

MEASUREMENT OF THERMAL DIFFUSIVITY OF KCl AT PRESSURES UP TO 35 KBAR AND TEMPERATURES UP TO 820°K

By

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Abstract

The thermal diffusivity of KCl has been measured up to 35 kb of pressure and up to 820°K of temperature using the Ångström method. The measurement was carried out through the phase transition from NaCl- to CsCl-structure occurring at about 19 kb. 66% of decrease of the diffusivity was observed at the transition point at 300°K, 56% at 610°K, and 71% at 820°K. The relative pressure derivative of the thermal diffusivity up to 19 kb was found to be 3.0%/kb at 300°K.

1. Introduction

It is well known that in the earth's interior there are several layers bounded by phase transitions. Knowledge of the behavior of the physical properties accompanied with the phase transitions is important to discuss the problems on the earth's interior. Thermal diffusivity is one of such properties. Yukutake [1974] reported that the thermal diffusivity of solid could be measured with fairly good accuracy under high pressures and temperatures. We attempted to measure the change of thermal diffusivity accompanied with phase transitions.

Preliminarily we found that the thermal diffusivity of KCl decreased largely through the phase transition from NaCl- to CsCl-structure occurring at about 19 kb. This is an interesting problem to know the heat transfer in the earth's interior. Furthermore, since it was investigated by Dobrestov and Peresada [1969] and Wang [1973] that the elastic constant C_{44} of KCl decreases with increase of pressure and Anderson and Demarest [1971] argued the abnormal behavior of the elastic constant C_{44} of the NaCl-structure like KCl near the phase transition, it is valuable to know the change of the phonon mean free path at the phase transition from measuring the thermal diffusivity. In this work, we measured the thermal diffusivity of KCl at pressures up to 35 kb and temperatures up to 820°K. The pressure dependence of thermal diffusivity was calculated based on the lattice model and compared with the experimental results.

2. Experimental method

Thermal diffusivity was measured by the Ångström method in which the peri-

odically varying thermal waves were sent from one end of the semi-infinite rod. The sample assembly in the pressure vessel is shown in Fig. 1. The apparatus used in this work was a single-stage piston-cylinder device of 12 mm in diameter of bore. Pressure was determined with a precision of ± 0.5 kb for all runs, by applying the correction for friction in the same apparatus determined previously by Shimada [1971].

The periodic variations of temperature were measured at the two points in distance L in the semi-infinite rod sample with two chromel/alumel thermocouples. The thermal wave generator was prepared by winding the nichrome wire on a thin tube of boron nitride with a narrow spiral groove on the surface. KCl rods of 5.3 mm in diameter and 10 mm in length were used. Powdered potassium chloride of Nakarai guaranteed reagent-grade was compressed at about 5 kb into rods. Single crystal rods cut in the [100] direction were also prepared from Optovac Inc. The accuracy of the direction was examined by X-ray diffractometry, being within $\pm 1^\circ$.

The basic equation of heat conduction in the x direction is

$$\kappa \frac{\partial^2 T(x,t)}{\partial x^2} = \frac{\partial T(x,t)}{\partial t} + \mu T(x,t), \quad (1)$$

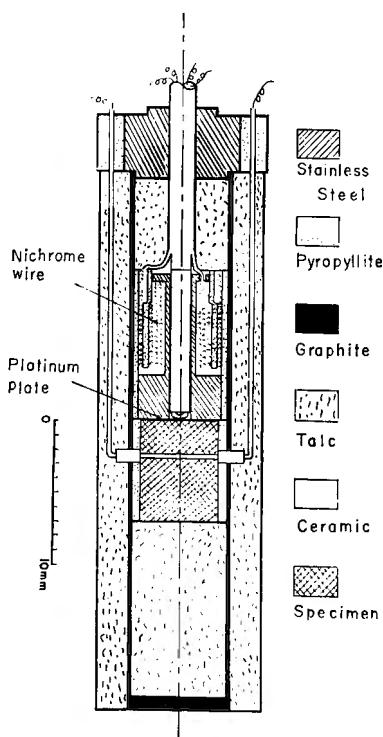


Fig. 1. The sample assembly in the pressure vessel.

where $T(x,t)$ is the temperature in the sample as a function of position x and time t , κ is the thermal diffusivity, and μ is a constant which determines the radial heat flux to the surrounding solid pressure medium.

