Experimental report

16/09/2018

Proposal: 7-01-456 **Council:** 4/2017

Title: Phonon density of states of PbFeBO4, PbMnBO4, and PbFe0.5Mn0.5BO4 studied by inelastic neutron scattering

Research area: Materials

This proposal is a new proposal

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Samples: PbFeBO4
PbMnBO4
PbFe0.5Mn0.5BO4

Instrument	Requested days	Allocated days	From	To
IN4	3	3	12/03/2018	15/03/2018
IN6	4	0		
IN6-SHARP	0	4	15/03/2018	19/03/2018

Abstract:

Mullite-type PbFeBO4, PbMnBO4 and PbFe0.5Mn0.5BO4 show negative thermal expansion in the a-axis below and above the spin-ordering temperatures. Grüneisen parameters of some low frequency optical modes are negative as obtained from the DFT calculations. Raman spectra showed strong softening/hardening effects, confirming the spin-phonon interactions. Temperature-dependent phonon density of states can provide both phonon-phonon and spin-phonon interactions, leading to understand the anisotropic lattice thermal expansion. We therefore ask for 7 days of beamtime at IN4C and IN6.

Report on experiment 7-01-456

Phonon density of states of $PbFeBO_4$, $PbMnBO_4$, and $PbFe_{0.5}Mn_{0.5}BO_4$ studied by inelastic neutron scattering

The crystal structure of $PbMBO_4$ was described in the space group *Pnam* [1,2], as shown in figure 1, where the edge-sharing MO_6 octahedra run along the **c**-axis. The planar BO_3 groups interconnect the MO_6-chain. Between two BO_3 groups the Pb^{2+} is located at the apex of a distorted PbO_4 square pyramid, where the $6s^2$ lone electron pair of Pb^{2+} is stereochemically active. The magnetic properties of $PbMBO_4$ was described as a Heisenberg 1D uniform chain model [1,3]. $PbFeBO_4$ shows AFM long-range order in the **c**-axis (T_N = 125 K and 280 K), where the AFM chains are ferromagnetically coupled. Upon substitution the spin-ordering temperature (T_N = 23 K) of $PbFe_{0.5}Mn_{0.5}BO_4$ significantly reduces. Both the intra- and inter-chain couplings in $PbMnBO_4$ are FM (T_C = 31 K) -a rare example of FM insulator. These phases are considered as excellent playgrounds to follow the Goodenough–Kanamori–Anderson [4] microscopic features. $PbFeBO_4$ [3], $PbMnBO_4$ and $PbFe_{0.5}Mn_{0.5}BO_4$ show negative thermal expansion (NTE) in the **a**-axis. While the elastic anomaly is associated in the **b**-direction the axial NTE in the **a**-direction is not well understood, worse even the microscopic sources of the NTE in the paramagnetic region. In search of sources of the NTE, we measured inelastic neutron scattering (INS) between 1.5 K and 520 K (Fig. 2) at IN4C and IN6, proving phonon density of states (PDOS). The dynamic structure factor *S(Q,E)* exhibits phonon dynamics across the T_Ns. The INS profile of $PbFeBO_4$ also shows steep magnon excitations up to ≃ 10 meV at the momentum transfer of q ≃ 1.1(1), 1.6(1) and 2.7(1) $Å^{-1}$, which are corresponding to acoustic spin-waves centered at (*010*), (*111*) and (*113*) AFM Bragg reflections, respectively. An AFM spin-wave velocity at d ≃ 0.57(1) nm is estimated to be 2.7(1) meV nm. *Ab initio* lattice dynamical calculations showed that most of the optically silent modes possess negative Grüneisen parameters. As such mode at 6.1 meV and 6.8 meV for $PbFeBO_4$ and $PbMnBO_4$, respectively exhibit hardening in increasing temperature as supported by the IN4C data. Interestingly, this mode shows thermal softening above 300 K as can be seen from the IN6 data. However, analysis of the temperature-dependent low-frequency phonon profile is challenging due to magnon-phonon interactions and strong paramagnetic background above the TNs. Of curious notes, the paramagnetic scattering still

