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Effect of pseudorotation on isochoric thermal conductivity of hydrocarbons in disordered phases

The isochoric thermal conductivity of solid five-membered heterocyclic compounds has been measured in orientationally ordered and orientationally disordered («plastic») phases on samples of different density in a wide interval of temperatures and pressures. The objects were: furan – C_4H_4O, cyclopentane – C_5H_{10}, thiophene – C_4H_4S. The aim of this research was to study the influence of the translation-orientational motion on the behavior of the isochoric thermal conductivity and to estimate the possible contribution of pseudorotation to the total heat transfer.

Key words: isochoric thermal conductivity, hydrocarbon compounds, translation-orientation movement.

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Влияние псевдовращения на изохорную теплопроводность углеводородов в неупорядоченной фазе

Изохорная теплопроводность твердых пятичленных гетероцикличных соединений была измерена в ориентационно-упорядоченной и ориентационно-разупорядоченной («пластичной») фазах образцов различной плотности в широком интервале температур и давлений. Объектами являлись: фуран - C_4H_4O, циклопентан -–C_5H_{10}, тиофен - C_4H_4S. Целью данного исследования было изучение влияния трансляционно-ориентационного движения на поведение изохорной теплопроводности и оценка возможного вклада псевдовращения в общую теплоотдачу.

Ключевые слова: изохорная теплопроводность, углеводородные соединения, трансляционно-ориентационное движение.

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Жалған айналымдардың реттелмеген фазадағы көмірсулардың жылу өткізгіштігіне әсері

Қатты бес мүшелі гетероциклды қосылыстардың изохоралық жылуөткізгіштігі әр түрлі тығыздықты үлгілердің бағдарлы-реттелген және бағдарлы-реттелмеген («пластикалық») фазаларында температураның және қысымның кең аралығында өлшенген. Зерттеу нысаны: фуран – C_4H_4O, циклопентан – C_5H_{10}, тиофен – C_4H_4S болды. Бұл зерттеудің мақсаты трансляциялық-бағдарланған қозғалыстың изохоралық жылуөткізгіштікке әсерін зерттеу және жалған айналымның жалпы жылу беруге үлесін бағалау болды.

Түйін сөздер: изохоралық жылуөткізгіштік, көмірсулы қосылыстар, трансляциялық-бағдарланған қозғалыс.

The isochoric thermal conductivity of solid five-membered heterocyclic compounds has been measured in orientationally ordered and orientationally disordered («plastic») phases on samples of different density in a wide interval of temperatures and pressures. The objects were: furan – C_4H_4O, cyclopentane – C_5H_{10}, thiophene – C_4H_4S. The aim of this research was to study the influence of the translation-orientational motion on the behavior of the isochoric thermal conductivity and to estimate the possible contribution of pseudorotation to the total heat transfer. Pseudorotation as a large amplitude motion may significantly affect the translation-orientation (TO) coupling in molecular crystals, and

therefore on the thermal conductivity, as much as it is determined by the nature as translational and orientational motion of molecules).

Long-term studies of the isochoric thermal conductivity established the basic regularities in the heat transfer of simple molecular crystals at T

D [1]. A strong translational orientational (TO) coupling contribute significantly to the thermal resistance. This, in turn, leads to large deviations of the isochoric thermal conductivity from the 1/T law owing to its approach to a lower limit min. The concept of the lower limit of the thermal conductivity comes from the idea that min is reached when the heat transfer occurs as diffusion of thermal energy between neighboring quantum-mechanical oscillators the life time of which is assumed close to one-half the period of the oscillations [2]. In orientationally ordered phases of molecular crystals large part of heat is transferred by «diffuse» modes, and thermal conductivity changes more weakly than the 1/T dependence. In orientationally disordered («plastic») phases of molecular crystals the «rotational» contribution to the total thermal resistance decreases sharply at gradual transition to weakly hindered rotation (freely rotatable molecules do not scatter phonons), so that the isochoric thermal conductivity increases with increasing temperature [1].

It is shown that the experimental data for all substances can be described in framework of a modified Debye model of thermal conductivity with allowance for heat transfer by both low-frequency phonons and «diffuse» modes. In phase II of cyclopentane the isochoric thermal conductivity is practically temperature – independent, but it increases smoothly with temperature in phase I. We attribute the increase of thermal conductivity to the translation – orientation interaction which becomes weaker as the rotational motion of the molecules enhances and the phonon scattering at the rotational exaltations attenuates. Thus, we can conclude that disinhibition of uniaxial rotation of the molecules in the cyclic hydrocarbons leads to the increase of the thermal conductivity with temperature like «plastic» phases of other molecular crystals.

References

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