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CONTRIBUTION OF "DIFFUSIVE" MODES TO ISOCHORIC THERMAL CONDUCTIVITY OF RARE GAS CRYSTALS

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Isochoric thermal conductivity of rare gas solids is analyzed within Debye approximation. The temperature dependences of isochoric thermal conductivity of solid Ar, Kr, and Xe are explained in the framework of a model where heat is transferred by phonons and above phonon mobility edge by "diffusive" modes migrating randomly from site to site. The mobility edge ω_0 is determined from the condition that the phonon mean free path restricted by the Umklapp processes cannot become smaller than half the phonon wavelength.

Key words: isochoric thermal conductivity, phonons, "diffusive" modes.

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I. INTRODUCTION

At present, there is no generally accepted theory that would adequately describe the experimental thermal conductivity of dielectric crystals in the high temperature region. Heat transfer in a dielectric solid, where the electrons are tightly bound to the atomic nuclei, is realized through the transport of phonons, quanta of energy associated with lattice vibrations. It is usually admitted that at temperatures close to or above the Debye temperature thermal conductivity of perfect crystals is determined mainly by phonon-phonon interactions. However, with the rising of complication of crystalline structure new types of thermal motions appear, which are able to affect thermal conductivity and complicate the analysis of its temperature dependence [1]. In this respect, the solidified inert gases are very convenient objects to compare the experimental results with theory, since in this case, the lattice dynamics is not complicated by the contribution of optical phonons, librons, and effects related to structural disorder. Theoretical models of heat transfer in solid dielectrics have predicted the lattice thermal conductivity behaviour $\Lambda \propto 1/T$ at the temperatures $T \geq \Theta_{\rm D}$ ($\Theta_{\rm D}$ is the Debye temperature) [1]. To obey the $1/T$ law, the volume of the crystals should remain invariable, because the modes would otherwise change and so would the temperature dependence of thermal conductivity. Nevertheless, isochoric studies of thermal conductivity of rare gas solids (RGS) show considerable deviations from the above dependence [2].

The aim of this work is to study the basic features of high-temperature heat transfer in solidified inert gases under isochoric conditions. This study attempts the following — to analyze isochoric thermal conductivity in the framework of the Debye model by using the concept of the lower limit of thermal conductivity and to define possible effect of the heat transfer by "diffusive" modes.

II. CALCULATION RESULTS AND COMPARISON WITH THE EXPERIMENT

The RGS are the simplest objects in the physics of solids and are therefore used traditionally for comparison of experimental and calculated data. In the solidified inert gases Ar, Kr and Xe the phonon-phonon interactions is the main mechanism determining the value and temperature dependence of thermal conductivity $\Lambda(T)$ at the Debye temperature and higher (He and Ne melt at temperatures much below $\Theta_{\rm D}$ [3]). If the scattering is not too strong and the model of elastic waves is appropriate, theory predicts that a high-temperature isochoric thermal conductivity should vary as $\Lambda \propto 1/T$ [4]. In actual fact, the experiment at the constant volume revealed appreciable deviations from this dependence at the highest temperatures, with the conductivity varying slower than $1/T$ [2]. Figure 1 shows the isochoric thermal conductivity of Ar, Kr, and Xe (black squares) [2,5]. As is seen in Fig. 1 the isochoric thermal conductivity decreases with the increasing of temperature as $\Lambda_p^{Ar} \propto T^{-0.93}, \Lambda_p^{Kr} \propto T^{-0.90}$, and $\Lambda_p^{Xe} \propto T^{-0.86}$. The latter qualitatively conforms to the case of strong phonon scattering when mean-free path of vibrational modes are substantially limited and approaches phonon wavelength. To provide an explanation for such temperature dependence of the isochoric thermal conductivity we used the Debye model and concept of the lower limit of thermal conductivity [6]. According to this model the lattice thermal conductivity is determined by integrating over all angular frequencies ω [7]:

$$\Lambda = \frac{k_{\rm B}}{2\pi^2 \upsilon^2} \int_0^{\omega_{\rm D}} l(\omega)\omega^2 d\omega, \qquad (1)$$

where $\omega_{\rm D}$ is the Debye frequency ($\omega_{\rm D} = \left(6\pi^2\right)^{1/3} \upsilon/a$), $l(\omega)$ is the phonon mean free path, υ is the polarization-averaged speed of sound, and a is the lattice parameter.

