Heat transfer by low-frequency phonons and «diffusive» modes in cryocrystal solutions: the Kr–Xe system

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The temperature and volume dependences of the thermal conductivity of the $Kr_{1-\xi}Xe_\xi$ solid solution are analyzed in a model in which heat is transferred by low-frequency phonons; above the phonon mobility edge this is done by «diffusive» modes migrating randomly from site to site. The phonon mobility edge ω_0 is determined from the condition that the phonon mean free path limited by umklapp processes and scattering on point defects cannot be smaller than one-half the phonon wavelength. The Bridgman coefficient $g = -(\partial \ln \Lambda / \partial \ln V)_T$ is the weighted mean over these modes, whose volume dependences differ strongly. It is shown that the amount of heat transferred by the «diffusive» modes above 100 K is quite large even in pure Kr and it increases with rising temperature and impurity concentration.

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Introduction

The solidified inert gases Ar, Kr, and Xe are among the simplest objects in the physics on the solids and are therefore used traditionally for comparison of experimental and calculated data [1]. At temperatures close to or above the Debye temperature ($T \geq \Theta_D$) the thermal conductivity of perfect crystals is determined solely by phonon−phonon scattering and it is expected to follow the law $\Lambda \propto 1/T$ [2]. To obey the law, the volume of the crystal should remain invariable, because the modes would otherwise change and so would the temperature dependence of the thermal conductivity [2,3].

However, isochoric studies of the thermal conductivity of heavy solid inert gases show a considerable deviation from the above dependence due to the approach of the thermal conductivity to its lower limit [4,5]. The concept of the lower limit of the thermal conductivity proceeds from the assumption that all the excitations are weakly localized in the regions whose sizes are half the wavelength, $\lambda/2$. As a result, the excitations can hop from site to site through thermal diffusion [6]. In this case the lower limit of thermal conductivity $\Lambda_{\min}$ of the lattice at $T \geq \Theta_D$ can be written as:

$$\Lambda_{\min} = \frac{1}{2}\left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3}(v_l + 2v_t), \tag{1}$$

where v_l and v_t are the longitudinal and transverse sound velocities, $n = 1/a^3$ is the number of atoms per unit volume, and k_B is the Boltzmann constant.

Further studies of heat transfer in the solid solutions $Kr_{1-\xi}(CH_4)_\xi$ ($0 \leq \xi \leq 1$) [7] and $Kr_{1-\xi}Xe_\xi$ ($0 \leq \xi \leq 0,14$) [8] have detected a gradual change from the thermal conductivity typical of a perfect crystal to the lower limit of the thermal conductivity $\Lambda_{\min}$ as the crystal becomes increasingly disordered. More recently the volume dependence of the thermal conductivity of the $Kr_{1-\xi}(CH_4)_\xi$ solid solution was analyzed in the framework of a model which assumes that the phonon mean free path cannot decrease infinitely [9]. In present study, the temperature and volume dependences of the thermal conductivity of the $Kr_{1-\xi}Xe_\xi$ solid solution are analyzed using the model mentioned above.

Model

We use Debye's expression for the thermal conductivity [10,11]

$$\Lambda = \frac{k_B}{2\pi^2 v^2} \int_0^{\omega_D} l(\omega)\omega^2 \, d\omega, \tag{2}$$

where v is the sound velocity; ω_D is the Debye frequency ($\omega_D = (6\pi^2)^{1/3} v/a$); $l(\omega)$ is the phonon mean free path determined by the U-processes and by scattering on point defects:

$$l(\omega) = (l_u^{-1}(\omega) + l_i^{-1}(\omega))^{-1}. \qquad (3)$$

The phonon mean free paths corresponding to each mechanism of scattering are described as [2,10,11]

$$l_u(\omega) = v\big/ A\omega^2 T, \quad A = \frac{18\pi^3}{\sqrt{2}} \frac{k_B \gamma^2}{\overline{M}\,\overline{a}^2 \omega_D^3} ; \qquad (4)$$

$$l_i(\omega) = v\big/ B\omega^4, \quad B = \frac{3\pi\Gamma}{2\omega_D^3} ; \qquad (5)$$

where the Grüneisen parameter $\gamma = -(\partial \ln\Theta_D / \partial \ln V)_T$, $\overline{M}$ is the average atomic weight of the solution: $\overline{M} = (1 - \xi) M_{Kr} + \xi M_{Xe}$; $\overline{a} = (1 - \xi) a_{Kr} + \xi a_{Xe}$.

