Heat transport in methane-palladium nanocomposites

R.V. Nikonkov, P. Stachowiak, and A. Jeżowski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences
PN 1410, Wroclaw 50-950, Poland
E-mail: R.Nikonkov@intibs.pl

The thermal conductivity of crystalline methane samples with spherical palladium nanoparticles of diameter 6, 8, 10, 12, 18 and 24 nm embedded in the CH_4 structure was determined in the temperature range 2–35 K. The spherical nanoparticles featured a low dispersion of the sphere diameter and the volume fraction of the nanoparticles in the nanocomposites amounted to 0.15. Time relaxation approximation analysis shows that the matrix resistive phonon scattering processes are dominated by diffuse scattering of phonons by matrix-nanoparticle boundaries. Other considered intensities of resistive scattering mechanisms of phonons, i.e., scattering by point defects, by dislocation strain fields and by phonons in *U*-processes remain almost the same in nanocomposites and pure methane crystal. In transfer of the heat through the investigated nanocomposites non-resistive scattering of phonons by the nanoparticles, such as phonon specular scattering and multiple scattering of phonons show very high intensity. The nanocomposites formed of 18 and 24 nm nanospheres show anomalous power increase of the thermal conductivity coefficient dependence on temperature, exceeding the values known for a typical dielectric crystal.

Keywords: methane-palladium nanocomposites, thermal conductivity, heat transport.

Introduction

Significant interest has recently been given to composites with nanoparticles due to their importance in electronics, optic and energy applications [1–3]. In such materials, small changes in the parameters of the ingredients can lead to significant changes in the overall properties. The heat transport through nanocomposites is expected to be strongly determined by the interface/surface effects. The energy carriers in composites experience different scattering processes, which ultimately determine the effective thermal conductivity of the material [4,5]. The prediction and understanding of the composite properties has been a complex subject of research since the properties of composite materials depend on several physical and chemical properties including the volume fraction, size, shape and orientation of the particles as well as the interfacial characteristics between the particles and matrix [6].

In turn, studies of methane and methane-based composites were triggered by the growing interest in using solid methane as a moderator for pulsed cold neutron sources, because from a neutronic point of view, this is the best moderator material known so far [7].

Methane is one of the most abundant hydrocarbon compounds known. Methane molecule can be depicted as a regular tetrahedron with hydrogen atoms at the vertex positions and carbon atom in the center [8]. Solid methane under equilibrium vapour pressure can exists in two crystalline modifications. In both modifications, the low-temperature phase II and high-temperature phase I, carbon atoms form an FCC lattice (space group *Fm*3*m* [9]). It is commonly supposed that in low-temperature phase hydrogen atoms are ordered in the lattice and can perform certain librational oscillations about the center of inertia of methane molecule and also reorientational hopping from one equilibrium position to another. In phase I, hydrogen atoms entirely lose the ordering and make "almost free spherical rotation" relatively to a mass center of carbon atom. The volume jump at the phase transition is about 0.3% [9].

In the current paper, we present our preliminary thermal conductivity experimental results obtained for methane-based nanocomposite. The investigated nanocomposites were obtained from solid methane with spherical palladium nanoparticles embedded in the crystal structure.

Experimental

In this work, the experimental results of thermal conductivity measurements were determined by steady-state heat flow method in temperature range 2–35 K. The methodology of the measurements and its technical aspects have been described in details in our previous paper [10].

The samples were grown and their thermal conductivity was measured in a glass chamber (with the inner diameter of 6 mm, the length of 50 mm) of the specially designed helium cryostat [11]. On the top and the bottom of chamber, the copper cups were glued. A gradient heater was attached to the top copper cover. Through that cover a thin-walled stainless steel capillary ran. The capillary allowed to pump out the cell and fill it with a gas. During the experiment, the bottom cap was fixed in a copper base of controlled temperature. Temperature and temperature gradient along the sample were measured by germanium resistance thermometers.

For obtaining the nanocomposite samples, methane gas of 99.9995% purity and palladium spherical nanoparticles of linear dimension 6, 8, 10, 12, 18 and 24 nm were used. Palladium nanoparticles were synthesized in the Institute for Low Temperatures and Structure Research PAS, Wrocław, Poland by solvothermal method. The size of the particles was determined by TEM microscopy methods. Standard deviation of the nanoparticle diameter did not exceed 3%.

At the very first stage in preparing the experiment, the glass ampoule was filled up with the nanopowder (in the gravity field, without any additional pressing) to its top. The nanoparticle volume fraction in the investigated samples (the ratio of the volume taken by the nanoparticle to the volume of the sample) was in the range 14.5–15%. The volume fraction was determined by the precise weighting of the nanopowder filling the known volume of the ampoule.

