EXPERIMENTAL SETUP FOR MEASURING THE ISOBARIC THERMAL CONDUCTIVITY OF MOLECULAR CRYSTALS

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The paper describes an experimental setup for the measurement of the isobaric thermal conductivity of molecular crystals in the temperature range from 80 K to 300 K. A scheme of the developed experimental setup for measuring the thermal conductivity by the linear-flow steady-state method under saturated vapor pressures has been presented. A modified heat potentiometer method with one thermometer was used, which allowed us to minimize the error in the estimation of the thermal conductivity due to the uncontrollable heat flows and different calibration of thermometers. The noncontrollable heat flows from thermal radiation were reduced considerably with a radiation shield on which the temperature field of the measuring cell was reproduced using a set of thermocouples and precision heat controllers. The total systematic error in the measurement of the thermal conductivity does not exceed 5%.

Key words: isobaric thermal conductivity, experimental setup, molecular crystals.

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I. INTRODUCTION

One of the most urgent and, at the same time, most difficult tasks in condensed matter physics is the problem of the study of energy transfer processes [1]. The transfer processes in molecular crystals associated with such a kinetic phenomenon as thermal conductivity \( \Lambda \) are of considerable interest to researchers. The thermal conductivity data provide important information on the dynamics of the crystalline lattice. There are a number of mechanisms responsible for thermal conductivity of molecular crystals, and a number of processes that limit the effectiveness of each of the mechanisms [1]. The thermal conductivity of molecular crystals is determined by the following factors: phonon–phonon interactions, phonon scattering by rotational excitations of the orientational subsystem, approaches the thermal conductivity to its lower limit \( \Lambda_{\text{min}} \), and the thermal expansion [2–5].

At temperatures close to or above the Debye temperature \( (T \geq \Theta_{D}) \), the general regularities of heat transfer in molecular crystals can be formulated as follows:

\[
\Lambda_{\text{min}} = \left( \frac{T}{6} \right)^{1/3} k_B n^{2/3} \sum_{i} v_i \left\{ \left( \frac{T}{\Theta_i} \right)^2 \int_{0}^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} \, dx \right\},
\]

(1)

The summation is over three (one longitudinal and two transverse) sound modes with the sound velocities \( v_i \); \( \Theta_i \) is the Debye temperature for each polarisation in Kelvin, \( \Theta_i = v_i (\hbar/k_B) (6\pi^2 n)^{1/3} \), \( n \) is the number of molecules per unit volume, and \( k_B \) is Boltzmann’s constant.

In molecular crystals with a relatively weak central interaction, the changeover from libration to a weakly hindered rotation is observed with an increase in tem-
temperature. With the temperature increasing, the rotational motion can in principle pass through the following stages: a growth of the libration amplitudes, the appearance of jump-like reorientations of the molecules, an increase in the frequency of the reorientations, a hindered rotation of the molecules and, finally, a nearly free rotation of the molecules [1,8]. In this case, the transition of the molecules from low-amplitude librations to a weakly hindered rotation is accompanied by a decrease in the translational–orientational component of the thermal resistance, and the general thermal conductivity can increase with an increase in the temperature [9,10]. The translation-rotation coupling also leads to a softening of elastic constants and affects phonon spectra.

Another characteristic feature of molecular crystals is a strong dependence of their thermal conductivity on the temperature and, as a consequence, a considerable discrepancy between the isochoric and isobaric data measured at high temperatures \( T \gtrsim \Theta_D \). Unlike crystals with a strong bonding, the density of molecular crystals can change by 10–20\% in the range of existence of the solid phase. The thermal expansion is accompanied by the softening of vibrational modes and a decrease in the potential barrier hindering free rotation of molecules.

It should be noted that at present, there is no generally accepted theory that would adequately describe the experimental thermal conductivity of molecular crystals in the high temperature region. Essentially all of the basic concepts of heat transfer were created mainly on the basis of the studies of the simplest crystalline structure atomic crystals, and features typical for molecular crystals were not taken into account in them [1,10]. Therefore, the initial problem, as always, consists in accumulating reliable experimental data over a wide range of temperatures for molecular crystals with different symmetries. The accumulation of experimental data, of course, contributes to the development of theoretical ideas about the processes of heat transfer. Moreover, it is extremely important not only to expand the list of the studied crystals and the temperature range of the study, but also to increase the accuracy of the measurements of the thermal conductivity coefficient using modern experimental techniques. In such studies, it is possible to identify new features in the behavior of thermal conductivity, which can be a convincing argument in favor of the use of one or another theoretical model. The purpose of this paper was to describe the specific peculiarities of the developed experimental setup, which allows isobaric thermal conductivity measurements of molecular crystals by the linear-flow steady-state method in the temperature range from 80 K to 300 K.

