Solid State Communications 197 (2014) 6–10

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Dissipation of phonons by subsystem of disordered molecules – Case of thermal conductivity of carbon monoxide crystal

Tetiana Romanova*, Piotr Stachowiak, Andrzej Jeżowski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

ARTICLE INFO

Article history:
Received 13 June 2014
Received in revised form
24 July 2014
Accepted 25 July 2014
by Merlin
Available online 2 August 2014

Keywords:
A. Carbon monoxide crystal
A. Molecular crystals
D. Dipolar disorder
D. Phonon scattering

ABSTRACT

Order or disorder in subsystem of dipolar constituents of a solid often significantly influences its physical properties. The results of investigation of the effect of glassy state in subsystem of carbon monoxide molecules on thermal conductivity of CO crystal in its equilibrium vapor pressure are reported. The thermal conductivity of a high quality carbon monoxide crystal was specified over the temperature range 1.2–45 K. The results of these measurements were analyzed within the frame of relaxation time approximation. It was shown that at low temperatures phonon scattering by subsystem of disordered CO molecules is the most significant dissipative mechanism of heat transfer in the investigated crystal.

1. Introduction

Some molecules possess a non-vanishing permanent electrostatic dipole moment. Although the non-zero permanent moment is rather typical feature of complex molecules of low symmetry, simple 2–4 atom molecules showing a non-zero electric dipole moment are known as well. In the condensed phase, the dipolar molecules – depending on mutual interactions and/or external conditions – may remain disordered or some kind of dipole ordering appears. The problem of dipole ordering/disordering in ferroelectric materials is essential for ferroelectric phase transition phenomenon [1]. Also properties of multiferroics – both bulk [2] and thin films [3] – are closely related to dipole ordering of molecules. Recently, the effect of dipolar ordering on thermal properties of the filled skutterudite $SmRu_4P_{12}$ was also discovered [4]. It turns out that ordering and disordering of molecular dipoles is also essential for understanding properties and processes observed in organic materials. The degree of static dipolar disorder in a polymer dielectric significantly influences the electronic density of states in adjacent organic semiconductor in organic–organic hetero-interfaces [5]. The disorder of dipolar molecules specifies charge carrier transport in organic materials [6]. The problem is also important for functions of biological membranes [7,8] and amyloid fibrils [9]. In some new functional materials, the molecular dipole ordering specifies unique properties of the materials making them appropriate for a particular use. The dipole–dipole ordering plays a crucial role in plasmonic gold nanoparticle chain networks [10]. Dipolar ordering influences the optical and electrical performance of the organic light-emitting diodes [11]. The effects related to the dipolar ordering are also of great importance for application of new materials in cooling techniques [12]. The list of examples given above is by no means exhaustive. In general, the molecular order or disorder conditions specify many observed properties of a matter. While in case of some of the properties being the result of enhancement of a local electric field due to the dipolar order, the particular properties of others are a consequence of disordering of the dipole molecules in a space-ordered structure and, therefore, a glassy state in the orientational subsystem of the crystal. In the present paper we attempt to show how such a dipolar disorder influences the thermal conductivity of carbon monoxide crystal.

The molecule of carbon monoxide (CO) is an example of the above mentioned simple diatomic system possessing a non-zero permanent electrostatic dipole moment which amounts to 3.7356×10^{-31} C m [13]. At low temperatures carbon monoxide forms a crystalline solid. In the temperature range 61.57–68.09 K the CO crystal shows a structure in which the linear molecules process over their mass centers located in an *hcp* lattice node. This is the so called β-phase of the crystal. At 61.57 K the crystal undergoes a structural phase transition: below that temperature it exists in orientationally-ordered *fcc* structure, known as the α-phase. The axes of the molecules are oriented along space diagonals of the elementary cubic cell. Due to the dipolar character of CO molecule, the molecules are displaced a little from the regular lattice positions. The symmetry of this structure belongs to the space group $P2_13$ [14]. Despite numerous theoretical propositions [14], the existence of a low-temperature phase of long-range

* Corresponding author. Tel.: +48 71 39 54 311.
E-mail address: t.romanova@int.pan.wroc.pl (T. Romanova).

http://dx.doi.org/10.1016/j.ssc.2014.07.020
0038-1098/

ordering of carbon monoxide dipoles in the α-phase was not confirmed. To the contrary, almost all experiments carried out so far have indicated disordering of the molecules down to temperatures below 1 K. Such a glassy state in the dipole subsystem of orientationally ordered phase of the CO crystal is supposed to be seen also in the thermal conductivity of the crystal. The low-temperature thermal conductivity of carbon monoxide crystal was measured before [15]; however the investigated crystals were of poor quality and the results of the measurements were dominated by phonon scattering by the crystal structure imperfections, which made impossible to see clearly other effects (such as, e.g., the influence of dipolar disorder on the thermal conductivity).

2. Experimental

In the reported experiment here, the measurements were performed over the temperature range 1.2–45 K with the steady-state heat flow method. The samples were grown and measured in a thin-wall stainless steel ampoule placed in the LHe cryostat described in Ref. [16]. It should be emphasized that particular care was taken to obtain a crystal of the highest possible quality.