Taking into account the difference ΔM between the atomic (molecular) masses of the impurity and the matrix and the lattice dilatation, the coefficient Γ can be written as [7]

$$\Gamma = \xi(1 - \xi)\left(\frac{\Delta M}{\overline{M}} + 6\gamma \frac{\Delta a}{\overline{a}}\right)^2, \qquad (6)$$

where $\Delta M = \overline{M} - M_{Xe}$; $\Delta a = \overline{a} - a_{Xe}$.

Expression (3) is not valid if $l(\omega)$ is of the order of one-half the phonon wavelength $\lambda/2 = \pi v/\omega$ or smaller. A similar situation was considered previously for the case of U-processes alone [11]. Let us assume that in the general case

$$l(\omega) = \begin{cases} v\big/(A\omega^2 T + B\omega^4), & 0 \le \omega \le \omega_0, \\ \alpha\pi v/\omega = \alpha\,\lambda/2, & \omega_0 < \omega \le \omega_D, \end{cases} \qquad (7)$$

where α is a numerical coefficient of the order of unity. There is evidence that the Ioffe–Regel criterion, which suggests localization, is not applicable for a phonon gas [12]. Nevertheless, we will refer to the excitations whose frequencies are above the photon mobility edge ω_0 as «localized» or «diffusive». Since completely localized states do not contribute to the thermal conductivity, we assume that the localization is weak and the excitations can hop from site to site diffusively, as was suggested by Cahill and Pohl [6]. The frequency ω_0 can be found from the condition

$$v\big/(A\omega_0^2 T + B\omega_0^4) = \alpha\pi v/\omega_0, \qquad (8)$$

as

$$\omega_0 = \frac{1}{(2\alpha\pi B)^{\frac{1}{3}}}\left[\sqrt[3]{1 + \sqrt{1 + u}} + \sqrt[3]{1 - \sqrt{1 + u}}\right], \quad (9)$$

where the dimensionless parameter u is

$$u = \frac{4\alpha^2\pi^2 A^3 T^3}{27B}, \qquad (10)$$

If $\omega_0 > \omega_D$, the mean free path of all the modes exceeds $\lambda/2$, and at $T \ge \Theta_D$ we obtain the well-known expression [11]:

$$\Lambda_{ph} = \frac{k_B}{2\pi^2 v} \frac{1}{\sqrt{ATB}} \arctan\sqrt{\frac{B}{AT}}\,\omega_D. \qquad (11)$$

At $\omega_0 \le \omega_D$ the thermal conductivity integral separates into two parts describing the contributions to heat transfer from the low-frequency phonons and the «diffusive» high-frequency modes:

$$\Lambda = \Lambda_{ph} + \Lambda_{loc} , \qquad (12)$$

In the high-temperature limit ($T \ge \Theta_D$) these contributions are:

$$\Lambda_{ph} = \frac{k_B}{2\pi^2 v} \frac{1}{\sqrt{ATB}} \arctan\sqrt{\frac{B}{AT}}\,\omega_0, \qquad (13)$$

$$\Lambda_{loc} = \frac{\alpha k_B}{4\pi v}(\omega_D^2 - \omega_0^2). \qquad (14)$$