II. SETUP FOR MEASURING THE ISOBARIC THERMAL CONDUCTIVITY OF MOLECULAR CRYSTALS

The study of the thermal conductivity of molecular crystals was carried out by various methods in a wide temperature range. At low temperatures, there is no signif-
at the initial stage of the evacuation of the system. In order to minimize heat losses due to thermal radiation, a radiation screen is used in the design of the measuring cell (Fig. 2). Reducing heat fluxes through contact connections with external devices is achieved by making connections from conductors of small diameters, as well as ensuring their direct thermal contact with a constant temperature surface (in this setup 80 K) and a large heat capacity. In order to minimize the effect of uncontrolled heat flows, measurements are carried out using the modified thermal potentiometer method [1] with the use of one thermometer, which also made it possible to avoid additional errors in the measured values of the thermal conductivity due to different calibrations of thermometers.

The measuring instrumentation unit of the setup consists of a potentiometer R-348 (accuracy class 0.002) and a digital voltmeter (DV). The potentiometer R-348 is used to measure voltage drops on germanium resistance thermometers and exemplary resistances with an accuracy of 10^{-4} V. A commutator is used in the circuit to switch potential channels that are fed to the input of R-348. In order to obtain information about the temperature of thermometers, an electric current circuit of the thermometers (Fig. 1) is used, which includes exemplary resistance \( R_{\text{ex}1} \), a voltmeter and a stabilized power source. The power supplied to the ampoule heater to create a controlled heat flow along the sample is measured out using an electric current circuit of the heater (Fig. 1). The circle consists of a heater, exemplary resistance \( R_{\text{ex}2} \), a voltmeter and a stabilized power source.

### III. MEASURING CELL

The peculiarities of the measurements of the high-temperature isobaric thermal conductivity of molecular crystals determined the specific design of the measuring cell. In this case, the term isobaric should be understood as the pressure of the intrinsic saturated vapor (the effect of saturation vapor on the thermal conductivity of crystals is not significant, see Section IV). The schematic diagram of the measuring cell is shown in Fig. 2. Measuring ampoule /9/, in which samples were grown, is made of thin-walled stainless-steel tube. A copper sleeve /7/ and a copper plate /13/ are soldered to the ends of the ampoule. On the copper sleeve /7/, a manganin heater /6/ is wound, which is used to control the sample temperature. The sleeve /7/ connects the ampoule /9/ with the inlet capillary /8/ used in the sample growth process. When growing the samples, the desired temperature of the capillary /8/ was maintained with the help of a manganin heater /2/ uniformly wound along the entire length of the capillary. In order to control the temperature of the measuring ampoule on the copper plate /13/, a heater /16/ was installed.

The required vacuum in the internal volume of the measuring cell was maintained by pumping it through channel /1/, which was also used to output the contact connections and the inlet capillary /8/ of the studied substance. The measuring cell was cooled through the contact of the copper plate /13/ with the cryostat vacuum casing /3/ placed in liquid nitrogen. Placed on the surface of the copper plate, the resistance thermometer /15/ is used to monitor the process of heating and cooling of the measuring cell.

Germanium resistance thermometers /12/ are used to measure the temperature gradient. They are placed on copper rings /11/ soldered to the surface of the ampoule in its middle part. In order to avoid losses of controlled power over the surface of the heater /6/ and the measuring ampoule, a radiation screen /10/ is used. It is made of a copper tube, the inner surface of which is a mirror. With the help of the heater /5/ and the copper-constantan differential thermocouple /4/, the temperature field distribution on the screen surface is maintained the same as on the surface of the measuring ampoule. The use of a radiation screen made it possible to expand the temperature range of the measurements of thermal conductivity to 300 K. The thermocouple /4/ is used to monitor the temperature difference in the upper parts of the screen and the measuring ampoule. Its contacts are placed on the copper sleeve /7/ and in the upper part of the radiation screen /5/. When a temperature difference occurs, the signal from the thermocouple is fed to the input of the potentiometer R-348.

### IV. GROWING SAMPLES

The system for growing samples (Fig. 1) consists of the manometer M2, balloons B1, B2, B3, the reducer R, inlet channels, the capillary, the measuring ampoule and heaters to maintain the required temperature conditions (Fig. 2). The gas (the study samples in a gaseous phase) is in the cylinder B2 under pressure; together with the reducer R it is used to maintain the required steady pressure when growing the samples. The manometer M2 shows the pressure drop during the samples’ growth from the gas phase. The gate vacuums GV3–GV6 are used to control the process of growing a sample and shut off the supply channels for the gas, liquid and helium being studied.

i) Growing polycrystalline samples from the gas phase.

