

MS34-O4**Analysis of the dynamics of a jumping crystal with Molecular Dynamics and TLS analysis from powder diffraction data**Jacco van de Streek¹

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Jumping crystals often shatter as a result of the phase transformation causing their jumping, making it difficult to analyse the structure after the phase transition.

For a compound for which the structure of the low-temperature phase was known from single-crystal analysis but where the disintegration of the crystals during the phase transformation prevented the elucidation of the high-temperature phase, we were able to observe a discontinuity in the unit-cell parameters when the temperature of the low-temperature phase was increased with Molecular Dynamics (MD). The new phase had a higher symmetry than the low-temperature phase and the anisotropic displacement parameters calculated from the Molecular Dynamics trajectory identified strong libration of the molecules as the cause of the phase transition.

Temperature-dependent powder diffraction experiments confirmed the structure of the new phase, but because anisotropic displacement parameters cannot be reliably refined against powder diffraction data, it seemed impossible to verify experimentally that molecular libration caused the phase transition.

This was solved by refining the anisotropic displacement parameters using a TLS (Translation-Libration-Skew) model, reducing the number of parameters required to describe the anisotropic motion of the non-hydrogen atoms by a factor of four. Additionally, the TLS approach allowed us to include the description of the anisotropic motion of the hydrogen atoms, even though only laboratory X-ray powder diffraction data were available. The results from the experimental TLS analysis were an excellent match with the results from the Molecular Dynamics calculations.

The combination of Molecular Dynamics simulations and TLS refinement against XRPD data therefore allowed a full characterisation, at the atomic level, of the anisotropy of the dynamics of the individual molecules leading up to, during and after a phase transition despite the destruction of the single-crystals during the phase transition.

Keywords: TLS, Molecular Dynamics, XRPD**MS34-O5****Is single-crystal diffraction a suitable technique to study jumping crystals in situ?**Michele Zema¹, Željko Skoko², Gennaro Ventrucci³, Jasminka Popović⁴, Serena C. Tarantino³

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Thermally induced mechanical properties of crystals, including the thermosalient effect manifested by some crystalline materials that jump many times their own size when heated or cooled, are known since the '80s. Modern analytical techniques have allowed deeper and deeper insights into the transformations that rule this phenomenon, and renewed the interest in a class of mechanically responsive materials that hold potential for a broad range of applications in electronics, soft robotics, regenerative medicine, and related fields [e.g., 1-2].

However, potential applications of the thermal-to-mechanical energy conversion through thermosalient effect require detailed understanding of the structural changes at the atomic/molecular level. This proves to be quite challenging, because of decreased crystal quality, latent/permanent crystal deformations, or simply because of technical difficulties of performing in situ single-crystal X-ray diffraction (SC-XRD) analyses. As a consequence, very few evidences on the atomic-scale mechanisms driving these transitions are available, mainly on non-molecular compounds [e.g., 3].

We have developed a new device and crystal mounting methods that make this technique flexible and fully versatile for studies under different heating (up to ca. 1100°C) and atmospheric conditions, with no limitations to the rotation of goniometer circles. Crystal mounting in quartz vials (in air; in closed atmosphere of virtually any conditions; under vacuum) by making use of quartz wool to avoid mechanical stress on crystal surfaces is compatible with this set-up and proved particularly efficient in the study of jumping crystals, as quartz fibres are flexible enough to accommodate crystal movements at the transition.

We present here the first results on three thermosalient crystals, oxitropium bromide (OTB), scopolamine methyl bromide (SMB) and hydrated SMB (SMBH). In all cases, in situ HT SC-XRD data were collected at regular intervals up to above the transition temperature and down to room temperature. All samples show negative thermal expansion of at least one cell parameter. OTB undergoes a structural transition at 330 K with some hysteresis on cooling. Variation of the unit-cell parameters with T shows a fairly large first-order jump. No discontinuities have been observed in the unit-cell parameters evolution with T for SMB, whereas SMBH clearly shows a sudden jump at ca. 320 K, also in this case reversible and with some hysteresis on cooling. Preliminary structure refinements indicate a single crystal-to-single crystal transformation due to a dehydration/re-hydration process rather than a phase transition.