Before the beginning the process of obtaining nanocomposite sample, the ampoule with powder placed in it was thoroughly pumped out at room temperature. Then the temperature of the ampoule was lowered to a little bit above the triple point temperature of methane and the gas was let to the ampoule where the condensation to its liquid phase began. During the condensation, the temperature of the upper part of the ampoule is maintained 7 K above the temperature of the bottom so that the liquid gradually filled the ampoule from its bottom to the top. In this way one obtained a liquefied matrix gas with nanopowder immersed in it. Finally, the temperature of ampoule was lowered (while maintaining a constant temperature gradient), therefore the liquid passed to the solid phase, forming a crystal with nanoparticles embedded in its volume. After the crystallization, the sample was cooled down to the temperature of the thermal conductivity measurements.

During the whole process obtaining of the sample, i.e., during the condensation of the gas, the solidification of the liquid and the cooling down, the sample was inspected visually. A good quality sample, showing reproducible measurement results after re-growing, featured a uniform dark opacity without any areas of different optical density seen in the passing-through light.

The random error of the thermal conductivity measurement in low temperatures did not exceed 1.5%, whereas above 20 K it increased to 3%, mostly due to effects connected with spurious heat leaks. The systematic error did not exceed 3%.

Results and discussion

Results of the measurements of dependence of thermal conductivity coefficient κ of the investigated nanocomposites on temperature T were shown in Fig. 1. In the figure, the data for the temperature dependence of the thermal conductivity of pure methane crystal was also depicted [12]. As it is easy to see from Fig. 1, the methane–Pd nanospheres composite feature lower thermal conductivity than that of pure methane. Most of the nanocomposites show dielectric crystal-like thermal conductivity with a low-temperature increase followed by a characteristic maximum and a decay at higher temperatures. Two of the samples, those obtained from the palladium nanospheres of the biggest investigated diameters — 18 and 24 nm do not display the typical dielectric crystal thermal conductivity. Their thermal conductivity which initially increases, attains a region of weak temperature dependence and then continues to increase resembles the thermal conductivity of an amorphous solid.

The value of the thermal conductivity coefficient obtained for the samples containing nanoparticles of diameter 6, 8, 10 and 12 nm are very close to each other. For all of them in the low-temperature part of the temperature dependence the thermal conductivity coefficient increases as T^3. This is a clear change of the character of the dependence when compared to the pure methane crystal, for which the $\kappa(T)$ follows T^2 dependence. The discrepancy is caused by different phonon scattering mechanism which dominate at low temperatures in pure matrix and the nanocomposite. The dominant phonon scattering mechanism in pure methane crystal at low temperature is not
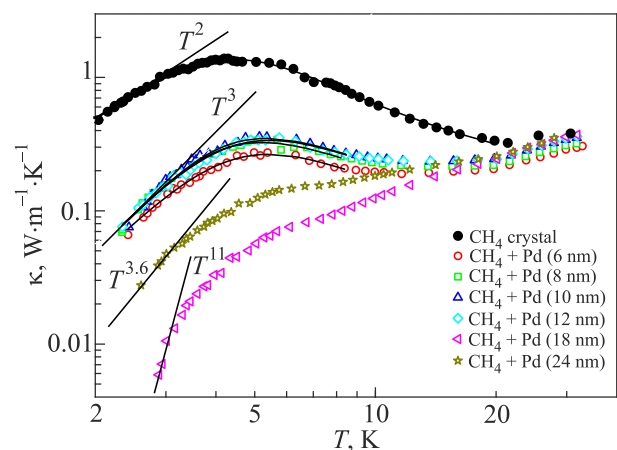

Fig. 1. Thermal conductivity κ of solid methane [12] and six nanocomposites of methane with palladium spherical nanoparticles of different diameters. Solid lines show the result of approximation of the data with Eq. (1).

clear [12] while that of the investigated nanocomposite seems to be independent of the phonon frequency. To get more information on scattering of phonons in the vicinity of the maximum of $\kappa(T)$, we fitted the Debye thermal conductivity expression, see, e.g., [13],

$$\kappa = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2}\,dx \qquad (1)$$

to the data obtained in our experiment.