Before the start of the growing procedure, the system is evacuated using VP and PVD pumps. When a vacuum of about 5 \times 10^{-6} mm of mercury is reached, the internal volume of the measuring ampoule and the inlet channels of the studied gas are flushed, then the system is evacuated again and the cryostat is immersed in a Dewar with liquid nitrogen. After cooling the cryostat using the heater /4/ (Fig. 2), a temperature gradient was created along the measuring ampoule, which was necessary for growing a sample from the gas phase using the Bridgman method. Moreover, the temperature of the lower part of the ampoule was maintained stable and close to the temperature of liquid nitrogen (\( \approx 80 \) K). The heater /2/ turned on during the sample growth (Fig. 2) allows...
the capillary inlet temperature to be maintained above the crystallization temperature and to avoid its blockage. When growing a crystal, the top temperature of the measuring cell gradually decreases so that the temperature front on the surface of the grown crystal is approximately 80 K. A significant deceleration (almost cessation) of the pressure drop on the manometer M2 indicated the block of the inlet channel of the studied gas by the crystalline sample and the end of the growing procedure. The growing procedure took 4–6 hours and was pre-tested on the example of a glass ampoule. The described procedure provided an opportunity to grow polycrystalline samples at a temperature close to the temperature of liquid nitrogen (≈ 80 K), which made it possible to avoid the samples’ detachment from the walls of the measuring ampoule. The structural features of the measuring cell (Fig. 2) provide the possibility of a free expansion of polycrystalline samples (without an increase in thermal pressure) when heated. This fact is a significant advantage of the developed experimental installation. After measuring the thermal conductivity coefficient, the polycrystalline samples melted, then cooled again to a temperature below the crystallization temperature. Within the experimental error (5%), the thermal conductivities of polycrystalline and the remelted samples near the melting point coincided.

Fig. 1. Setup scheme for measuring the coefficient of the isobaric thermal conductivity of molecular crystals by the linear-flow steady-state method.

ii) Growing monocrystalline samples from the liquid phase.

In contrast to the previous case, when growing from the liquid phase, the samples were monocrystals. The samples were obtained by condensation into a liquid state from the gas phase or by direct cooling of the studied liquid (the studied samples in the liquid phase). Pre-washed with the studied gas, the empty measuring ampoule was cooled to the temperature of the liquid phase. Then the gas from the cylinder B2 under the pressure of ≈ 1 atm. was condensed into the internal volume of the measuring cell. During the condensation procedure, the temperature of the capillary inlet of the studied substance was maintained above the evaporation temperature. The stop of the pressure drop on the manometer M2 was an indicator of the filling of the measuring ampoule with the studied liquid. Subsequent cooling of the measuring ampoule to a temperature below the corresponding crystallization temperature made it possible to obtain monocrystalline samples.

The monocrystalline samples during their cooling detached from the walls of the measuring ampoule and quite often cracked (their thermal conductivity decreased sharply). The thermal contact of the monocrystalline sample with the walls of the ampoule and in the cracks of the single crystal was restored using helium gas, which was inflated into the internal volume of the measuring ampoule through the inlet channel of the studied substance under pressure close to 1 atm. In order to fill all cracks with helium, the ampoule remained in this state for 24 hours. Test measurements showed that the thermal conductivity of a monocrystalline sample, after filling the ampoule with gaseous helium, was restored after about 18-20 hours.

V. MEASUREMENT OF THERMAL CONDUCTIVITY COEFFICIENT

The main requirements in the study of thermal conductivity by stationary methods is the accurate measurement of the temperature gradient and power output by the heater, provided that the temperature is maintained stable. Fulfilling these requirements in the measurement process is associated with certain difficulties, in particular, the difficulties in providing a thermal contact of
the sample with a heater and thermometers, as well as uncontrolled thermal losses. All these factors influence the accuracy of determining the coefficient of thermal conductivity. The method that allows avoiding the influence of contact resistances and uncontrolled heat loss on the measurement results is a modified method of thermal potentiometer. This is a stationary method flat in the form of the temperature field, in which the heat flow is distributed along the sample, and the temperature difference is measured in the middle part. With such a geometry and a stationary temperature field, the temperature gradient does not depend on the contact thermal resistances. In order to take into account the heat flow that is distributed along the walls of the measuring ampoule, preliminary measurements were made of the temperature dependence of the thermal conductivity of the empty ampoule (Fig. 3).

The direct procedure for measuring the thermal conductivity of the studied sample was as follows. At first, the measuring cell was set to a temperature $T_0$, which was kept constant throughout the entire experiment and which was measured by a lower resistance thermometer /15/ (Fig. 2). Then, the temperature $T_1$ of the upper thermometer /12/ (Fig. 2) was measured without power supply to the heater /6/ and with it determined the temperature gradient $\Delta T$, which was used in the calculations of the coefficient of thermal conductivity.

