The influence of silica nano-inclusions on the structure of methane crystal observed in thermal conductivity experiment

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ARTICLE INFO

ABSTRACT

The preliminary results of experimental investigations of the thermal conductivity of nanocomposites built of amorphous silica nanoparticles embedded in the structure of crystalline methane are presented. The investigations were carried out on the samples containing the particles of linear dimensions of 5, 10–20 and 42 nm. The measurements were performed with steady-state heat flow method in the temperature interval 2–35 K.

A very simple thermal conductivity model shows that the dependence of the thermal conductivity coefficient of the investigated nanocomposites on temperature can be successfully described by taking into account only two mechanisms of the heat carrier dissipation: scattering of phonons by methane crystal grain boundaries and phonon-phonon interaction in U-processes. It was found that the low-temperature phonon mean free path is inversely proportional to the linear dimension of the nanopowder particles embedded in the methane crystal structure.

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1. Introduction

Due to unique physical properties, the nanosized and nanostructured objects have become the focus of researchers attention relatively long time ago, see e.g. Refs. [1,2] and references therein. On the wave of the attention, a tremendous increase of interest into thermal properties of nanocomposite crystalline materials consisted of nanoinclusions embedded in crystalline matrix structure has been observed over the recent decade. The reason for the interest is twofold: 1. Application-motivated, caused by a potential of usage of the materials in a technology, and 2. purely investigative, aiming to understand and explain thermal excitation and heat transfer phenomena in the materials of this kind. The former is obvious: The unique physical properties of the nanostructured materials allow to design new devices. In some of them a significant amount of heat may be locally generated during their normal work and therefore – depending on the work regime – the heat diffusivity (or the thermal conductivity) becomes a crucial process for appropriate dissipation of the excess heat. In some others, maintaining a significant temperature gradient in a device is a basic issue, therefore, again, the knowledge of the thermal conductivity coefficient of the material is necessary. As an example of the

application-motivated interest towards thermal properties of the nanocomposites one can give the investigations of thermoelectric material candidate such as SiC nanoparticles embedded in ZnSb crystal structure [3]. For the same reason the nanocomposites consisted of Au nanodot/Bi_2Te_3 nanotube in the Bi_2Te_3 matrix were investigated towards their thermoelectric performance (the figure of merit) [4] and in Ref. [5] the thermal conductivity of composites of tungsten-coated diamond particles bound with copper or silver was analyzed.

Understanding and successful describing of the thermal excitation and thermal transport phenomena in such nanostructured materials has not only the cognitive importance, a fundamental thing for the basic science, but also provides a good rudiments to design the functional materials featuring optimal thermal properties. Therefore the phenomena are being recently intense studied, both experimentally and theoretically. For example, for better understanding of the physics of thermal excitations, thermal conductivity and specific heat of nanosize disks of Laponite in water ice were measured and analyzed [6]. In Ref. [7] the effect of embedding Ge nanoparticles as extrinsic phonon scattering centers on the lattice thermal conductivity of bulk semiconductor $Si_{0.7}Ge_{0.3}$ alloy crystals was investigated. Theoretical investigation of the dependence of the thermal conductivity of nanocomposites on the shape and size of particle inclusions in a crystal matrix was also carried out [8]. Another example is theoretical investigation of nanocom-

posites regarding both size and dimensionality dependent phonon conductivity of PbTe-PbSe nanocomposites by considering three configurations: superlattice, embedded nanowire and embedded nanodot [9]. Also, theoretical studies of more complex problems such as the strain effects on the lattice thermal conductivity of low-dimensional silicon and carbon materials: silicon nanowires (one dimensional) and thin-films (two dimensional), single-walled carbon nanotube (SWCNT, one dimensional) and single-layer graphene sheet (two dimensional) were conducted [10]. It also should be mentioned here the works which do not concentrate on any particular nanocomposite system but are devoted to general understanding of physics of phonons in the nanocomposites [11–14].

In the current paper we present our preliminary thermal conductivity experimental results obtained for a model crystalline nanocomposite. The matrix for investigated nanocomposites was solid methane. In the crystalline matrix of methane the amorphous silica nanoparticles (at relatively high volume density of the nanopowder) were embedded. The experiment was carried out on a number of samples containing nanoparticles of different mean linear dimensions and different dispersion of the dimensions. The choice of the nanocoposite constituents was dictated by relative simplicity both of the methane matrix and the SiO_2 nanopowders. It also should be emphasized that solid methane belongs to one of best known dielectric crystals.

A molecule of methane can be pictured as a regular tetrahedron with hydrogen atoms at the vertex positions and carbon atom in the center. Such a symmetry causes the molecule to exhibit permanent octupolar electrostatic moment, which is essential for the crystal structure at low temperatures. At the equilibrium vapor pressure, methane (CH_4) solidifies at 90.66 K and shows unchanged crystallographic structure, called phase I, down to 20.4 K which is the temperature of phase transition to phase II. In both phases, the carbon atoms of the methane molecule occupy sites of the face-centered cubic lattice [15].