The dependence of the thermal conductivity on the specific volume is characterized by the Bridgman coefficient [3,13]:

$$g = -(\partial \ln \Lambda/\partial \ln V)_T . \qquad (15)$$

Taking into account that $(\partial \ln A/\partial \ln V)_T = 3\gamma + 2q - 2/3$, where $q = (\partial \ln \gamma/\partial \ln V)_T$, and that $(\partial \ln B/\partial \ln V)_T = 3\gamma$ (as follows from Eqs. (4), (5)) and $(\partial \ln\Gamma/\partial \ln V)_T \approx 0$, we have:

$$g = \frac{\Lambda_{ph}}{\Lambda} g_{ph} + \frac{\Lambda_{loc}}{\Lambda} g_{loc} , \qquad (16)$$

where

$$g_{ph} = -\left(\frac{\partial \ln \Lambda_{ph}}{\partial \ln V}\right)_T = 2\gamma + q +$$

$$+ \frac{\sqrt{\dfrac{B}{AT}}\,\omega_0}{\left(1 + \dfrac{B}{AT}\omega_0^2\right)\arctan\sqrt{\dfrac{B}{AT}}\,\omega_0}\left(\gamma_0 + q - \frac{1}{3}\right), \quad (17)$$

$$g_{loc} = -\left(\frac{\partial \ln \Lambda_{loc}}{\partial \ln V}\right)_T = -\gamma + \frac{1}{3} +$$

$$+ \frac{2}{\omega_D^2 - \omega_0^2}(\omega_D^2\gamma - \omega_0^2\gamma_0), \qquad (18)$$

$$\gamma_0 = -\left(\frac{\partial \ln \omega_0}{\partial \ln V}\right)_T = \gamma + \frac{u^{\frac{1}{3}}}{6\sqrt{1+u}} \times$$

$$\times \left[\sqrt[3]{1+\sqrt{1+u}} - \sqrt[3]{1-\sqrt{1+u}}\right](6\gamma + 6q - 2). \quad (19)$$

Results and discussion

The isochoric thermal conductivity of the $Kr_{1-\xi}Xe_\xi$ ($\xi = 0.034, 0.072, 0.14$) solid solution was studied on samples of different densities in the interval of temperatures from 80 K to the onset of melting. The choice of the system, concentrations, and temperature interval was dictated by the following.

The phase diagram of the $Kr_{1-\xi}Xe_\xi$ solid solution is well known [14]. The liquid and solid phases have a point of equal concentrations at 114.1 K and $\xi = 0.15$. Between 75 and 114 K the components form an fcc solid solution for all $1 \geq \xi \geq 0$. When samples are grown with a temperature gradient along the measuring cell, the solid solution can become layered at $\xi > 0.15$. The highest Xe concentration was therefore limited to 14%.

The isochoric thermal conductivities of pure Kr and the $Kr_{1-\xi}Xe_\xi$ solution, for which the isochoric condition comes into play at 80 K are shown in Figs. 1−4 (black squares). The computer fitting of thermal conductivity using Eqs. $(12)-(14)$ was performed by the least squares method, varying the coefficients A and α. The parameters of the Debye model for thermal conductivity used in the fitting (a, v [1,14]; Γ — coefficients calculated by Eq. (6)), and the fitted values A and α are listed in Table along with the Bridgman coefficients obtained in the experiment and calculated by Eqs. $(16)-(19)$. The calculation was done using the values $\gamma = 2.5$ and $q = 1$ [1,14].
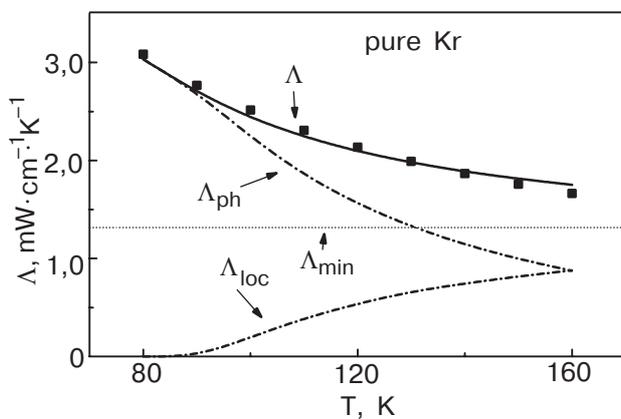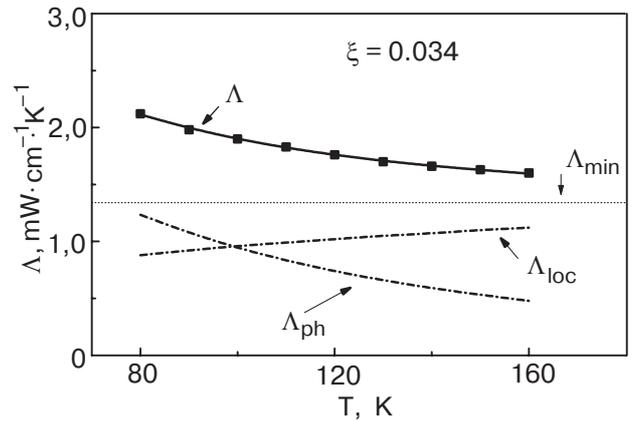

