with temperature, indicative of umklapp processes between phonons. Phonon scattering by isotopes and chemical impurities is important only near the maximum which occurs between 13 and 15°K. The use of the Callaway expression generates a curve in good agreement with the experimental data.

(2) In the reduced samples, two additional scattering mechanisms are present; the usual point-impurity term as well as a scattering process which is important below the maximum and not well understood at present. Re-oxidation proved useful in separating the two terms for the vacuum-reduced sample and a reasonable value was obtained for the scattering by point defects.

(3) The anisotropy ratio K_c/K_a is about 1.5 above 25°K where only phonon-phonon scattering processes are important. In the temperature range of boundary scattering, the ratio is close to 1.

(4) The thermoelectric power has a very large phonon-drag component at low temperatures as a consequence of the large phonon mean free path and the small elec-

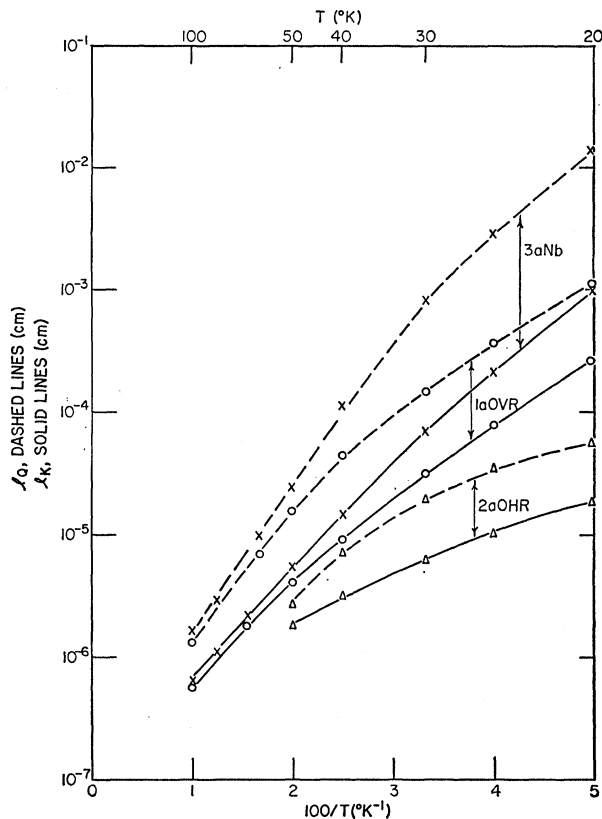


FIG. 9. The phonon mean free path from the thermal-conductivity data and that from the phonon-drag thermoelectric power plotted as a function of reciprocal temperature for three of the semiconducting rutile samples.

tron mobility. A comparison of the phonon mean free paths computed from the phonon-drag thermoelectric power and from the heat conductivity indicates that the same group of phonons is influential in both phenomena.

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