It should be noted that the same thermometer is used in this measurement procedure at two stages of measurement. This is a significant advantage of this method of measurement, since it allows us to avoid the influence of uncontrolled heat flows and the difference in the calibration of the thermometers on the measured value of the thermal conductivity. The coefficient of thermal conductivity was calculated according to the formula:

$$\Lambda = \frac{Lq}{S\Delta T},$$

where $S$ is the cross-sectional area of the sample, $L$ is the distance between the thermometers, $\Delta T = T_2 - T_1$ is the difference between the readings of the upper thermometer when the power is supplied to the heater and without the supply, respectively, $q = Q - q_{\text{amp}}$ is the portion of the heat flow that passes directly through the sample, $Q$ is the heater power, and $q_{\text{amp}}$ is the part of the heat flow transmitted through the walls of the ampoule (determined from previous studies of the thermal conductivity of an empty ampoule).

Heat loss through the capillary inlet of the test gas and the contact conductors do not exceed 1 $\mu$W. It should be noted that the heat fluxes along the walls of the ampoule and through the test sample are approximately equal. The measurement of the thermal conductivity was carried out on at least two samples. In the process of growing the sample, the internal volume of the ampoule was gradually filled. When the sample reached the lower end of the capillary /8/ (Fig. 2), the growth process was blocked by the sample itself. If part of the internal volume of the ampoule remained unfilled, then the thermal conductivity of the sample decreased sharply. In this case, the sample was re-grown. Before taking measurements, in order to relieve internal stresses, the sample was heated (several times) sequentially and cooled over the entire temperature range of the studies.

$$\Lambda = \frac{Lq_{\text{amp}}}{S\Delta T}.$$
VI. CONCLUSIONS

Measuring the coefficient of the isobaric thermal conductivity of molecular crystals is associated with a number of difficulties, among which are the following: ensuring the measuring process in the field of low temperatures (up to 80 K); avoidance of the studied samples' detachment from the walls of the measuring ampoule in the process of decreasing the temperature; ensuring a free expansion of the crystal inside the measuring ampoule while increasing its temperature; minimization of heat losses due to heat radiation and uncontrolled heat fluxes; ensuring the required accuracy of the measurements. The described experimental setup for measuring the isobaric thermal conductivity of molecular crystals makes it possible to positively solve these problems. It should also be noted that the developed experimental installation has several advantages: a wide range of temperatures (80–300 K) for the thermal conductivity measuring, a free thermal expansion of studied samples, compactness, and efficiency in the use of the substances under study.

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У статті описано експериментальну установку для вимірювання ізобарної теплопровідності молекулярних кристалів в інтервалі температур від 80 К до 300 К. Наведено схему цієї установки для вимірювання коефіцієнта теплопровідності плоским стаціонарним методом під тиском власних насичених парів. Розроблене дослідницьке середство має певні переваги перед своїми прототипами, що застосовуються для вимірювання теплопровідності молекулярних кристалів, зокрема: можливість вимірювати коефіцієнт теплопровідності в широкому діапазоні температур (220 К), вільне теплове розширення досліджуваних зразків, компактність і економічність у використанні досліджуваних речовин та охолоджувальної рідини (азот). Описано методи вирощування полікристалічних та монокристалічних дослідних зразків з газової фази за методом Бріджмена та методом прямого охолодження відповідно. Показано конструкцію вимірювальної комірки, яка забезпечує вільне теплове розширення (без наростання термічного тиску) досліджуваних молекулярних кристалів у широкому діапазоні температур. Описано безпосередню процедуру визначення коефіцієнта ізобарної теплопровідності молекулярних кристалів за допомогою розробленої експериментальної установки. Перед проведенням вимірювань коефіцієнта теплопровідності для зняття внутрішніх напруг проводиться обов'язкове послідовне (декілька разів) нагрівання й охолодження дослідного зразка за всім температурним діапазоном вимірювань. Для врахування теплового потоку, що розповсюджується по стінках вимірювальної комірки, попередньо вимірюють температурну залежність коефіцієнта теплопровідності порожньої вимірювальної комірки. Неконтрольовані потоки тепла, зумовлені термічним випромінюванням із поверхні вимірювальної ампули, мінімізуються за допомогою радіаційного екрану, на поверхні якого відтворюється поле температур вимірювальної ампули. Для вимірювання теплопровідності використано метод перетворення з одним термометром, що дозволило уникнути похибок у значеннях коефіцієнта теплопровідності молекулярних кристалів за рахунок неконтрольованого температурного впливу та різного калібрування термометрів і суттєво підвищити точність вимірювань. Загальна похибка під час вимірювання коефіцієнта теплопровідності молекулярних кристалів не перевищує 5%.