Diffusive modes as a defect for explanation of isochoric high-temperature thermal conductivity deviations of rare gas solids from law of 1/T

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This paper discusses the analysis of the isochoric high-temperature thermal conductivity of the atomic cryocrystals exceeding over the law of 1/T within the frames of Callaway method using the hypothesis of the phonon Raileigh scattering influence on the local diffusive modes. It demonstrates that with the temperature and frequency of the dominant phonons growth in these crystals is possible the weakening of the effective thermal resistance due to the transition from mechanism of Raileigh scattering to the independent from wavelength one. The effect is the acoustic analogue of the sky color change from blue to white due to air pollution by the impurity particles with wider length than the wavelengths of the optical photons.

Keywords: rare gas solids, isochoric high-temperature thermal conductivity, phonon scattering by diffusive modes, Callaway method.

Проведено аналіз перевищення ізохорної високотемпературної теплопровідності атомарних кріокристалів над законом 1/T в рамках методу Каллауея з використанням гіпотези про вплив релеївського розсіяння фононів на дифузних локальних модах. Показано, що із зростанням температури і частоти найбільш істотних фононів в таких кристалах можливе послаблення ефективного теплового опору внаслідок переходу від релеївського механізму розсіяння до незалежного від довжини хвилі. Ефект є акустичним аналогом зміни кольору неба з голубого на білий внаслідок туману або забруднення атмосфери частинками, розміри яких перевищують довжини хвиль оптичних фотонів.

Ключові слова: атомарні кріокристали, ізохорна високотемпературна теплопровідність, розсіяння фононів дифузними модами, метод Каллауея.

Проведен анализ превышения изохорной высокотемпературной теплопроводности атомарных криокристаллов над законом 1/T в рамках метода Каллауэя с применением гипотезы о влиянии релеевского рассеяния на диффузных локальных модах. Показано, что с ростом температуры и частоты наиболее существенных фононов в таких кристаллах возможно ослабление эффективного теплового сопротивления вследствие перехода от релеевского механизма рассеяния к независящему от длины волны. Эффект является акустическим аналогом изменения цвета неба с голубого на белый вследствие тумана или загрязнения атмосферы частицами, размеры которых превышают длины волн оптических фотонов.

Ключевые слова: атомарные криокристаллы, изохорная высокотемпературная теплопроводность, рассеяние фононов диффузными модами, метод Каллауэя.

Introduction

The isochoric thermal conductivity of the molecular cryocrystals for temperatures higher than Debay`s temperatures identifies the systematic excesses over the law of 1/T. It was explained by reducing of the libron scattering due to the gradual moving rotational molecular motions, while the sample was heated [1], and with the additional thermal transfer by the diffusive modes [2]. The effect is so powerful that it changes the thermal conductivity behavior with its transition from decrease to increase. As an explanation, in addition to the libron mechanism, the diffusive local modes concept is used [3, 4]. It occurs under conditions of gradual weakening of phonon thermal transfer mechanism of the thermal energy transfer when it begins to propagate diffusively from one localized area of excitation to another one. It is found that the minimum of thermal conductivity of the diffusive thermal transfer in solids has not been achieved yet (Figure 1). Therefore, for the high-temperature field (near and above the Debye`s temperature) the conclusion was made that the phonon mechanism and the diffuse modes in the heat transfer work simultaneously, competing with each other [5].

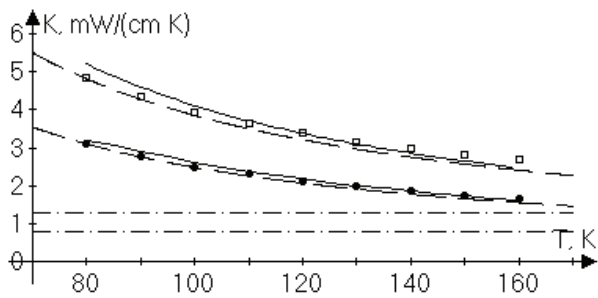However, it should be noted that the high-temperature isochoric thermal conductivity excesses over the law

Fig. 1. Thermal conductivity temperature dependencies of solid argon and crypton. Squares are the argon experimental data [8]. Circles are the crypton experimental data [9]. Dashed lines is 1/T dependences (upper for Ar and bottom for Kr). Dotted straight lines is minimal thermal conductivity (for diffusive transfer, upper for Ar and bottom for Kr). Solid curves are the calculation results of the thermal conductivity by Callaway method.