In the above equation k_B and $\hbar$ are Boltzmann and Planck constants, respectively. v is phonon group velocity, averaged over velocities for two longitudinal and one transverse vibrations. For the current approximation ms^{-1} [14] was applied. θ is Debye temperature of the matrix crystal ($\theta = 144$ K) $x = \hbar\omega/k_B T$, where ω is phonon frequency and τ_c is combined phonon relaxation time

$$\tau_c^{-1}(x) = \sum_i \tau_i^{-1}(x).$$

Here τ_i is phonon relaxation time for ith phonon scattering mechanism.

In our fitting we have taken into account scattering of phonons by grain boundaries (τ_b), point defects (τ_p), dislocation strain fields (τ_d) and by other phonons in U-processes (τ_b). The used relaxation rates (reciprocal of the relaxation time) were:

$$\tau_b^{-1} = a_b,$$

$$\tau_p^{-1} = a_p x^4 T^4,$$

$$\tau_d^{-1} = a_d x T,$$

$$\tau_U^{-1} = a_{U1} x^2 T^3 \exp[-a_{2U}/T].$$

In the fitting procedure, a computer program varied parameters (a_i) of the relaxation times to get the best agreement between the Debye thermal conductivity Exp. (1) and the data obtained in the experiment. The best-fit parameters were shown in Table 1 and the results of the fitting were displayed in Fig. 1 by solid lines.

As one can see from Fig. 1, the applied model well describes the results of the experiment. The obtained values of the fitted parameters carry information regarding-contribution of each of the processes to an overall scattering of phonons. The parameters of phonon scattered by point defects, dislocation strain fields and U-processes shown in the consecutive columns in Table 1 are close to each other for the four nanocomposites and also close to those obtained for pure matrix crystal. This means that the introduction of palladium nanoparticles into the crystalline matrix does not change significantly the original density of point defects, the density of dislocations nor the dynamics of the lattice. The only exception is the parameter which describes the scattering by grain boundaries. While for all four nanocomposites the boundary scattering parameters are again close to each other, the one for pure methane crystal is by three orders of the magnitude smaller than that for the nanocomposites. Using a dependence $a_b \approx v/l$ [13], from the parameter a_b one can obtain a rough estimate of phonon free path l for the scattering by "grain boundaries". Therefore, while for pure methane crystal $l \sim 10^{-3}$ m, in the analyzed composites $l \sim 10^{-6}$ m. The shortening of the phonon free path in nanocomposites is caused by diffusive scattering of phonons by the boundaries of two media: the crystalline matrix and the material of nanoparticle (palladium). Here it should be emphasized that the obtained for the nanocomposites value $l \sim 10^{-6}$ m is very much longer than the average internanoparticle distance in the investigated samples — if one assumes a uniform distribution of the nanoparticles in a hypothetic cubic lattice, for the nanoparticle volume density of 0.15 the average distance between the nanospheres amounts to approximately two diameters of the nanoparticle. Therefore, in our samples the average distance of the neighboring palladium nanoparticles is $\sim 10^{-8}$ m. The conclusion from this estimation is that just one out of one hundred phonons incident on the nanoparticle gets scattered in a diffusive way. To understand the phenomenon of phonon scattering by the nanoparticles one additionally has to take into account specular scattering by the intermedia (the boundary of the matrix and the nanoparticle material) and also multiple phonon scattering described as follows: the matrix phonon incident on the boundary penetrates the nanoparticle, leaves it and then,

Table 1. Value of the parameters a_i, for which the experimentally obtained dependence of the thermal conductivity of the investigated nanocomposites is best approximated by Eq. (1)

	a_b	a_p	a_d	a_{U1}	a_{U2}
CH$_4$ pure crystal	$3.64\cdot10^6$	$3.32\cdot10^3$	$4.89\cdot10^7$	$1.91\cdot10^7$	$1.59\cdot10^1$
CH$_4$ + Pd (6 nm)	$3.53\cdot10^9$	$6.98\cdot10^3$	$6.29\cdot10^7$	$6.28\cdot10^7$	$1.61\cdot10^1$
CH$_4$ + Pd (8 nm)	$3.11\cdot10^9$	$2.52\cdot10^3$	$3.59\cdot10^7$	$5.18\cdot10^7$	$1.56\cdot10^1$
CH$_4$ + Pd (10 nm)	$3.84\cdot10^9$	$1.25\cdot10^3$	$3.45\cdot10^6$	$4.77\cdot10^7$	$1.58\cdot10^1$
CH$_4$ + Pd (12 nm)	$3.59\cdot10^9$	$4.29\cdot10^3$	$9.19\cdot10^5$	$4.71\cdot10^7$	$1.59\cdot10^1$

without interaction with other phonon or crystalline structure defects penetrates a neighboring one, and so on, and so on. Both of the postulated additional mechanisms can be considered non-resistive and therefore are not directly seen in the thermal conductivity data, resulting in elongation of the effective phonon free path. The latter one may potentially enhance the thermal conductivity of the nanocomposite since the thermal conductivity of palladium is higher than that of methane. However this is not the case: At the highest investigated temperatures, where the thermal conductivity is specified by the crystalline matrix U-processes, the experimental data points are close to each other, both for pure CH_4 crystal and the nanocomposites. The lack of increase of the thermal conductivity above the U-processes limit denotes that multiple phonon scattering is not particularly significant phonon dissipation mechanism in the investigated nanocomposites.