Fig. 1. Fitting results for the isochoric thermal conductivity and calculated relative contributions of low-frequency phonons and «diffusive» modes to the thermal conductivity of pure Kr (molar volume is 28,5 cm^3/mole).

Fig. 2. Fitting results for the isochoric thermal conductivity and calculated relative contributions of low-frequency phonons and «diffusive» modes to the thermal conductivity of the $Kr_{1-\xi}Xe_\xi$ ($\xi = 0.034$) solid solution (molar volume is 29.1 cm^3/mole).

The fitting results are shown in Figs. 1−4 (solid lines). The same figures show the contributions (dash-dot lines) to the thermal conductivity from the low-frequency phonons, Λ_{ph}, and from the «diffusive» modes, Λ_{loc}. The dashed line in the figures indicate the lower limits of the thermal conductivity Λ_{min}, which were obtained as asymptotes of the $\Lambda(T)$ dependence at $T \to \infty$.

It is seen in Fig. 1 that in pure Kr the «localization» of the high-frequency modes starts above 90 K. As the temperature rises, the amount of heat transferred by the «diffusive» modes increases, and at 160 K it becomes equal to the heat transferred by the low-frequency phonons. In the solution with $\xi = 0.034$ (see Fig. 2) the «localization» of the high-frequency modes starts at 30 K and above 100 K most of the heat is transferred by the «diffusive» modes. As the tempe-
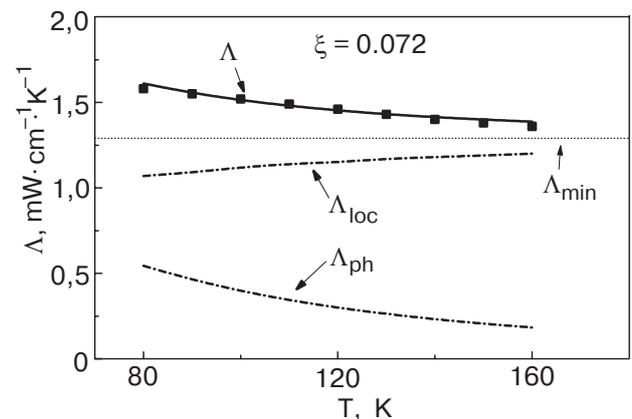

