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Report:

The low-frequency vibrational properties of glasses and other disordered systems are a topic of long-term interest in condensed matter physics [1]. Especially the microscopic origin of the Boson peak is a recent matter of debate. We have applied nuclear inelastic absorption (NIA) to an organometallic compound, octamethyl-ethinyl-ferrocene (OMFA), which was recently found to undergo a first-order solid-solid phase transition to a rotator phase above $T_{pc} = 248$ K [2,3]. NIA is a powerful tool for element-selective studies of the vibrational dynamics of crystalline solids and glasses [4]. It yields the vibrational density of states (VDOS) selectively for the resonant Mößbauer nuclei in a material at a resolution that is now comparable to standard infra-red and Raman measurements, and it provides background-free measurements because only the resonant nuclei contribute to the delayed signal.

The issue of the present experiment was twofold:

1. First, to find out whether the orientationally disordered state might be undercooled, yielding an orientational glass. Thus, in one and the same compound the acoustic modes and in particular the Boson peak might be investigated both for the orientationally ordered and the orientationally disordered state.
2. Second, to obtain precise phonon densities of states above and below the order-disorder phase transition and to identify the phonons whose DOS undergoes significant changes at T_{pc} and thus possible the driving forces for the phase transition on a microscopic basis.

The experiment was carried out at the Nuclear Resonance Beamline ID18, using a three-bounce high-resolution monochromator (HRM) with two highly asymmetrically cut Si (9 7 5) reflections and a Ge(3 3 1) symmetrically cut crystal that ensures an approximately horizontally outgoing beam. A new set of crystals providing an energy resolution of about 0.5 meV was used. Within this bandwidth, a high flux of $3 \cdot 10^8 \text{ s}^{-1}$ was achieved by collimating the beam in front of the HRM by a compound refractive lens. The sample, a pellet of about 0.35 mm thickness, was mounted between thin Be sheets into a copper holder sealed with Kapton windows in a closed-cycle cryostat.

The extraction of the one-phonon contribution and the evaluation of the phonon DOS was carried out using DOS V2.1 [5]. Five spectra were measured, four for OMFA cooled down slowly from room temperature and one for OMFA quenched by immersion into liquid nitrogen. The percentage of subtraction of the elastic line was optimized as described in [6].

Fig. 1 shows the reduced DOS $g(E)/E^2$ for both the slowly cooled (annealed) and the quenched substance for the same temperature (60 K). Whereas frozen orientational disorder is expected to enhance the Boson peak intensity, the opposite effect is observed, namely a cut-off of the reduced VDOS for lowest energies, much like the VDOS of glassy ferrocene/dibutylphthalate in nanopores [6]. Whether this can be attributed to phonon confinement owing to the formation of nanostructured domains in the undercooled crystal is unclear at the moment. The phase transition itself is seen to yield an abrupt further increase of the number of very-low-energy modes.

Fig. 2 shows the partial Fe VDOS of OMFA at 60 K together with a room-temperature Raman spectrum. Owing to different selection rules, the acoustical phonons are not visible to Raman but to NIA. Moreover, the relative intensities of the optical phonons, which appear rather well separated from the acoustical phonons, differ strongly in both methods. In particular, the modes between 10 and 30 meV belong mainly to vibrations of the carbon framework of the substituted cyclopentadienyl units with only a low vibrational amplitude of the central iron atom.

Fig. 3 shows a part of the optical phonon spectrum for 60, 230, and 240 K (set temperature of cryostat), in comparison to the RT Raman spectrum. Error bars for the NIA spectra are about 3–4 times the symbol size. For the sake of clarity, the upper two NIA spectra and the Raman spectrum are offset, and the Raman spectrum has in addition been rescaled.

Some changes in the optical phonons can be observed clearly in the 240 K spectrum but also appear to start already 10 K below: the 40 and 51 meV bands disappear, and the band for 60.5 meV splits. The latter phenomenon is also observed in the Raman spectrum. An assignment of the phonon bands to different molecular modes should allow us to explain this possible interplay of intra- and intermolecular vibrational modes.

A precise determination of the low-temperature phase of OMFA, which might help to interpret some of the phenomena observed in this study more in detail, is under way.

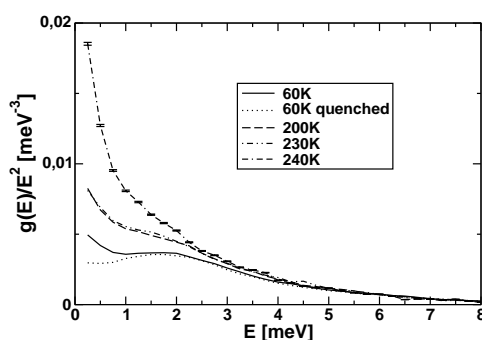


Fig. 1

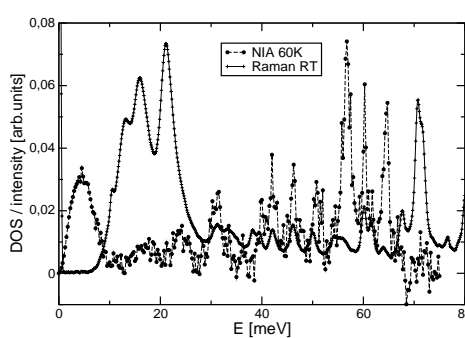


Fig. 2

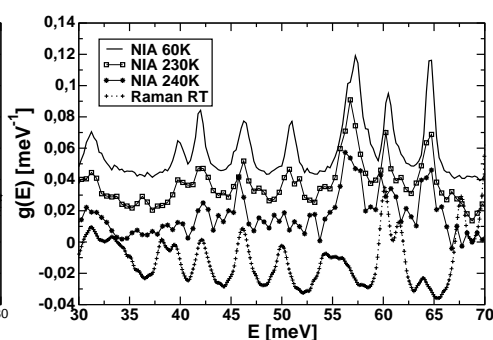


Fig. 3

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