of 1/T. It was also observed in the rare gas solids, even though those gases have no molecular rotational degrees of freedom (Figure 1). Explanation of this phenomenon is based on the concept of need to renormalize the phonons oscillation spectrum in conditions when the sample's temperature increasing. However, we can propose another explanation of this phenomenon. The reason consists of the thermal conductivity excess over the law of 1/T dependence is connected with mechanism that is similar to the optical high-frequency photons molecular scattering in atmosphere. According to some earlier studies [3], diffusive modes appear in conditions where the free phonons path *l* become close to their wavelengths ($l = \lambda / 2$, where λ – wavelength). It is clear, that those not correlated local areas will transmit heat energy much worse than the flow of phonons. Therefore, diffusive modes are defects of the flow of phonons, because these fluctuation formations disturb the general correlation of the directive wave-like movements of the non-equilibrium crystalline sample.

Statement and solution of the problem

We will consider that local diffuse modes as spherical formations, which scatter phonons by Rayleigh mechanism, that is proportionally to the fourth degree of the frequency. At a constant length of these centers with Rayleigh scattering mechanism, which predominates over other on the thermal conductivity curve while T increases, thermal conductivity behavior will appear as the dependence of 1/T [7, 15], because the parameter $x = \hbar\omega/kT$ for dominant phonons must remain constant and nearly equal to 4. It satisfies maximum of function $x^4 e^x / (e^x-1)^2$ in the integral expressions for the thermal capacity and the thermal conductivity in the frames of Debye model. It seems clear under the condition of the heat transfer phonon mechanism still works.
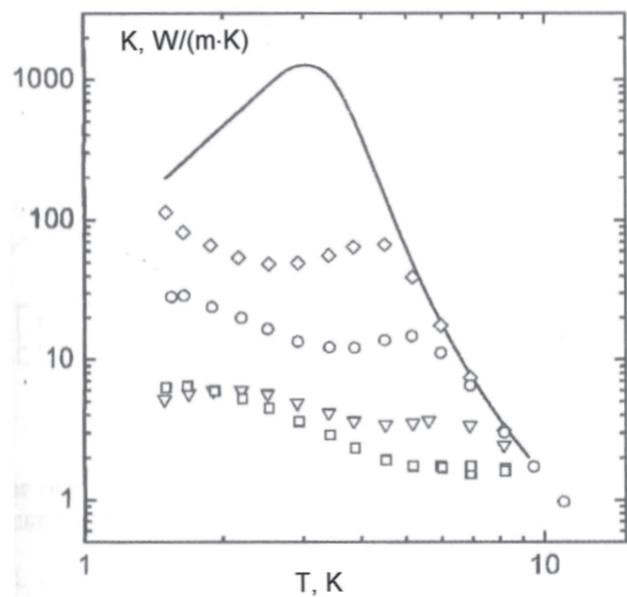

Fig. 2. The thermal conductivity of solid hydrogen with neon impurity [8, 12] for the following Ne concentrations (curves are going down): rhombus are 0.0001%, circles are 0.001%, triangles are 0.012%; squares are 0.099%. Solid line is pure hydrogen.

The appropriate example for this case is solid parahydrogen with doped neon impurity [8]. In Figure 2, in a double logarithmic scale, the experimental results are shown obtained for the thermal conductivity temperature dependence with the different concentrations of neon impurity. It is evident that on the right wing from the maximum of pure solid hydrogen thermal conductivity (solid line) it decreases faster than dependence of T^3 growing on the left wing. This is due to the solid hydrogen is a quantum crystal with a melting temperature is much lower than Debye temperature (118.5 K). However, addition of spherical impurities of the constant size (atomic Ne) gradually reduces the slope of the curve. It becomes close to the law of 1/T for the biggest concentrations of Ne. An appropriate Rayleigh dependence T^4 is shown on Figure 3 for effective scattering rate $\tau^{-1}=Cv^2/3K$ (thermal capacity of solid hydrogen with Ne impurity were taken from [9]).

