Measurement of phonon dispersion relation in negative thermal expansion compound ZrW$_2$O$_8$

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Abstract. Isotropic negative thermal expansion (NTE) is found in cubic AX$_2$O$_8$ (A=Zr, Hf; X=W, Mo) up to high temperatures (1050 K). Anharmonicity of low energy phonon modes plays an important role in leading to the NTE behaviour. Earlier we verified our predictions of large phonon softening for low energy phonons (below 8 meV) through high-pressure inelastic neutron scattering measurements on powder samples at ILL, France. Now we have measured the phonon dispersion relation from a single crystal of ZrW$_2$O$_8$. The measurements are useful to verify our prediction of highly anharmonic nature of specific phonon branches, in particular the transverse acoustic branch, and other branches up to 10 meV. These modes below 10 meV mainly contribute to the NTE in ZrW$_2$O$_8$.

1. Introduction

Studies of oxide materials exhibiting negative thermal expansion (NTE) are of interest both from a fundamental scientific angle and their potential applications. Large and isotropic negative thermal expansion is found [1-3] in cubic AX$_2$O$_8$ (A=Zr, Hf; X=W, Mo) up to high temperatures (1050 K). The compounds can be used for the preparation of controlled thermal expansion composites where the NTE material compensates for the positive thermal expansion of the other components. The AX$_2$O$_8$ compounds have a framework structure consisting of corner linked AO$_6$ octahedral and XO$_4$ tetrahedral units.

Recent measurements [4] of the temperature dependence of the elastic constants for ZrW$_2$O$_8$ show that the bulk modulus in ZrW$_2$O$_8$ decreases by about 40 % with increase of temperature from 0 to 300 K. The analysis [5-7] of the observed NTE, specific heat and phonon density of states measurements in ZrW$_2$O$_8$ and HfW$_2$O$_8$ suggested that low energy phonon modes play an important role for understanding of the NTE behavior. High-pressure inelastic neutron scattering experiments conducted [8,9] by us on polycrystalline samples of cubic ZrW$_2$O$_8$ and ZrMo$_2$O$_8$ confirm the expected phonon softening under pressure. The unusual phonon softening of low energy modes is able to account for the NTE in these compounds. Our lattice dynamical calculations [8-12] for ZrW$_2$O$_8$ and HfW$_2$O$_8$ reproduce the observed anomalous thermal expansion in these compounds. They predict unusually dominant contributions of the transverse acoustic, librational and translational optic modes below 8 meV leading to a large NTE. Now we have measured the low energy part of the phonon dispersion
curves at 10 K from a single crystal of ZrW$_2$O$_8$ in order to check the predictions of our model. The temperature dependence of a few selected frequencies was also measured over 10-300 K to examine their anharmonicity.

2. Results and discussion

ZrW$_2$O$_8$ has a cubic structure with space group P2$_1$3 and four formula units per primitive cell [1]. There are 132 distinct dispersion branches along [100] direction. The 132 phonon modes along [100] direction can be classified as $\Delta = 66\Delta_1 + 66\Delta_2$. The lattice dynamical model [1] was used for the calculation of the one-phonon structure factors in the (100) - (110) plane. These calculations are required for selection of the most appropriate Bragg points for the detection of particular phonons. Furthermore, calculations are very important for assignments of the various inelastic signals to specific phonon branches.

The experiment was carried out on a single crystal of ZrW$_2$O$_8$ (8 mm $\times$ 4 mm $\times$ 2 mm) using the 1T1 spectrometer at LLB, Saclay. This instrument is equipped with vertically and horizontally focusing monochromators and analyzers resulting in high neutron intensity. Measurements in the (100)-(011) scattering plane were done with pyrolithic graphite (PG002) as a monochromator and analyzer, respectively.

![Figure 1](image.png)

**Figure. 1** Constant-energy scan taken at the (0,4,4) reciprocal lattice point in ZrW$_2$O$_8$ at 11 K.

The crystal quality was found to be rather poor. The largest grain found has a relatively poor mosaic spread which severely affects the q-resolution. Moreover, there is strong evidence that the large grain used for the phonon measurements is by far not 100 % of the crystal volume, but possibly only about 50 %. The misoriented grains contribute to the background, which moreover has some structure. Still, we could measure some useful data using this crystal. This is demonstrated by the constant-energy scan taken at the (0,4,4) reciprocal lattice point in ZrW$_2$O$_8$ at 11 K shown in figure 1.

The phonon data measured during four days of beam time are summarized in figure 2. The branches shown are a kind of guess from both the experimental data and the lattice dynamical calculations. The experimental results confirm the calculated (figure 2) optic phonon branches. On the other hand, the predicted slope of transverse acoustic branch is too low.

The temperature dependence of a few selected phonons (figure 3) was also measured at 10 K and 330 K to examine their anharmonicity. Phonons around 4 meV were found to harden by 0.15 to 0.25 meV. A similar, although slightly larger, hardening was deduced from the temperature dependence of the
Figure. 2 Upper panel shows the Low-energy phonon dispersion in ZrW$_2$O$_8$ as deduced from measurements at T = 11 K. The solid lines are guide to the eye in the upper panel. Calculated phonon dispersion relations for ZrW$_2$O$_8$ are shown as dashed and solid lines in the upper and lower panels respectively.

A strong anharmonicity of the 4 meV phonons is further evidenced by their large line widths at T = 330 K. This broadening makes it difficult to precisely measure the frequency shift with respect to low temperature as it leads to strong overlap with phonons at higher energies. The unusual hardening of the 4 meV phonons with increasing temperature is another indication of their anomalous character.

3. Conclusions
The experimental results show that our lattice dynamical model is realistic enough to serve as a basis for an understanding of the unusual phonon properties of the NTE compounds. On the other hand, they also show the need for further improvement of our lattice dynamical model.
Figure 3 Constant Q scans for few selected phonons at 10 K and 330 K

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