The boundary conditions are

$$\left. \begin{aligned} T(0,t) &= A_a + A_b \cos \omega t, \\ T(\infty,t) &= 0, \end{aligned} \right\} \quad (2)$$

where ω is the angular frequency, A_a is the mean temperature of the sample and A_b is the amplitude of the thermal wave. The solution of Eq. (1) with the boundary conditions (2) is

$$T(x,t) = A_a \exp\left(-\sqrt{\frac{\mu}{\kappa}} x\right) + A_b \exp\left(-\sqrt{\frac{\sqrt{\mu^2 + \omega^2} + \mu}{2\kappa}} x\right) \times \cos\left(\omega t - \sqrt{\frac{\sqrt{\mu^2 + \omega^2} - \mu}{2\kappa}} x\right). \quad (3)$$

The time dependent parts of temperatures measured at the points $x=0$ and $x=L$, are from (3)

$$\left. \begin{aligned} T(0,t) &= A_b \cos \omega t, \\ T(L,t) &= A_b \exp\left(-\sqrt{\frac{\sqrt{\mu^2 + \omega^2} + \mu}{2\kappa}} L\right) \cos\left(\omega t - \sqrt{\frac{\sqrt{\mu^2 + \omega^2} - \mu}{2\kappa}} L\right). \end{aligned} \right\} \quad (4)$$

We determined the thermal diffusivity κ and the constant μ by (4), measuring the ratios of the maximum amplitude at the point $x=0$ to that at the point $x=L$ for the thermal waves with different frequencies. This method was described in detail elsewhere (Yukutake [1974]).

In the compressible materials like KCl, it is very difficult to measure the distance between two thermocouple junctions accurately under pressures. This difficulty leads large uncertainty in determining the absolute value of thermal diffusivity. The sample in the side of the thermal wave generator was caved in by the thermocouple junction under pressures, though a platinum plate was placed between the junction and the sample in order to reduce the cave-in. The correction of this effect was approximately done by measuring the distance after each run, though the pressure excursion passed the transition point. The effects of pressure and temperature on the sample length were corrected by using the compressibility and the thermal expansion coefficient from Clark's table [1966]. The volume change accompanied with the phase transition, 18.3% (Weir and Piermarini [1964]) was also taken into account. The correction was not made for the plastic deformation of the sample due to nonhydrostatic condition.

3. Experimental results

The thermal diffusivity of powdered potassium chloride at 300°K is shown in Fig. 2 as a function of pressure. As pressure increases, the thermal diffusivity increases and suddenly decreases at about 22 kb. This pressure corresponds to the transition pressure of KCl from NaCl- to CsCl-structure occurring at 19 kb almost independently of temperature (Pistorius [1964]). In the piston-cylinder apparatus with talc pressure medium, the transition pressure of KCl is apparently about 15% too high at room temperature, and this discrepancy decreases almost linearly with increase of temperature becoming zero above about 450°C (Pistorius *et al.* [1967], Shimada [1971]). This temperature effects are seen in Figs. 3 and 4.

In low pressure region below about 6 kb, the thermal diffusivity rises rapidly. The rapid rise in thermal conductivity of KCl was observed by Hughes and Swain [1967]. On the other hand, Alm and Bäckström [1974] obtained a linear increase of thermal conductivity up to 19 kb and suggested that the rapid increase was caused by the loose contact of the thermocouples with the sample at low pressures. Since in our observation the rise became weaker in the pressure cycles after the first loading, the rapid rise at low pressures was regarded as the same effect as the suggestion by Alm and Bäckström [1974]. We obtained the linear pressure dependence of thermal diffusivity from the results at the higher pressures. In the NaCl-structure, the thermal diffusivity was found to increase at a rate of 3.0%/kb, which agreed well

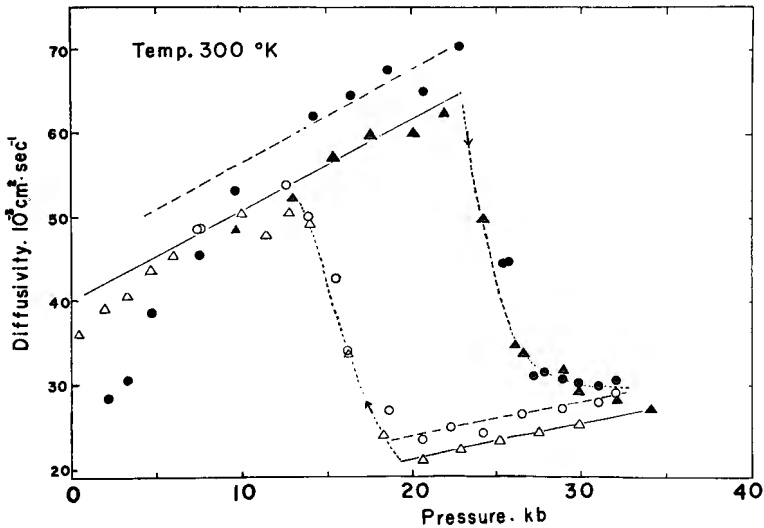


Fig. 2. Thermal diffusivity of powdered potassium chloride at 300°K as a function of pressure. Broken lines are the results from the first pressure cycle and solid ones from the second cycle. Closed and open circles indicate the measured values from the first loading and unloading runs, respectively. Triangles indicate those from the second cycle.