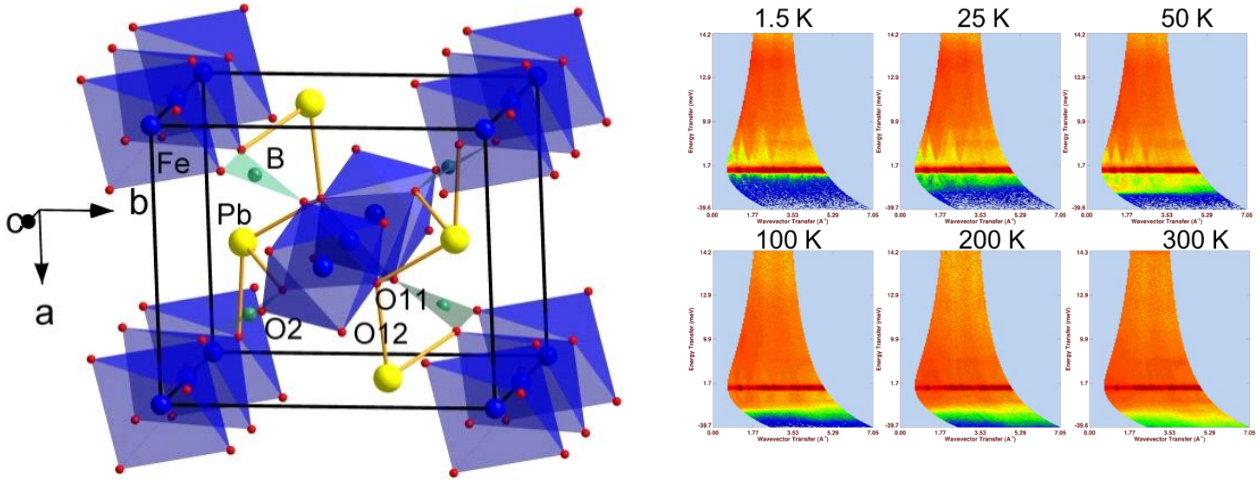

Figure 1: Crystal structure of $PbFeBO_4$. (left). Temperature-dependent evolution of the dynamical structure factor *S*(*Q,E*) of $PbFeBO_4$ (right). Logarithmic scale is used, where dark-red and dark-blue refer to strong and weak intensity, respectively.