Unlike neon atoms, the size of the diffusive modes increases with temperature increase, and it could become bigger than wavelength of dominant phonons. It happens because the appropriate frequency of the dominant phonons increases. Under those conditions, it is possible to predict the opportunity of scattering mechanism change on diffusive modes with its transition from Raileigh mechanism to the independent from the phonon's frequency. A multiplier in Raileigh expression for the relaxation velocity must be taken into account in those circumstances. This transition to the new scattering mechanism leads to weaker temperature dependence of the isochoric high temperature thermal conductivity of atomic crystals than the law of 1/T. As one

of the active phonon scattering mechanisms it could take place in other molecular crystals and has an influence on the high temperature thermal conductivity together with libronic and others [2]. It is important to mention that the exponential influence in the expression for the *U*-processes relaxation velocity decreases with temperature increasing (see expression for $\tau_U{}^{-1}$ below).

The calculation results for the isochoric thermal conductivity in cases of classical pure atomic cryocrystals Ar and Kr in comparison with experimental data and classical dependence the law of 1/T are shown in Figure 1. Besides the normal processes and U-processes hypothetical phonon scattering mechanism on diffusive modes was also taken into account. Relaxation Callaway method was used for calculations when in addition to resistive mechanisms we considered the special role of normal phonon-phonon processes. For pure substances and high-quality samples, the normal processes remain important for high temperature range (here we can not consider K_2 as an insignificant). Phonon thermal conductivity K is determined within the frameworks of this relaxation model with two components [4]:

$$K = K_1 + K_2 \text{, where}$$

$$K_1 = \frac{k}{2\pi^2 v}\left(\frac{k}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau_C x^4 e^x}{(e^x - 1)^2} dx \; ;$$

$$K_2 = \frac{k}{2\pi^2 v}\left(\frac{k}{\hbar}\right)^3 T^3 \frac{\left[\int_0^{\theta/T}(\tau_C/\tau_N)x^4 e^x(e^x-1)^{-2}dx\right]^2}{\int_0^{\theta/T}(\tau_C/\tau_N\tau_R)x^4 e^x(e^x-1)^{-2}dx} \; .$$

Integration parameter $x = \hbar\omega/kT$, where $\hbar$ *is* Planck's constant, ω is cyclic frequency, T is crystal temperature, Θ is characteristic Debye temperature. Reciprocal combinational time of phonon relaxation $\tau_C{}^{-1}$ (or average frequency of collisions) is determined by the expression:

$$\tau_C^{-1} = \tau_R^{-1} + \tau_N^{-1},$$

where $\tau_N{}^{-1}$ is frequency of normal processes, that is the way those phonon-phonon collisions that occur without loosing of quasi-momentum:

$$\tau_N^{-1} = A_N T^5 x^2 .$$

Here $\tau_R{}^{-1}$ is frequency of all resistive processes as the sum of all such frequencies. It was calculated in case of perfect single crystal with such mechanisms: boundary scattering (*v* - speed of sound, *L* - characteristic size of the bulk sample):

$$\tau_{bound}^{-1} = v / L \text{ , where } L = 3 \text{ mm;}$$

inelastic phonon-phonon interactions (*U*-processes):

$$\tau_U^{-1} = A_U T^3 x^2 e^{-\frac{E}{T}} \; ;$$

modified Rayleigh relaxation velocity $\tau_{dif}{}^{-1}$ on diffusive local modes:

$$\tau_{dif}^{-1} = f\omega^4$$

where $f = A/T^n$ (n <4). The exponent of power n is considered the parameter, which together with the coefficient A is determined by matching of the theoretical models with thermal conductivity experimental curve. Some of parameters are shown in Table 1.

At this point, we will do the comparison of dominant wavelength phonons at different temperatures for the parahydrogen and rare gas solids with the size of the local diffusive modes which we can consider as the fluctuating volumes. Square of it can be written [17, 18] as

$$< \delta V^2 > = kT \left(\frac{\partial V}{\partial p}\right)_T .$$

For example, at T = 10 K for 1 mole of ideal gas under the normal pressure the isothermal compressibility

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{V_{mol}}{p} = -\frac{RT}{p^2} = \frac{8,31\cdot 10}{10^{10}} \approx 10^{-8} m^6 .$$

Then, the fluctuation per one molecule will be:

$$\delta V_1 = (< \delta V^2 >)^{1/2} / N_A =$$
$$= \left(\frac{kTV_{mol}}{p}\right)^{1/2} / N_A =$$
$$= \left(1,4\cdot 10^{-30}\right)^{1/2} / 6\cdot 10^{23} \approx 10^{-39} m^3$$

Since the compressibility of these crystals is six orders less then for ideal gas [1, 19] despite the weak intermolecular bond in these substances, the corresponding volume magnitude δV_1 will be also smaller.

