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Quasi-elastic (QENS) and inelastic neutron scattering (INS) on hexamethylbenzene

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Abstract

The Quasi-elastic Neutron scattering (QENS) spectra of polycrystalline hexamethylbenzene (HMB) were measured for temperatures from 10 K to room temperature (phase III and phase II) for momentum transfer 1.9 $Å^{-1}$. The Inelastic Neutron scattering (INS) and QENS spectra for momentum transfer 0.5–2.9 $Å^{-1}$ were measured at $T = 20$, 100 and 130 K for energy transfer up to 200 meV. The low-resolution diffraction patterns, used as the phase indicator, were also obtained.

In the phase III (below 117 K), we see practically no quasi-elastic broadening. In phase II, the broadening changes with the temperature are in good agreement with the Arrhenius law. The estimated activation barrier to reorientation is 6 kJ/mol. The fitted mean time between instantaneous 120° jumps of CH_3 groups changes from 10^{-11} s at $T = 130$ K to 2×10^{-13} s at room temperature.

On the basis of EISF versus momentum transfer dependency it is hardly possible to decide what is the geometry of the reorientation. Both reorientation of the CH_3 groups around the three-fold symmetry axis and reorientation of the whole molecule around the six-fold symmetry axis of the benzene ring could describe our results, the former being more probable.

The measured INS spectra are compared with the quantum chemical ab initio calculations performed for an isolated HMB molecule.

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1. Introduction

Since many years, hexamethylbenzene (HMB) has been studied by various experimental methods. Results of crystallographic [1,2], calorimetric [3–5] NMR [6–10] and neutron scattering studies [11–16] were reported. However, neither structure nor dynamics of the HMB is as yet fully understood.

The calorimetric studies show the existence of three phases in solid HMB: phase I from the melting point at 483K to 383 K, phase II—from 383 to 117 K and phase III below 117 K. The structure of phase I is orthorhombic, Fmmm, with four molecules per unit cell [2]. In phase II, the arrangement of molecules in the planes changes resulting in a triclinic structure with one molecule per unit cell [11,12]. Following Ref. [2], phase III has the same symmetry as phase II but with slightly different lattice parameters. In Ref. [14], the refinement of phase III structure was done: the phase has a pseudo-rhombohedral space group symmetry with the normal to the plane of the benzene rings along the (1 1 1) direction. Within a single HMB molecule, all the ring carbons lie within a plane with alternating methyl groups tilted above and below the plane by 3.3°.

There are some inconsistencies about the results of experimental studies of the dynamics of HMB. According to NMR studies [6], a reorientation of methyl groups is found in phases III and II and is characterized by an activation energy of about 7.9 and 6.7 kJ/mole, respectively. The reorientation of the molecules about the six-fold axis of the molecule exists above 150 K. These results were confirmed in Ref. [7] where the values of the activation barriers for different molecular processes are given.

The NMR studies [8] seem to suggest reorientations of the whole molecule around the six-fold axis in phase II and methyl group rotation in phase III. This should be compared with conclusions of the calorimetric study [3] in which an existence of a hump in the specific heat around 117 K is interpreted as due to rotational oscillations or reorientation of the methyl groups which begins in phase III and continues on in phase II.

Inelastic neutron scattering (INS) studies [11,12] assigned two modes: one at 60 cm^{-1} for phases II and III as an overall libration and the other at 137 cm^{-1} for phase III and 120 cm^{-1} for phase II, as torsional motion of the methyl groups. These studies revealed an existence of distinct quasi-elastic component in phase II and a lack of such a component in phase III. At the high-temperature phase transition at 383 K, the onset of reorientation between six equilibrium positions around six-fold axis of HMB molecules occurs [11,12].

As one can see there is no clear image neither of the structure nor the dynamics of solid-state HMB phases. Therefore, we decided to study this compound by quasi-elastic neutron scattering (QENS) and INS. The results are important also as a part of a research project concerning charge transfer complexes with HMB as one of the components of the complexes.

2. Experimental

The QENS spectra of polycrystalline HMB were measured using two spectrometers: TOF, operating at the JEEP II reactor at the Institute of Energy Technology, Kjeller, Norway and NERA, inverted geometry spectrometer installed at the IBR-2 pulsed reactor of the Institute for Nuclear Research in Dubna, Russia. The incoming neutrons of the TOF spectrometer come from a cold neutron source and are monochromatized to the energy of 4.66 meV by Bragg scattering from a pyrolytic graphite crystal. The NERA spectrometer is installed at the end of a 100 m flight path. It is an inverted geometry spectrometer i.e. it operates with a fixed energy of scattered neutrons. This is achieved by the Bragg scattering from PG monocrystals and a Be filter installed before the detectors. The fixed energy of scattered neutrons was 4.65 meV.

The measurements performed using TOF spectrometer covered the temperatures from 10 K to room temperature (phase III and phase II) not reaching the high-temperature phase transition (phase II/phase I) at 383 K. The QENS spectra were measured for one scattering angle 80°, corresponding to the momentum transfer of 1.9 $Å^{-1}$. The energy resolution of the TOF spectrometer was ~120 μeV (HWHM). In the case of NERA spectrometer, QENS measurements covered momentum transfer range from 0.5 to 2.9 $Å^{-1}$ and