The thermal conductivity coefficient dependence on temperature for two of not-discussed-yet nanocomposites made of palladium nanospheres of diameter 18 and 24 nm unlike the remaining ones is not typical for a dielectric crystal. As was noticed above, at first glance the dependence is similar to that of amorphous solid. However, a little bit closer look shows that this is not the case. A feature common for all glassy materials is low-temperature T^2 dependence of thermal conductivity coefficient. In case of the 18 and 24 nm palladium sphere nanocomposites the thermal conductivity at low temperatures may be approximated by a power law, however, the dependence (see Fig. 1) being $\sim T^{11}$ and $T^{3.6}$ for 18 and 24 nm composites, respectively, is distinctly stronger than for glasses. This is a very intriguing finding. On one hand, the nanocomposites feature the lowest investigated thermal conductivity while on the other they show low-temperature increase indicating an enhancing thermal transport phonon scattering mechanism. The way the hypothetic mechanism works is easy to see in a plot showing the dependence of phonon mean free path l_m on temperature, displayed in Fig. 2. The dependence was obtained from thermal conductivity data by use of the following equation, see, e.g., [15],

$$l_m = \frac{3\kappa}{Cv}$$

where C is the specific heat of a unit of volume of the investigated sample. For the calculations, the specific heat of methane crystal obtained from the Deby'e model were utilized. The unusual behavior is best seen for the 18 nm Pd sphere sample where the phonon mean free path initially increases, then attains at ~ 4 K a maximum followed by a typical for a dielectric crystal decrease. The low-temperature increase leading to the formation of the maximum resembles, to some extent, an effect caused by the Poiseuille flow of phonons [13]. This finding requires further investigations.
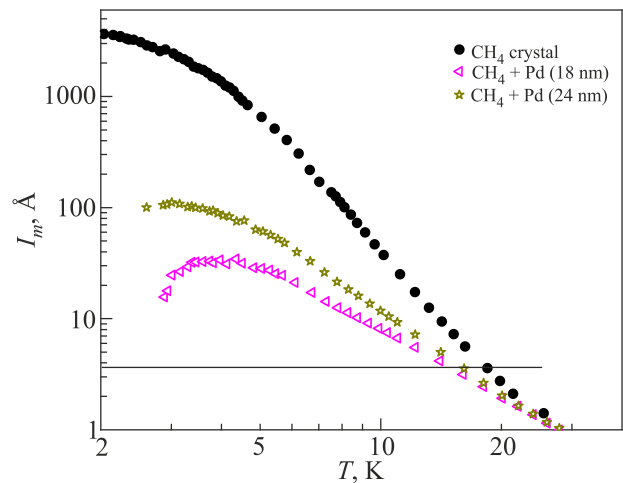

Fig. 2. Phonon mean free path l_m in methane crystal and CH_4–Pd nanocomposites containing palladium nanospheres of diameter 18 and 24 nm. The horizontal line shows the average internanosphere distance in 18 nm composite.

Summary

The thermal conductivity of six crystalline methane samples with embedded spherical palladium nanoparticles of different diameters was determined in the temperature range 2–35 K. Four of the investigated nanocomposites display a typical dielectric crystal temperature dependence of the thermal conductivity while the remaining two show an unusual low-temperature behavior. In the typical dielectric crystal nanocopmosites, the low-temperature thermal resistivity is dominated by diffusive scattering of phonons by the matrix-nanoparticle boundaries. However, the efficiency of this mechanism is low. In the complete picture of matrix phonon interaction with the nanoparticles one also needs to consider non-resistive interactions such as specular and multiple phonon scatterings.