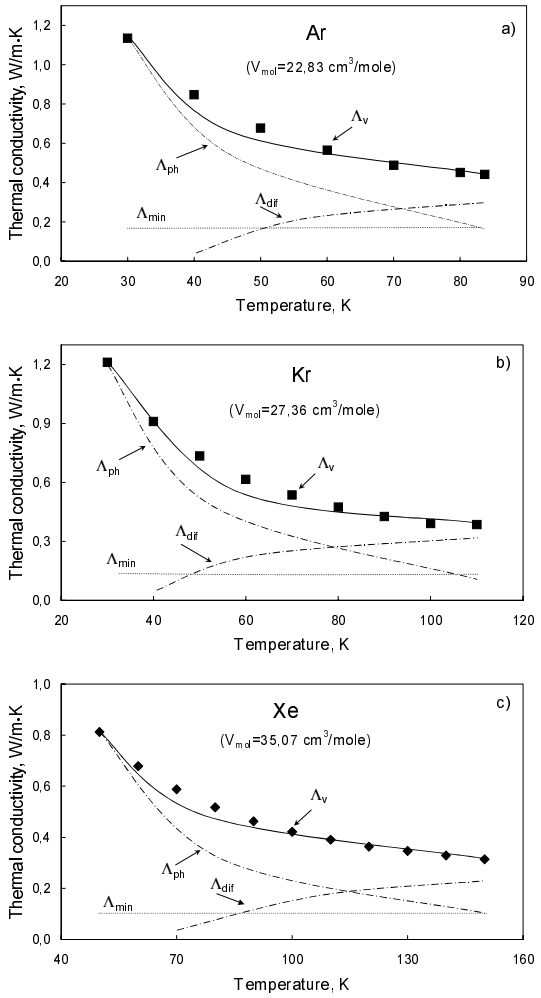

Fig. 1. Isochoric thermal conductivity of solid Ar (a), Kr (b), and Xe (c). Solid lines are the fitting curves for isochoric thermal conductivity. $\Lambda_{\rm ph}$ and $\Lambda_{\rm dif}$ are contributions of phonons and "diffusive" modes to heat transfer, respectively. The lower limit of thermal conductivity $\Lambda_{\rm min}$ is calculated according to equation (3).

The concept of the minimal thermal conductivity assumes that the phonon mean free path decreases with temperature, but it cannot become smaller than half the phonon wavelength $\lambda/2$. If all vibrational modes scatter for the distance of $\lambda/2$, thermal conductivity reaches its lower limit $\Lambda_{\rm min}$ and can be written as [8]

$$\Lambda_{\rm min} = \left(\frac{\pi}{6}\right)^{1/3} k_{\rm B} n^{2/3} \upsilon_i \left(\frac{T}{\Theta_i}\right)^2 \int\limits_0^{\Theta_i/T} \frac{x^3 e^x}{\left(e^x-1\right)^2} dx, \quad (2)$$

for one polarization with the speed of sound υ_i, where Θ_i is the Debye cut-off frequency for each polarization in Kelvins: $(\Theta_i = \upsilon_i \left(\hbar/k_{\rm B}\right)\left(6\pi^2 n\right)^{1/3})$, $n = 1/a^3$ is the number of atoms per volume unit [2,5]. To get the total thermal conductivity, we add the contributions from two transverse and one longitudinal oscillatory modes. In the limit of high temperatures, $T > \Theta_{\rm D}$, Eq. (2) becomes [8]

$$\Lambda_{\rm min} = \frac{1}{2}\left(\frac{\pi}{6}\right)^{1/3} k_{\rm B} n^{2/3} \left(\upsilon_\ell + 2\upsilon_t\right), \quad (3)$$

where υ_t and υ_ℓ are transverse and longitudinal speeds of sound, respectively [9,10].