with the results of the thermal conductivity by Alm and Bäckström [1974] considering the increase of density of 0.5%/kb. The discrepancy between the results of the first and the second pressure cycles (the broken and the solid lines in Fig. 2, respectively) is caused mainly by the error from the determination of the distance L as mentioned in the previous section. The absolute values is considered not so

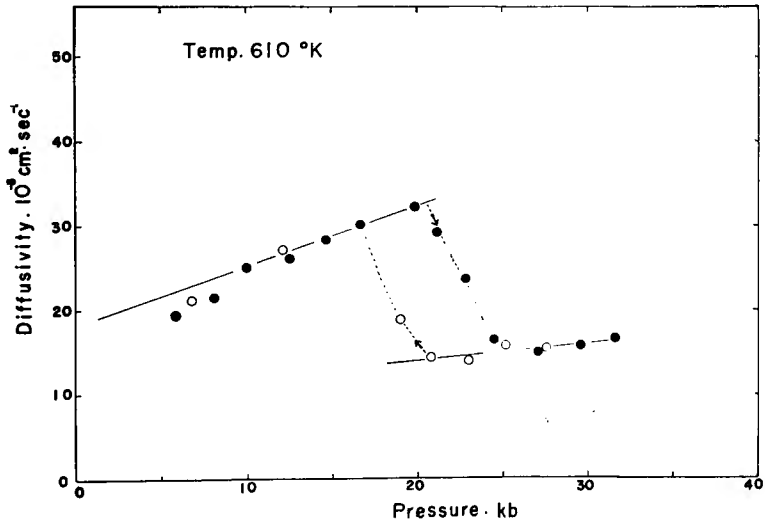


Fig. 3. Thermal diffusivity of powdered potassium chloride at 610°K as a function of pressure.

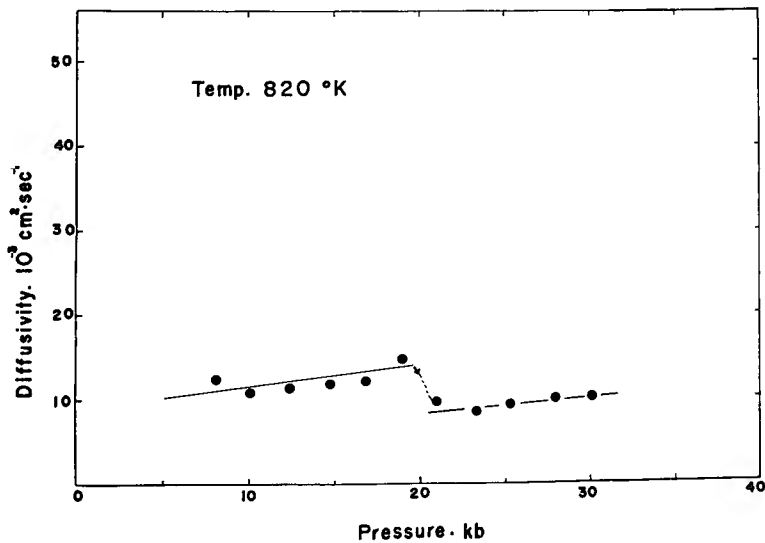


Fig. 4. Thermal diffusivity of powdered potassium chloride at 820°K as a function of pressure.

reliable as the relative ones.

66% of decrease of the diffusivity was observed at the transition point at 300°K. The decrease was not sharp but sluggish as illustrated by the dotted curves in Fig. 2, which was considered due to the use of the solid pressure medium, the large size of sample, and the shear strength of potassium chloride or the sluggishness and the smearing-out of the transition at lower temperatures (Shimada [1971]). The relative pressure derivative on the CsCl-structure was determined only from the unloading

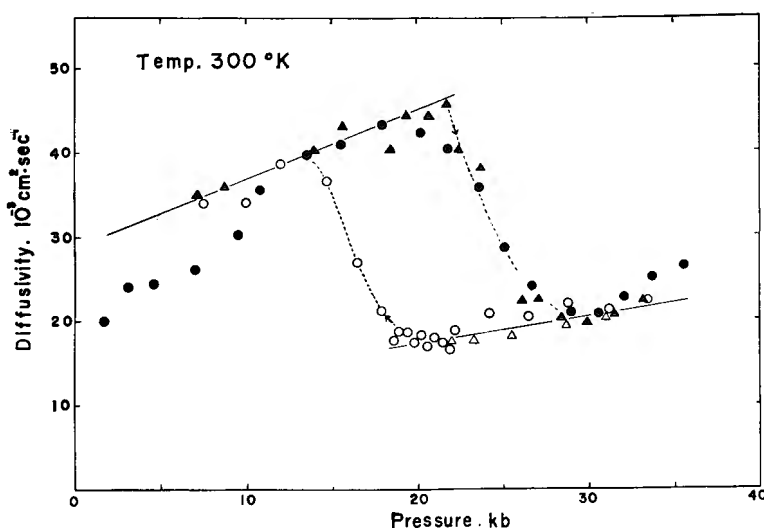


Fig. 5. Thermal diffusivity of single crystal in the direction [100] of potassium chloride at 300°K as a function of pressure. For explanation of symbols, see Fig. 2.