1. R.G. Yang and G. Chen, *Phys. Rev. B* **69**, 10 (2004).
2. Y. Ma, R. Heijl, and A.E.C. Palmqvist, *J. Mater. Sci.* **48**, 2767 (2013).
3. M.L. Lee and R. Venkatasubramanian, *Appl. Phys. Lett.* **92**, 5, 053112 (2008).
4. P.M. Saulnier, M.P. Zinkin, and G.H. Watson, *Phys. Rev. B* **42**, 2621 (1990).
5. R. Prasher, *ASME J. Heat Transfer.* **128**, 627 (2006).
6. G.W. Milton, *The Theory of Composites*, Cambridge University Press, Cambridge, New York (2002).
7. O. Kirichek, A.J. Church, M.G. Thomas, D. Cowdery, and S.D. Higgins, *Cryogenics* **52**, 9, 325 (2012).
8. G. Hertzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, Krieger, Malabar (1991).
9. V.G. Manzhelii, A.I. Prokhvatilov, V.G. Gavrilko, and A.P. Isakina, *Structure and Thermodynamic Properties of*

Cryocrystals, Begel House, Ink., New York, Wallingfort, U.K. (1998).

10. R.V. Nikonkov, P. Stachowiak, A. Jezowski, and A.I. Krivchikov, *Int. J. Heat Mass Transfer.* **112**, 913 (2017).

11. A. Jeżowski and P. Stachowiak, *Cryogenics* **32**, 601 (1992).

12. P. Stachowiak, E. Pisarska, A. Jeżowski, and A.I. Krivchikov, *Phys. Rev. B* **73**, 134301 (2006).

13. R. Berman, *Thermal Conduction in Solids*, Clarendon, Oxford (1976).

14. L.M. Tarasenko, *Fiz. Nizk. Temp*. **1**, 1434 (1975) [*Low Temp. Phys.* **1**, 688 (1975)].

15. C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons Inc., New York (1966).

Тепловий транспорт у метан-паладієвих нанокомпозитах

Р.В. Никонков, P. Stachowiak, A. Jeżowski

В інтервалі температур 2–35 K виміряно теплопровідність зразків кристалічного метану зі сферичними наночастинками паладію діаметром 6, 8, 10, 12, 18 та 24 нм, вбудованими в структуру CH$_4$. Сферичні наночастинки мали низьку дисперсію діаметра сфери, а об'ємна частка наночастинок у нанокомпозитах складала 0,15. Аналіз апроксимації часу релаксації показує, що у процесах резистивного розсіяння фононів переважає дифузне розсіяння фононів на границях матриця–наночастинка. Для інших механізмів резистивного розсіяння фононів, тобто розсіяння на точкових дефектах, полях дислокаційних деформацій та фононах в *U*-процесах, розглянуті інтенсивності лишаються практично однаковими в нанокомпозитах та кристалі чистого метану. При передачі тепла через нанокомпозити, які досліджено, нерезистивне розсіяння фононів на наночастинках, а також фононне дзеркальне розсіяння фононів демонструють дуже високу інтенсивність. У нанокомпозитів, які сформовані з наносфер розміром 18 та 24 нм, спостерігається аномальне зростання залежності коефіцієнта теплопровідності від температури, що перевищує значення, які відомі для типового діелектричного кристала.

Ключові слова: метан-паладієві нанокомпозити, теплопровідність, тепловий транспорт.

Тепловой транспорт в метан-палладиевых нанокомпозитах

Р.В. Никонков, P. Stachowiak, A. Jeżowski

В интервале температур 2–35 K определена теплопроводность образцов кристаллического метана со сферическими наночастицами палладия диаметром 6, 8, 10, 12, 18 и 24 нм, встроенными в структуру CH$_4$. Сферические наночастицы имели низкую дисперсию диаметра сферы, а объемная доля наночастиц в нанокомпозитах составляла 0,15. Анализ аппроксимации времени релаксации показывает, что в процессах резистивного рассеяния фононов преобладает диффузное рассеяние фононов на границах матрица–наночастица. Для других механизмов резистивного рассеяния фононов, т.е. рассеяния на точечных дефектах, полях дислокационных деформаций и фононах в *U*-процессах, рассматриваемые интенсивности остаются практически одинаковыми в нанокомпозитах и кристалле чистого метана. При передаче тепла через исследуемые нанокомпозиты нерезистивное рассеяние фононов на наночастицах, а также фононное зеркальное и многократное рассеяние фононов демонстрируют очень высокую интенсивность. У нанокомпозитов, сформированных из наносфер размером 18 и 24 нм, наблюдается аномальное возрастание зависимости коэффициента теплопроводности от температуры, превышающее значения, известные для типичного диэлектрического кристалла.

Ключевые слова: метан-палладиевые нанокомпозиты, теплопроводность, тепловой транспорт.