The phonon mean free path limited by three phonon scattering processes equals

$$l_u\left(\omega\right) = \upsilon / AT\omega^2, \quad (4)$$

$$A = \frac{18\pi^3}{\sqrt{2}} \frac{k_{\rm B}\gamma^2}{ma^2\omega_{\rm D}^3}, \quad (5)$$

where the Grüneisen parameter $\gamma = -\left(\partial \ln \Theta_{\rm D}/\partial \ln V\right)_T$, V is the volume, and m is the average atomic weight.

When the temperature rises, the phonon scattering length decreases and can become comparable with the phonon wavelength. In this case expression (4) is not applicable. Proceeding from [6] it is possible to assume that the mean free path is restricted to a distance close to half the phonon wavelength $\alpha\lambda/2 = \alpha\pi\upsilon/\omega$, where α is the numerical coefficient of the order of unity. In this case the lattice vibrations is separated into two types: presenting the phonons (mean free path larger than $\alpha\lambda/2$) and "diffusive" (mean free path reaches $\alpha\lambda/2$) modes, and then equation (4) becomes

$$l\left(\omega\right) = \begin{cases} \upsilon/A\omega^2 T & 0 \le \omega \le \omega_0, \\ \alpha\pi\upsilon/\omega & \omega_0 < \omega \le \omega_{\rm D}, \end{cases} \quad (6)$$

The "diffusivity" edge ω_0 can be expressed from the condition

$$\frac{\upsilon}{AT\omega_0^2} = \frac{\alpha\pi\upsilon}{\omega_0}, \quad (7)$$

as

$$\omega_0 = 1/\alpha\pi AT, \quad (8)$$

If $\omega_0 > \omega_{\rm D}$, the mean free path of all modes exceeds $\lambda/2$ and thermal conductivity is determined solely by the processes of phonon scattering, and we have the known $1/T$ law. At $\omega_0 \le \omega_{\rm D}$ the integral of thermal conductivity (1) is subdivided into two parts describing the contributions to the heat transfer from the low-frequency phonons $\Lambda_{\rm ph}$ and high-frequency "diffusive" modes $\Lambda_{\rm dif}$

$$\Lambda = \Lambda_{\rm ph} + \Lambda_{\rm dif}, \quad (9)$$

Substituting (6) in (1) we have:

$$\Lambda_{\rm ph} = \frac{k_{\rm B}\omega_0}{2\pi^2\upsilon AT}, \quad (10)$$

$$\Lambda_{\rm dif} = \frac{\alpha\, k_{\rm B}}{4\pi\,\upsilon}\left(\omega_{\rm D}^2 - \omega_0^2\right), \quad (11)$$

The average (according to Debye) speed of sound υ at a specified temperature was computed from the relationship

$$\frac{3}{\upsilon^3} = \frac{1}{\upsilon_\ell^3} + \frac{2}{\upsilon_t^3}, \quad (12)$$

In the present study, we do not separate relative contributions of transverse and longitudinal phonons to the total heat transfer. They can be determined as the corresponding contribution from transverse and longitudinal oscillatory modes which propagate in crystal with υ_t and υ_ℓ, respectively. Here, we concentrate our attention on high temperature thermal conductivity as a function of two main (in our opinion) mechanisms of heat transfer: phonon heat transfer and heat transfer by "diffusive" modes.

Substances	a, 10^{-10} m	υ, m/s	A, 10^{-16} s/K	α	$\omega_{\rm D}$, 10^{12} s^{-1}
Ar	1.93	1021.5	2.90	2.45	11.8
Kr	2.18	843.2	2.85	3.20	9.18
Xe	2.16	804.2	2.20	2.65	8.06

Table 1. The quantities used in the theoretical simulation.

The computer fitting of thermal conductivity using Eqs. (9)–(11) was performed by the least square technique by varying the coefficients A and α. The best agreement with experiment was obtained with parameters of the model for thermal conductivity and fitted values A and α listed in Table 1. The fitting to smoothed experimental isochoric thermal conductivity is shown in Fig. 1 (solid line). The same figure shows the contributions (dot-and-dash lines) to the heat transfer from the low-frequency phonons $\Lambda_{\rm ph}$ and the high-frequency "diffusive" modes $\Lambda_{\rm dif}$ [calculated by Eqs. (10,11)]. The dotted line shows the lower limit of thermal conductivity $\Lambda_{\rm min}$ calculated according to Eq. (3). As temperature rises the amount of heat transferred by "diffusive" modes increases. The solid curves calculated with fitting parameters (Fig. 1) adequately describe the behavior of the temperature dependencies of isochoric thermal conductivity and agree with the results of direct investigations into isochoric thermal conductivity of Ar, Kr, and Xe [2] for the same conditions (P, V, T).

