Acoustic phonon softening in tetragonal $BiVO_4$

Izumi Tomeno,[A] Naomi Sato,[A] Yoshinosuke Sato,[A] Kunihiko Oka,[B] YorihikoTsunoda[C]
[A]*Akita Univ.*, [B]*AIST*, [C]*Waseda Univ.*

Bismuth vanadate $BiVO_4$ undergoes a second-order ferroelastic phase transition at T_c=525 K.[1] The high-temperature paraelastic phase has a body-centered tetragonal scheelite structure with a centrosymmetric space group $I4_1/a$ (C_{4h}^6).

We studied the TA phonon propagating on the (001) plane polarized on this plane in $BiVO_4$ above T_c=525 K. The energies of the TA phonon dispersion curve along $[0.7\xi, \xi, 0]$ are slightly lower than those along $[\xi, \xi, 0]$, indicating that the acoustic symmetry direction deviates from the high-symmetry $[\xi, \xi, 0]$ direction. The deviation is related to the fact that the oxygen site at the tetrahedral VO_4 has the lowest site symmetry C_1 above T_c.

The present study shows the considerable softening of the TA phonon mode along $[0.7\xi, \xi, 0]$ in the range $\xi < 0.2$. Figure 1 shows the temperature dependence of the TA phonon mode along the $[0.7\xi, \xi, 0]$ direction. The TA phonon branch along $[0.7\xi, \xi, 0]$ is almost temperature independent between 673 and 873 K. Below 673 K, the TA phonon curve in the range $0 < \xi < 0.2$ shifts downward with decreasing temperature. In Fig.1 the dashed lines around $\xi = 0$ represent the extrapolations of the sound velocities determined by Brillouin scattering experiments.[2] The sound velocity $v_{min} \approx 8.2 \times 10$ m/s at T_c indicates an extreme flat TA dispersion in the vicinity of the zone center. The extrapolated intercept of the observed TA branch at 538 K with the horizontal axis gives a upper bound of the wave vector $q = [0.013, 0.019, 0]$ for the extreme flat dispersion region. The TA phonon branch along $[0.7\xi, \xi, 0]$ at 538 K should have a significant upward curvature at the small q range. On the other hand, the TA phonon mode along $[\xi, 0.176\xi, 0]$ exhibits a hardening with decreasing temperature toward T_c. This tendency is the normal behavior in an anharmonic lattice.

An elastic central peak emerges at $[0.7\xi, \xi, 0]$ in addition to the soft TA mode. The width of the central peak is comparable to the instrumental resolution. We found out that the central-peak intensity for $q = [\xi, \xi, 0]$ is significantly higher than that for $q = [0.7\xi, \xi, 0]$. The elastic diffuse scattering distributed along $[1,\bar{1},0]$ suggests that the narrow central-peak at $[0.7\xi, \xi, 0]$ has no direct connection the softening of the TA mode. A possible interpretation is that static or quasi-static defects appear along $[\xi, \bar{\xi}, 0]$ with decreasing temperature toward T_c.

[1] J.D. Bierlein and A. W. Sleight, Solid State Commun. 16, 69 (1975).
[2] H. Tokumoto and H. Unoki, Phys. Rev.B27, 3748 (1981).

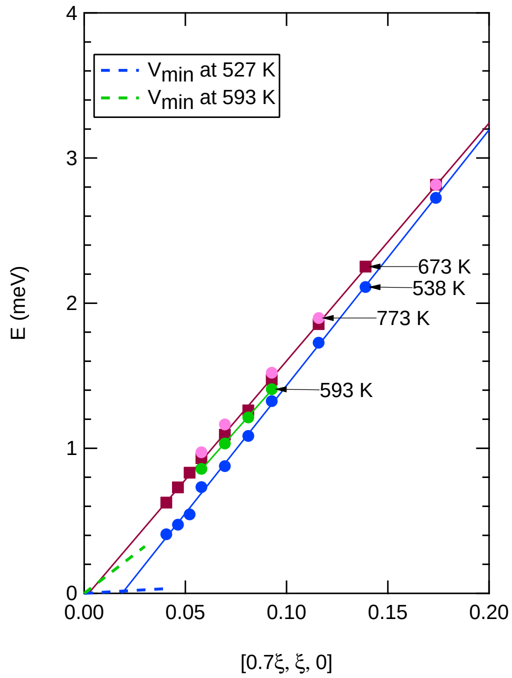

Fig. 1. Temperature dependence of TA mode along $[0.7\xi, \xi, 0]$