doi:10.1017/S1431927622006687
Microsc. Microanal. 28 (Suppl 1), 2022

Exploring Vibrational Spectroscopy of Quantum Materials in the Scanning Transmission Electron Microscope

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Quantum materials promise to be transformative to our modern world. Quantum materials host emergent phenomena, such as phonon and magnon quasiparticles. Understanding how the bonding and local structures affect emergent phenomena is of particular interest in obtaining a more fundamental knowledge of these materials. Traditional vibrational spectroscopy methods, such as Raman, can be a powerful tool to detect these phenomena in novel materials, but they provide relatively delocalized information about the sample. The next step in the evolution of vibrational spectroscopy is to leverage the flexibility and spatial resolution of scanning transmission electron microscopy (STEM) to collect localized vibrational data using electron energy-loss spectroscopy (EELS) [1].

More sensitive detectors, better spectrometers, and brighter electron sources have pushed the energy resolution of STEM-EELS far enough that vibrational spectroscopy can be performed on commercially available microscopes [2]. Figure 1 shows preliminary data recorded at an energy resolution of 69 meV on a ThermoFisher Themis Z instrument, showing that a phonon signal can be detected in hexagonal boron nitride (*h*-BN). A resolution of <25 meV is achievable on this instrument which will be sufficient for initial characterization studies on our materials. Higher resolution investigations will then be conducted at the Center for Nanophase Materials Science at Oak Ridge National Laboratory.

Previous work has established that STEM-EELS can be used to detect the phonon signal in *h*-BN with atomic-scale contrast [3]. The existing literature regarding phonon spectroscopy using STEM-EELS is heavily focused on *h*-BN, primarily because its vibrational properties make it well suited to the study of spatial resolution [4]. This study plans to expand the list of studied materials to include $MnPSe_3$, a two-dimensional material with antiferromagnetic ordering below 74 K, the structure of which is shown in Figure 2. $MnPSe_3$ has several Raman-active phonon modes which this study will experimentally demonstrate are also observable with STEM-EELS [5].

Due to the antiferromagnetic ordering, $MnPSe_3$ also hosts magnon modes. A recent study using magneto-Raman spectroscopy observed magnon-phonon coupling between a two-magnon excitation and two E_g phonons [5]. This study further plans to explore the effect of magnon-phonon coupling on the observable phonon peaks in the EELS low-loss spectrum.

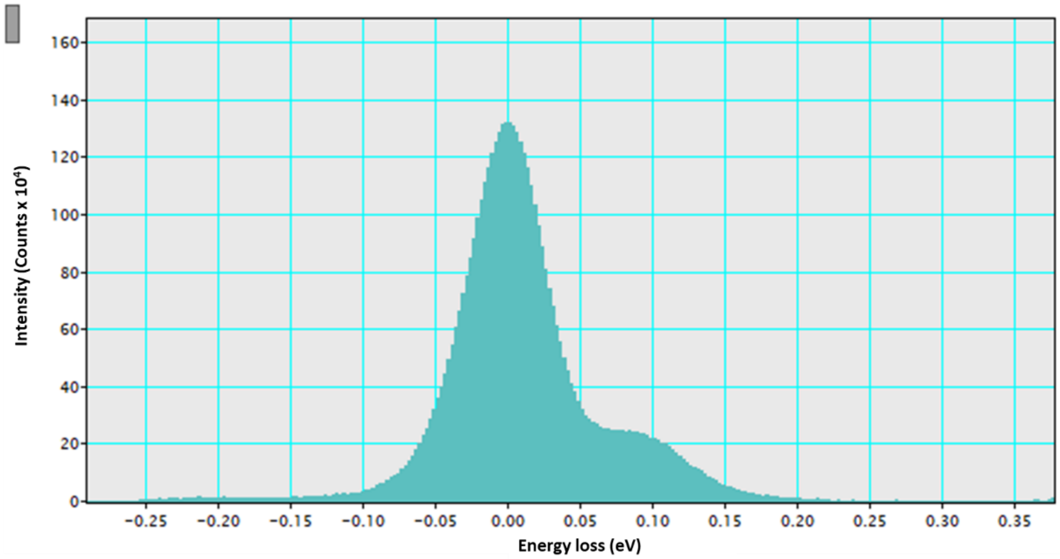

Figure 1. EELS spectrum of *h*-BN collected on the Themis Z at 60kV. The spectrum is summed from several pixels of a spectrum image. The convergence and collection angles were 27.4 and 22.8 mrad, with a spectrometer entrance aperture of 2.5mm and a dispersion of 0.002eV per channel. The FWHM is 69meV.

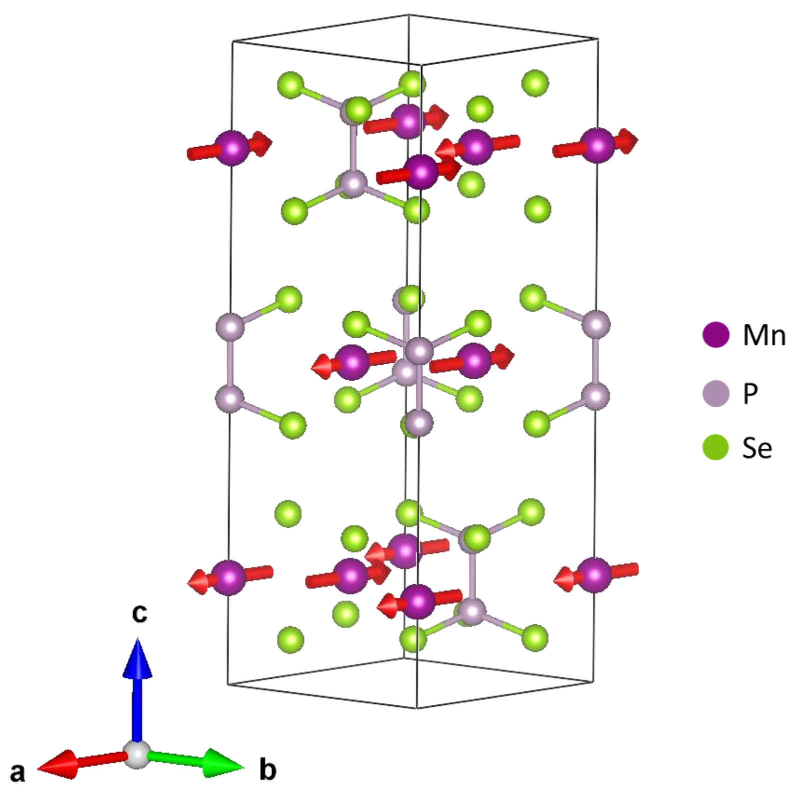

Figure 2. The structure of $MnPSe_3$. The red arrows in the manganese atoms indicate the direction of magnetic spin. $MnPSe_3$ is antiferromagnetically ordered below 74 K.

https://doi.org/10.1017/S1431927622006687 Published online by Cambridge University Press

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[6] The authors gratefully acknowledge funding from the Center for Emergent Materials at The Ohio State University, an NSF MRSEC (DMR- 2011876).