The phonon mobility edge ω_0 for RGS calculated by Eq. (8) is presented in Fig. 2. As the temperature rises, the "diffusivity" edge decreases for all crystals. It is seen that "diffusive" behavior of the high-frequency oscillatory modes in solids Ar, Kr, and Xe appears above 40 K, 37 K, and 65 K, respectively. During our calculation we proceeded from the assumption that the minimal phonon mean-free path equals one half of the wavelength. But it should be noted that this is only one of possible assumptions. For example, Slack [4] supposed that scattering length equals the phonon wavelength.

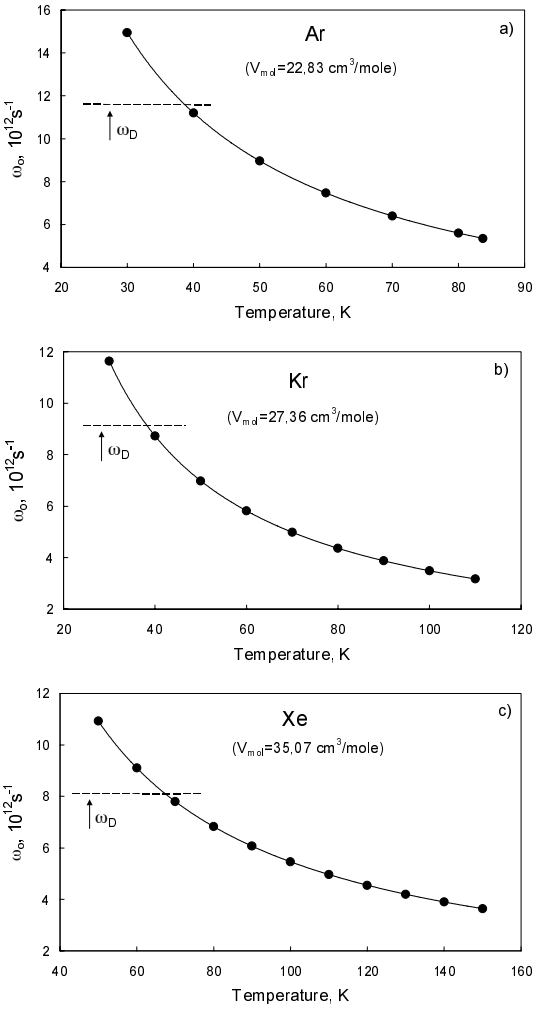

Fig. 2. Temperature dependence of the "diffusivity" edge ω_0 of solid Ar (a), Kr (b), and Xe (c), $\omega_{\rm D}$ is the Debye frequency.

III. CONCLUSIONS

The results obtained in the present study demonstrate that the isochoric thermal conductivity of RGS can be described in a model where heat is transferred by phonons and above phonon mobility edge by "diffusive" modes migrating randomly from site to site. Our calculations data show that with the temperature rises the amount of heat transferred by "diffusive" modes increases. It seems, therefore, warranted to conclude that the main reason for essential deviations of isochoric thermal conductivity of RGS from the $1/T$ dependence is heat transfer by "diffusive" modes.

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ВНЕСОК "ДИФУЗНИХ" МОД В ІЗОХОРНУ ТЕПЛОПРОВІДНІСТЬ КРИСТАЛІВ ІНЕРТНИХ ГАЗІВ

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Ізохорну теплопровідність кристалів інертних газів проаналізовано в наближенні Дебая. Температурну залежність ізохорної теплопровідности твердих Ar, Kr та Xe пояснено в межах моделі, у якій тепло переноситься фононами, а вище від межі рухливости фононів — "дифузними" модами. Межу рухливости фононів знаходимо з умови, що довжина вільного пробігу фонона, яка визначається U-процесами, не може стати меншою від половини довжини хвилі.