Fig. 3. Fitting results for the isochoric thermal conductivity and calculated relative contributions of mobile low-frequency phonons and «diffusive» modes to the thermal conductivity of the $Kr_{1-\xi}Xe_\xi$ ($\xi = 0.072$) solid solution (molar volume is 29.4 cm^3/mole).
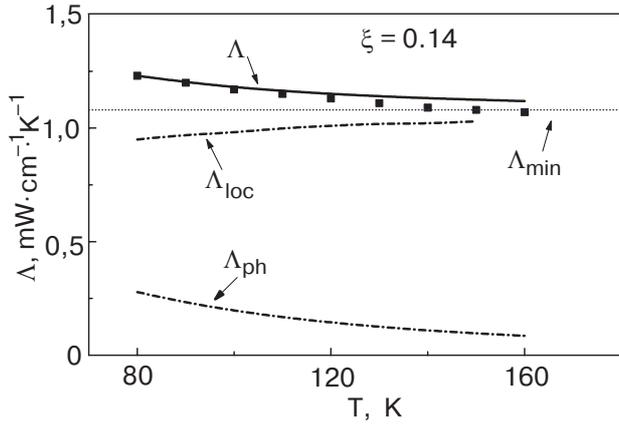
Fig. 4. Fitting results for the isochoric thermal conductivity and calculated relative contributions of mobile low-frequency phonons and «diffusive» modes to the thermal conductivity of the $Kr_{1-\xi} Xe_\xi$ ($\xi = 0.14$) solid solution (molar volume is 29.8 $cm^3/mole$).
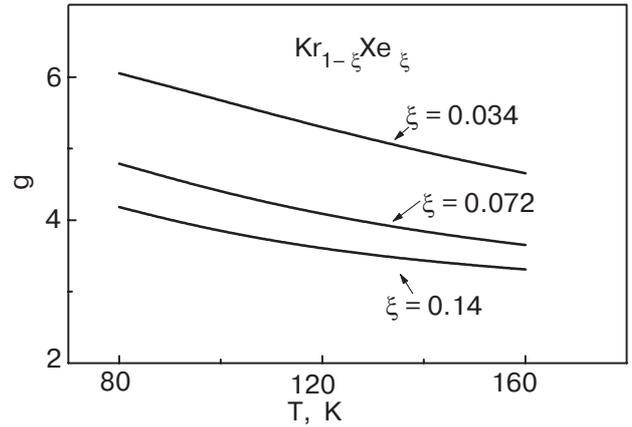

Fig. 5. Calculated temperature dependence of the Bridgman coefficient $g = -(\partial \ln \Lambda / \partial \ln V)_T$ for the $Kr_{1-\xi} Xe_\xi$ solid solution.

rature and the impurity concentration increase, so does the amount of heat transferred by the «diffusive» modes. For $\xi = 0.14$ (see Fig. 4) practically all the heat at $T \geq \Theta_D$ is transferred by the «diffusive» modes. The lower limit of thermal conductivity found by fitting is 1.1−1.2 times higher than Λ_{min} calculated by Eq. (1).

As is seen in Table, the experimental and calculated Bridgman coefficients are in fairly good agreement if one notes that the value of g is estimated with large uncertainty and the model disregards phonon dispersion and the real density of states. The temperature dependence of the Bridgman coefficients $g = -(\partial \ln \Lambda/\partial \ln V)_T$ of the $Kr_{1-\xi} Xe_\xi$ solid solution calculated by Eqs. (16)−(19) is shown in Fig. 5. Equations (16)−(19) describe the general tendency of the Bridgman coefficient g to decrease as the crystal becomes increasingly disordered and most of the heat transferred by the «diffusive» modes.

Table

Parameters of the Debye model for thermal conductivity used in the fitting: a, v, and Γ, obtained through fitting A and α; calculated g_{th} and experimental g_{exp} Bridgman coefficients

ξ	$a \cdot 10^{-8}$, cm	v, km/s	Γ	$A \cdot 10^{-16}$, s/K	α	g_{exp}	g_{th}
0	3.62	0.86	0	3.1	1.2	9.4	9.2
0.034	3.64	0.86	0.1	3.8	1.2	8.0	5.7
0.072	3.65	0.87	0.19	6.4	1.2	5.5	4.6
0.14	3.67	0.87	0.29	9.8	1.1	4.0	3.8

Conclusions

It is shown that the temperature and volume dependences of the thermal conductivity of the $Kr_{1-\xi} Xe_\xi$ ($\xi < 0.14$) solid solution can be described in the framework of a model in which heat is transferred by low-frequency phonons; above the phonon mobility edge, heat is transferred by the «diffusive» modes migrating randomly from site to site. The phonon mobility edge ω_0 is found from the condition that the phonon mean free path determined by the umklapp processes and scattering on point defects cannot become smaller than one-half the phonon wavelength. The Bridgman coefficient $g = -(\partial \ln \Lambda/\partial \ln V)_T$ is the weighted mean over these modes, which differ strongly in their volume dependence. It is shown that the amount of heat transferred by the «diffusive» modes is quite large above 100 K even in pure Kr and it increases with rising temperature and impurity concentration.

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