Table 1. Pressure dependence of thermal diffusivity of KCl and decrement accompanied with the transition from NaCl- to CsCl-structure

Sample	Temperature, K	Relative pressure derivative, %/kb		Decrement of κ accompanied with the transition, %
		NaCl structure*	CsCl structure**	
Powdered KCl	300	3.0	1.9	66
	610	3.6	1.8	56
	820	2.8	2.1	71
Single crystal in direction [100]	300	2.8	1.9	63

* Calculated from $\frac{\kappa(P) - \kappa(0)}{\kappa(0)} \cdot \frac{100}{P}$, where $\kappa(P)$ is the thermal diffusivity at pressure P in kb, and $\kappa(0)$ is the extrapolated value to zero pressure.

** Calculated from $\frac{\kappa(P) - \kappa(20)}{\kappa(20)} \cdot \frac{100}{P-20}$, where $\kappa(20)$ is the value at 20 kb.

runs, being 1.9%/kb.

The pressure dependence of the thermal diffusivity of powdered potassium chloride at 610°K is shown in Fig. 3 and that at 820°K is shown in Fig. 4. The results on the single crystal of KCl in the direction [100] at 300°K is shown in Fig. 5. The relative pressure derivatives of thermal diffusivity for the NaCl- and the CsCl-structures and the decrements accompanied with the transition are summarized in Table 1. It is shown that the powdered sample and the single crystal have the nearly same values of the relative pressure derivatives and of the decrements at the transition point.

4. Discussion

The lattice model can be used to interpret the present results on the pressure derivatives. From Debye's expression, we have $\kappa = 1/3 V_m l$, where V_m and l denote the phonon velocity (the mean sound velocity) and the phonon mean free path, respectively. According to Dugdale and MacDonald [1955], the mean free path $l = A_0 K_T / C_v \rho \gamma^2 T$, where A_0 , K_T , C_v , ρ , γ and T are the lattice constant, the isothermal incompressibility, the specific heat, the density, the Grüneisen's ratio and the absolute temperature, respectively. From this expression, the relative variation of the thermal diffusivity with pressure may be approximately written by the following form (see Fujisawa *et al.* [1968], Yukutake [1974]),

$$\kappa(P) \simeq \kappa(0) \left[1 + \left\{ \frac{1}{K_{T0}} \left(\frac{\partial K_T}{\partial P} \right)_0 + \frac{1}{V_{m0}} \left(\frac{\partial V_m}{\partial P} \right)_0 \right\} P \right] / \rho(P), \quad (5)$$

where the subscripts 0 refer to the zero-pressure quantities. Using Eq. (5) and the elastic constants of KCl for the NaCl-structure determined by Bartels and Schuele [1965], we obtained the pressure dependence of thermal diffusivity of 2.6%/kb at room temperature. This value agrees, though somewhat smaller, with the observed value shown in Table 1.

We attempted to determine the pressure dependence for the CsCl-structure in the same manner above mentioned. The pressure dependence of the phonon velocity of KCl in the CsCl-structure was roughly estimated from the elastic wave velocities measured by Ahrens and Katz [1962]. From the values of the compressibility up to 45 kb obtained by Vaidya and Kennedy [1971], the incompressibility at 20 kb and its pressure derivative were estimated at 380 kb and 7.2, respectively. Using Eq. (5), we can estimate the pressure dependence of the thermal diffusivity of KCl in the CsCl-structure. The calculated value was 2.0%/kb at room temperature being in close agreement with the present experimental result (Table 1).

The changes of thermal diffusivity accompanied with the transition have been studied by few workers. Fujisawa *et al.* [1968] found that the thermal diffusivity of Fe_2SiO_4 was increased by about 50% at the transition from olivine- to spinel-structure. Soga *et al.* [1972] found that the thermal conductivity of high-pressure polymorph

of GeO_2 (rutile-type) was about 4.5 times that of low-pressure polymorph (quartz-type). Generally, these behavior will be reasonable from the viewpoint of the lattice thermal conductivity theory.

On the other hand, we found that the thermal diffusivity of KCl largely decreased at the transition point. To interpret this decrease, further studies are required experimentally and theoretically. It may be considered that at the transition point of KCl the abnormal decrease of the phonon mean free path predominates over the change of the phonon velocity.

Acknowledgement

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