In phase I all the tetrahedral molecules are orientationally disordered, performing rotations which do not show any long-range correlation. In the low-temperature phase II, the orientation-dependent octupole-octupole interaction leads to a partial orientational ordering. The structure of methane crystal with six orientationally ordered and two disordered sublattices belongs to the space group *Fm3c*. In this phase the orientationally ordered molecules perform collective librations, while those at disordered positions rotate almost freely down to the lowest temperatures. Anharmonic effects in the libration motions play a major role in the behavior of the thermal conductivity of methane crystal [16,17].

2. Experimental

Thermal conductivity of methane-based nanocomposite samples was measured in the temperature range from 2 K to 35 K by the steady-state heat flow technique. Growth of the samples and determination of their thermal conductivity coefficient took place in the measuring chamber of a home designed and made helium cryostat [18]. The central part of the measuring chamber of the cryostat was a glass ampoule the diagram of which was shown in Fig. 1. Both ends of a glass tube of an inner diameter of 6 mm, a wall thickness of 1 mm and a length of 60 mm were closed with copper caps and vacuum tightened with a low-temperature epoxy. The bottom of the ampoule was fixed to a block of controlled temperature. The top cap of the cell was equipped with a stainless steel capillary which was used to admit a matrix gas to the ampoule from the outside of the cryostat. The bottom-top differential thermocouple and electric heater wound on the top cap were used to
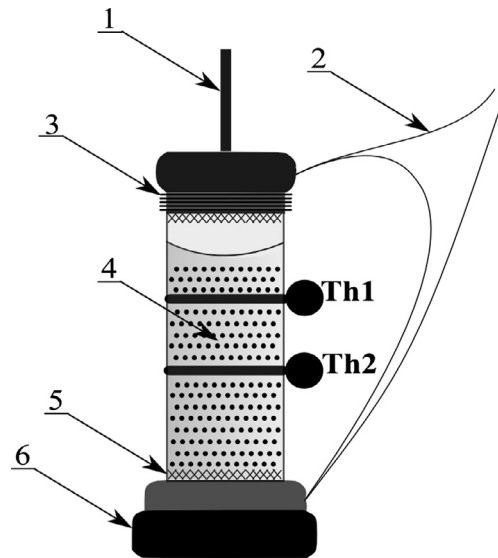

Fig. 1. The experimental cell diagram. 1 – stainless steel capillary admitting the matrix gas into the ampoule, 2 – differential thermocouple, 3 – copper top cap of the ampoule along with electrical heater, 4 – glass tube, 5 – epoxy binding and sealing the copper and glass parts of the cell, 6 – copper bottom cap of the ampoule, Th1 and Th2 – germanium resistance thermometers.

control the temperature of the upper part of the ampoule during the sample growth and thermal processing. The same heater – along with two germanium thermometers attached to the wall of the ampoule – were utilized for realization of the steady-state heat flow thermal conductivity measurement method. For details of the technique of the thermal conductivity measurement see e.g. Ref. [19].

To obtain the nanocomposite sample, at the very beginning, after fixing the bottom cap to the glass tube, the powder of amorphous silicon dioxide of well-defined size of particles (grains) was placed into the experimental cell. The glass ampoule was filled up with the powder (in the gravity field, without any additional pressing) to its top and then the top cap was fixed with an epoxy. The nanopowders of an average linear dimension of 5 nm, 10–20 nm and 42 nm were used for separate samples. The sizes of the particles were earlier determined by BET method, and confirmed by TEM microscopy. The surface area of the powders was 533.6, 143.2 and 64.1 m^2/g for 5 nm, 10–20 nm and 42 nm nanoparticles, respectively. The average volume fraction of silica in the chamber was 6.5% in each case – it did not depend on the dimension of the powder particles. The volume fraction was determined by precise weighting of the powder filling the volume of the ampoule. At the volume fraction amounting to 6.5% the average distance between the nanoparticles $a \approx 2d$, where d is an average diameter of the particle. The low-dispersion powders of 5 nm and 42 nm (a standard deviation of linear dimensions of the particles did not exceeded 5% of their mean value) were obtained in the Institute for Low Temperatures and Structure Research, PAS, Wrocław while the high dispersion one, 10–20 nm, was purchased from Sigma-Aldrich Ltd.

Before growing of the nanocomposite sample, for each of nanopowders a "blanc" measurement was carried out: after pumping out, the cell was cooled down to the liquid helium temperature and after admitting some heat exchanging gaseous helium, the dependence of thermal conductivity coefficient of the powder itself on temperature was determined.

Obtaining of the nanocomposite sample was preceded by thorough pumping out of the ampoule at room temperature. Then the temperature of the ampule was lowered to a little bit above the