The crystal specimens were obtained directly from gaseous phase. The temperature and pressure of condensation were slightly below the triple-point values of carbon monoxide, and were maintained constant during the whole crystal growth procedure. Following appropriate choice of temperature gradient along the ampoule and the rate of lowering of temperature of the bottom of the ampoule, the crystal gradually (at a constant rate of approximately 1 mm/h) filled the ampoule from its bottom to the top. Afterwards, the crystal was annealed for 12 h at the growth temperature. Next, the sample was carefully cooled down: initially, in the vicinity of 61 K (the temperature of $\alpha \rightarrow \beta$ phase transition) at the rate of 0.1 K/h, and then down to the temperature 45 K at the rate of 0.2 K/h. The measurements started after admitting to the ampoule heat-exchanging gaseous He^4 at a pressure of about 1 kPa. In order to be able to take into account the part of heat transferred by the wall of the ampoule, the thermal conductivity coefficient dependence on temperature of the stainless steel was specified in a separate measurement. The CO gas used in the experiment had natural isotope composition and chemical purity of 99.999%.

The random and systematic errors of the thermal conductivity determination did not exceed 3% in the whole investigated temperature range.

3. Results and discussion

At low temperatures, the transport of heat in simple dielectric crystals is realized exclusively by collective translational vibrations of its constituents, atoms or molecules, the quanta of which are Bose particles called acoustic phonons. The phonons carrying thermal energy interact with each other and with the imperfections of the crystallographic lattice. These interactions specify the dependence of the thermal conductivity coefficient κ of a crystal on temperature T. In the simplest case, at the lowest temperatures, the scattering of phonons is dominated by the scatterings by the crystal (or its grains) boundaries. This interaction results in a $\kappa \sim T^3$ dependence. In the intermediate temperatures, the phonon scattering processes are dominated by highly-resistive three-phonon U-processes which produce characteristic exponential decay of the thermal conductivity with increasing temperature, resulting in formation of a maximum of the thermal conductivity. At higher temperatures, the exponential dependence gradually becomes weaker and finally attains the dependence $\kappa \sim T^{-1}$. Crystal structure defects and, therefore, presence of additional to the mentioned above phonon scattering mechanisms change this simple picture. Influence of crystal structure imperfections such as dislocations or point defects on thermal conductivity is particularly well seen in the lowest temperature region, in the vicinity of the thermal conductivity maximum [17]. The examples of the dependence of the thermal conductivity coefficient on temperature are depicted in the inset in Fig. 1. In the main field of the figure, the results of reported thermal conductivity experiment carried out on pure carbon monoxide crystal are shown. Besides our current measurement results, the data published earlier [15] have also been shown.

At the upper limit of the investigated temperature range, our current data agree very well with the previously obtained ones. At these temperatures, thermal conductivity of an undoped dielectric crystal is specified by three-phonon U-processes and hardly depends on the crystal structure imperfections. Therefore, the consistency of the data at high temperatures testifies to overall correctness of the measurements. At the same time, the significantly higher thermal conductivity of the investigated crystal shows that the current procedure of growth and thermal treatment of the sample allowed us to obtain a crystal of much better quality than the previous ones. The low concentration of the crystal structure imperfections diminishes the phonon–imperfection interaction occurrence and, therefore, facilitates more convenient observing the effects of other phonon-scattering mechanisms on the investigated thermal conductivity. One can clearly see that this low concentration of structure defects results not only in high value of the thermal conductivity coefficient, but also unveils a new character of $\kappa(T)$ dependence. Notice that the shape of the maximum is different from that of other simple molecular crystals such as solid oxygen [18], nitrogen [19] or carbon dioxide [20], and other dielectric crystals such as neon [21] or glycerol [22], see inset in Fig. 1.

The maximum of $\kappa(T)$ dependence newly obtained is rounded, relatively wide, stretched over the temperature range of a few Kelvins and does not show any clear power increase in the region of the lowest investigated temperatures. We assumed that the untypical shape of the maximum is a result of some additional (when compared to other simple crystals) mechanism of scattering of phonons – the scattering by disordered dipoles of carbon monoxide molecules.

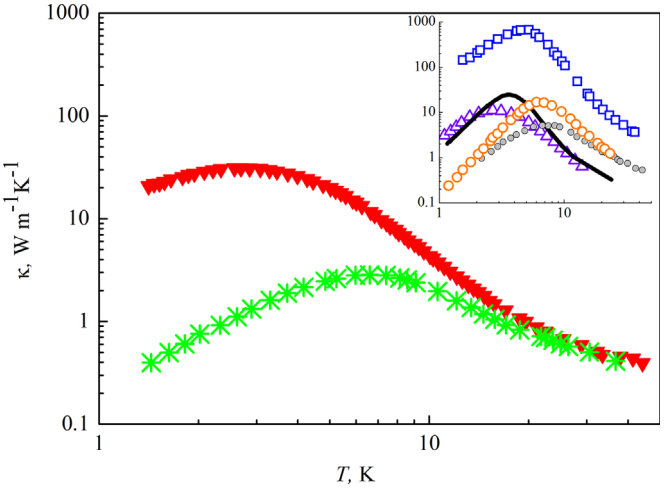

Fig. 1. (Color online) Dependency of the thermal conductivity coefficient of crystals on temperature. In the main graph data for solid carbon monoxide: close triangles – current measurements; stars – previous results [15]. In the inset, the crystals of: solid line – nitrogen [19], open triangles – neon [21], close circles – glycerol [22], open squares – carbon dioxide [20], open circles – oxygen [18].