Hence the order of estimate for an ideal gas fluctuation size per one particle is equal 10^{-13}m. This magnitude is even less than the size of the one molecule. On the contrary, dominant phonon wavelength near 10K is much more. Indeed, from $\hbar\omega/kT = 4$ we will have $\omega = 4kT/\hbar$ or $\lambda_{dom} = 2\pi c/ \omega = \pi c\hbar/2kT = 1\cdot 10^{-9} m$, where c is the speed of sound. The speed of sound was set in the calculations as equal to 1 km/s. Thus, phonon Raileigh scattering of this fluctuating formations for solid parahydrogen (right wing of thermal conductivity curve, Figure 2) is weak. However, in experiments with temperature conductivity of solid argon and krypton the fluctuation magnitude per molecule increases more than an order. The dominant phonon wavelength conversely decreases. Keep in mind that the local diffusive mode is forming by the fluctuations of many molecules, the situation with excess dimensions of diffusive modes above the dominant phonon's wavelengths for the highest temperature of experiments with Ar i Kr
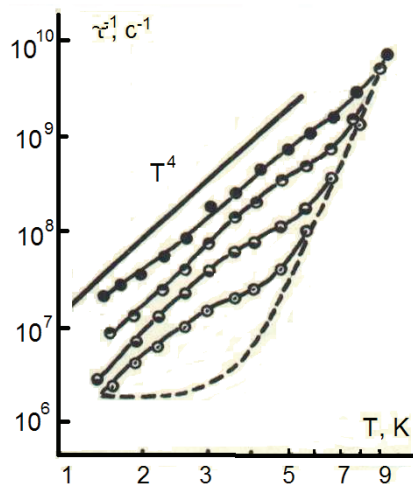
Fig. 3. The temperature dependence of the effective scattering rate $\tau^{-1}=Cv^2/3K$ of solid hydrogen with neon impurity [16]. The concentrations are the same as in Figure 3 (curves are going up with concentration growth). Dashed line is pure hydrogen. The solid line is T^4 dependence.

(Figure 1) seems likely. It should be also noted that in the latter case the length of the phonon does not depend on the temperature and size of it and has the order of magnitude 10^{-10} m (the temperatures of the experiments exceed the Debye temperature, see Table 1). Therefore, scattering of phonons could not have the Raileigh character. The question of the size growth the volume fluctuations till to 10^{-10} m remains open. It requires further investigation.

Conclusion

Thus, thermal conductivity excess in atomic cryocrystals over the law of 1/T could be explained by phonons scattering on diffusive modes when the dominant phonon wavelengths become shorter than their size with the temperature increasing. This effect can be also active in other molecular crystals [1, 2, 11, 12]. However, the excess over the law of 1/T is much higher for molecular crystals due to other mechanism's action, in particular for case of the libronic scattering. The libronic scattering also weakens in conditions of a gradual putting into action of molecular rotational movements with the temperature growth. It seems that phonons as carriers of heat energy must be much more active for the heat transfer than diffusive modes. The scattering of the phonon flow by diffusive modes and libronic mechanism weakens as the temperature increases.

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Table 1

Cryocrystals parameters used for thermal conductivity calculations in the frames of relaxation Callaway method with taking into account the special role of normal processes:

Substance	Molecular volume V, cm³/mole	Debye theory of solids, Θ, K	A_N, $c^{-1} K^{-5}$	A_U, $c^{-1} K^3$	E, K
H_2	23.16	118,5	$6.7\cdot10^4$	$2.9\cdot10^{-15}$	39.9
He	17.3	43	$4.2\cdot10^6$		
Ne	13.53	74.6	$4.5\cdot10^5$		
Ar	22.57	93.3	$9.62\cdot10^3$	$1\cdot10^{-16}$	26
Kr	27.13	71.7	$2.11\cdot10^4$	$1.13\cdot10^{-16}$	25
Xe	34.55	64	$1.59\cdot10^4$		

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