ESRF	**Experiment title:** Dispersion of an OH-valence vibration	**Experiment number:** HS-3474
Beamline: ID28	**Date of experiment:** from: 19.09.2007 to: 22.09.2007	**Date of report:** 26.02.2008
Shifts: 9	**Local contact(s):** M.Krisch, A. Bossak	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
B. Winkler[1,⋆], A. Friedrich[1,⋆], M. Krisch[2,⋆], A. Bossak[2,⋆]

1 Geowissenschaften, Goethe-Universität, Altenhoeferallee 1, D-60438 Frankfurt a.M., Germany
2 ESRF, BP 220, Grenoble, F-38000 France

Report:

Summary
The dispersion relations of the hydrogen stretching frequencies of diaspore, α-AlOOH, where the hydrogen atoms participate in a hydrogen bond of intermediate strength, have been predicted by density functional perturbation theory and have been confirmed experimentally by inelastic x-ray spectroscopy using the spectrometer ID28@ESRF. The results show that the OH-stretching frequency has an appreciable wave vector dependence and that it is possible to measure this dispersion relation with IXS at energies around 400 meV.

Introduction
Hydrogen bonds influence structure-property relations in a very large variety of compounds. Consequently, numerous experimental techniques are employed to study the detailed atomic arrangement and the dynamics of $R-O-H\cdots O-R'$ groups, where R and R' represent parts of a structure, O-H represents a significantly covalent bond with a typical distance of $d(\mathrm{OH}) \approx 1$ Å, and d(H...O) represents the hydrogen bond between the hydrogen and the acceptor atom, with a typical distance of $d(\mathrm{H}\cdots\mathrm{O}) \approx$ 1.5 - 1.72 Å. The only technique currently available to probe the dispersion relation of high-frequency OH-stretching vibrations is inelastic x-ray spectroscopy, IXS, but to the best of our knowledge, this has not been demonstrated yet.

Density functional perturbation theory predicted an unexpectedly large dispersion of the OH-stretching frequency in diaspore, α-AlOOH (Fig.1). Calculations for the dynamical structure factors showed that the splitting of the OH-stretching frequencies should be observable with two IXS measurements at different points in the BZ (Fig. 1).

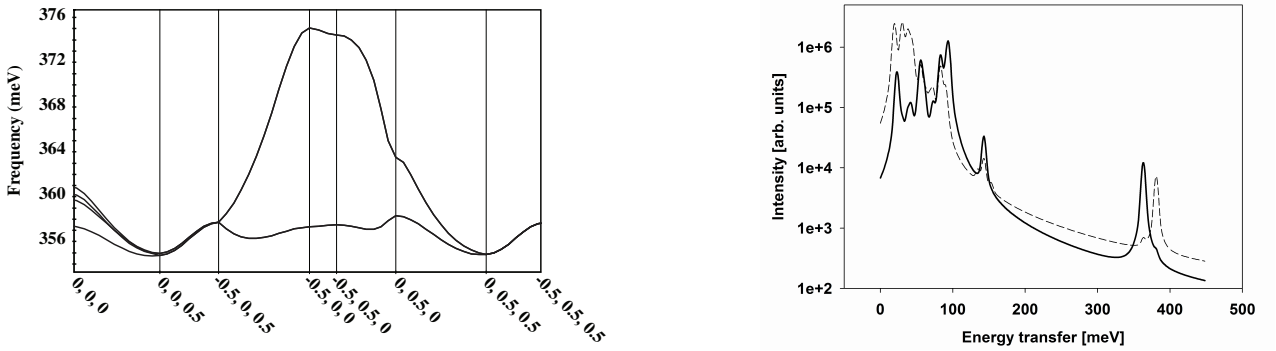

Fig. 1. Left: Predicted dispersion of the OH-stretching frequencies of diaspore. Right: predicted IXS spectra, showing that the splitting at $\approx$ 370 meV would be observable by two measurements at (2.5 0 0) (continuous line) and (2.5 0 $\bar{1}$) (dashed line).

The experiments confirmed the predictions. We observed the same splitting (17 meV) of the frequencies that we had predicted (Fig 2) and, using the other 6 analyzers, the dispersion relation.

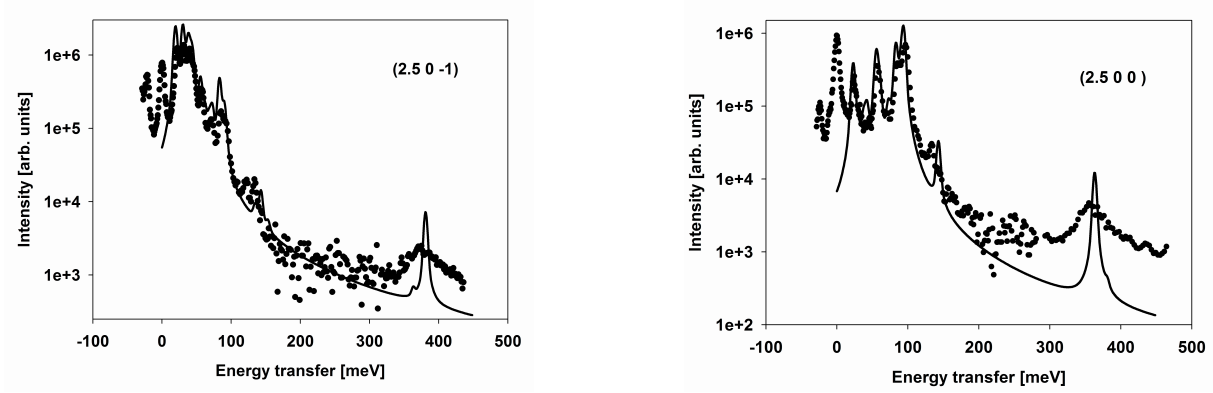

Fig. 2. Predicted (lines) and observed (points) inelastic spectra. The excellent agreement allows to use the DFPT calculations to explore the lattice dynamics of diaspore in great detail.

In summary, the agreement of the DFPT results with experiment for high frequency is as good as it is for low frequency phonons. The experiments show that the OH-stretching frequencies of hydrogen bonds of intermediate strength can have a wave vector dependence. However, this technique will generally not be applicable to study the pressure dependence of the dynamics of hydrogen bonds, as diamond anvil cell experiments require thin samples, which would lead to unreasonable counting times. In contrast, temperature dependent measurements are unproblematic, and hence IXS can be used to study the origin of phase transitions governed by the dynamics of the hydrogen bonds.