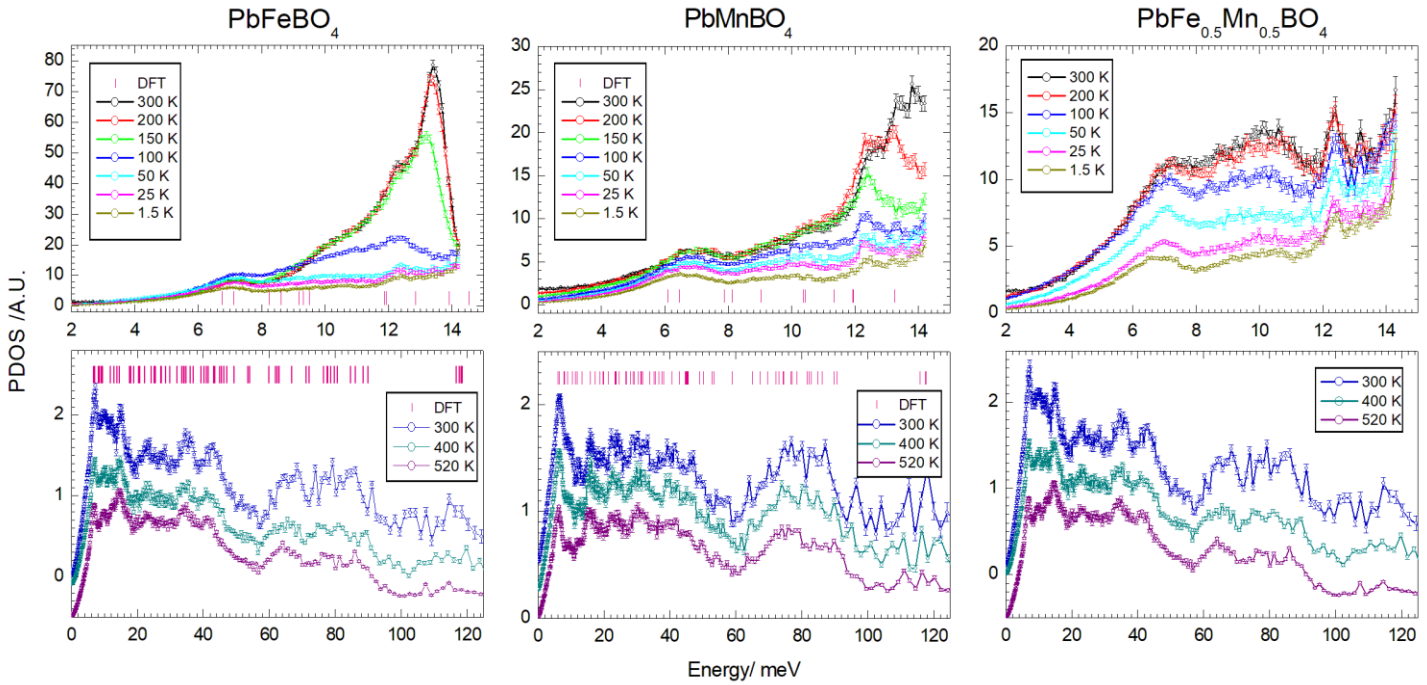

Figure 1: Temperature-dependent phonon density of states (PDOS) of $PbMBO_4$. Top and bottom panel datasets are collected using the Stokes and anti-Stokes facilities of the IN4 and IN6 spectrometers, respectively.

below the T_N is not so far understood. Moreover, the low-temperature spectra are far reaching to the boron-dominated cutoff of ~ 160 meV within the resolution. The dataset also limits observing the spin-phonon coupling. To get a complete story from these INS datasets representative PDOSs without the paramagnetic contributions are of crucial necessity. It is therefore necessary to measure temperature-dependent INS of some structural analogues such as $PbAlBO_4$, $PbGaBO_4$ or $PbAl_{0.5}Ga_{0.5}BO_4$. Since their metric parameters of these non-magnetic phases are close to those of the magnetic $PbFeBO_4$ and $PbMnBO_4$ or $PbFe_{0.5}Mn_{0.5}BO_4$. phases, respectively, one can extract the missing information from the PDOS of the magnetic phases from their non-magnetic counterparts. In the upcoming proposal round, we intend to propose/measure PDOS of these phases for a complete story of the lattice dynamics of $PbFeBO_4$, $PbMnBO_4$, and $PbFe_{0.5}Mn_{0.5}BO_4$.

Additionally, DFT constant pressure constrained geometry optimizations were performed, providing bulk elastic properties and the PDOSs. Raman spectra were collected between 78 K and 700 K. Temperature-dependent neutron elastic scattering data were collected at POWGEN, SNS and at D20, ILL. The lattice thermal expansion was simulated using Debye-Einstein-Anharmonicity (DEA) model [2]. Debye temperatures extracted from the respective volume thermal expansions are close to those calculated from the averaged mass-weighted values of the isotropic atomic displacement parameters; however, either of them is significantly lower than the highest-frequency optical mode.

Reference

[1] H. Park, R. Lam, J. E. Greedan, J. Barbier; Chem. Mater. 15 (2003) 1703.
[2] M. M. Murshed, C. B. Mendive, M. Curti, G. Nénert, P. E. Kalita, K. Lipinska, A. L. Cornelius, A. Huq, Th. M. Gesing Mat. Res. Bull. 59 (2014) 170.
[3] H.-J. Koo, M.-H. Whangbo, Solid State Comm. 149 (2009) 602.
[4] U. Schwingenschlögl, C. Schuster, Phys. Rev. Lett. 99 (2007) 237206.