

Research Description

Current research

In Professor Wenzcovitch's group, I mainly investigate high temperature and pressure properties of materials with *ab initio* calculations. Interesting topics I have been studying include pressure induced phase transition, thermodynamic and thermoelastic properties. My research efforts can be summarized into four aspects:

1. Develop an effective method to include the anharmonic effects of lattice vibrations.

The quasi-harmonic approximation (QHA), assuming that the phonon frequency only depends on the volume and is independent of the temperature, is not good enough to describe the thermodynamic properties at high temperature and low pressure ($T > 1000\text{K}$ for MgO at zero pressure) where the intrinsic anharmonic effects ignored by QHA become very obvious. There are no effective methods to include anharmonic effects up to now because of the complicity of such effects. In our method, the temperature dependence of renormalized phonon frequencies is expressed in implicit way by volume modification, whose advantage is that we can get a reasonable temperature dependence of renormalized frequencies based on the anharmonicity character even if we do not know clear about anharmonicity. Only an adjustable constant c is introduced and QHA becomes a special case in our method. We test our method with MgO and our results are excellently consistent with the experimental observation up to maximum temperature measured (see Fig.1). The anharmonicity can be divided into two types depending on whether or not the adjustable constant c is larger than 0. If adjustable constant is negative, heat capacity at constant volume (C_v) will go beyond the Dulong-Petit limit at high temperature. We found that forsterite (α phase of Mg_2SiO_4) has a negative adjustable constant. The temperature where C_v crosses the Dulong-Petit limit is about 1500K, which is consistent with the experimental result.

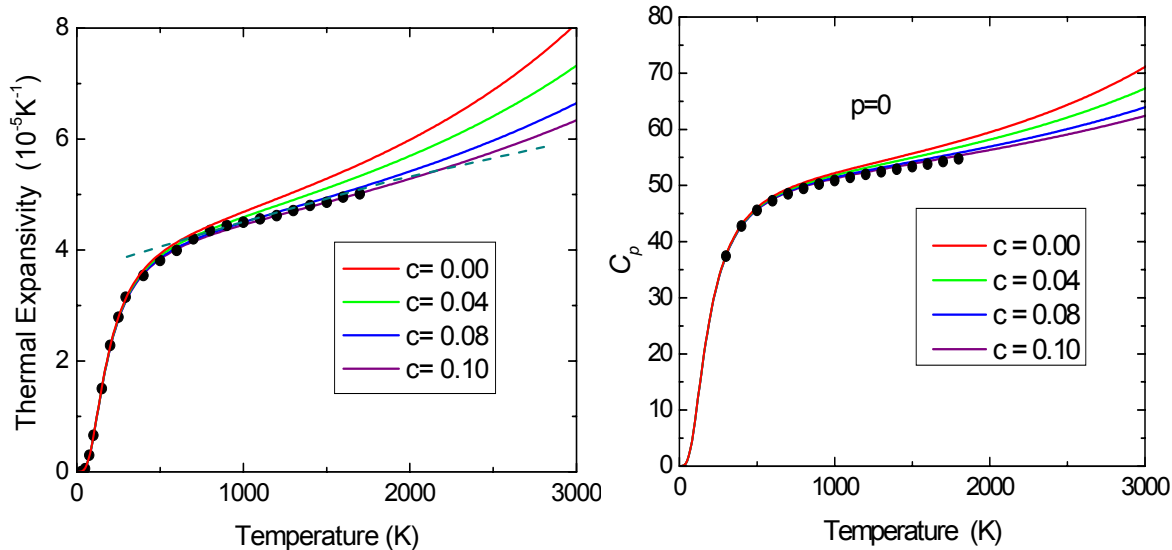


Fig.1. Temperature dependence of (a) thermal expansivity and (b) isobaric specific heat at 0 GPa with various anharmonic adjustable constant c . $c=0$ correspond to QHA

2. A high Pressure-Temperature (PT) scale of MgO based on density functional calculations.

Current high PT standards of calibration produce too large uncertainties to the point of inhibiting clear conclusions regarding the importance of certain phenomena for planetary processes at these high PTs, e.g., the post-perovskite transition in Earth's mantle. We propose a calibration based on thermal equations of state (EoS) of MgO obtained from LDA quasiharmonic (QHA) calculations. The anharmonic effects are also included in our calculation by adopting our method, which considerably expand the PT range of validity of our calculation. These EoSs agree perfectly with shock wave data (see fig.2). Post-perovskite phase transition boundary is more matched to the seismic discontinuity by using our scale than other widely used scales.

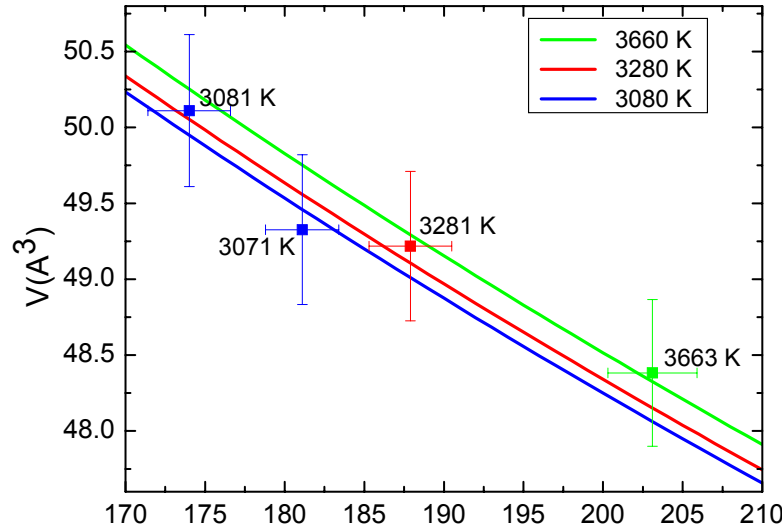


Fig.2. Equation of state of MgO at high temperature and pressure. Perfect consistence with shock wave data (solid square) indicates our EoS can be used as pressure calibration at such high pressure.

3. Vibrational and thermodynamic properties of wadsleyite (beta phase of Mg_2SiO_4).

Mg_2SiO_4 is the major compound of the Earth's upper mantle. It undergoes a series phases including olivine (α), wadsleyite(β), and spinel (γ) phase with increasing pressure (or depth). The knowledge of physical properties of these polymorphs is very important to clarify the nature of the Earth's mantle. The vibration properties of Mg_2SiO_4 wadsleyite has been calculated based on density functional perturbation theory (DFPT) over a wide pressure range. Both the frequencies and their dependence on volume consist with available Raman and infrared experimental data. Our calculations provide detailed vibration properties that are still not available experimentally. These vibration results are used to calculate the Helmholtz free energy within the quasi-harmonic approximation (QHA) and other thermodynamic variables without further approximation.

4. Develop a method to get thermoelastic constant without calculating the phonon DoS of strained structure.

The elastic constant of Earth material at high temperature and pressure is indispensable to understand most issue of geophysics. Thermal elastic constant can be calculated with first principles and quasi-harmonic approximation. However, the total computation time is very long. Especially for crystal with large primitive cell (general case for mineral) computation time generally is too long to endure because density of state (DoS) of phonon for each strained structure needs be calculated. For example, for the orthorhombic crystal, DoSs for at least 8 volume and 15 strained structures for each volume are required to get the nine elastic constant at high temperature and pressure. Can we get the thermoelastic constant without phonon DoS calculations of strained structure? We analyzed the temperature effect on elastic constant in detail and derived the equations to describe the relation of the elastic constants and temperature. Based on these equations, we figured out a

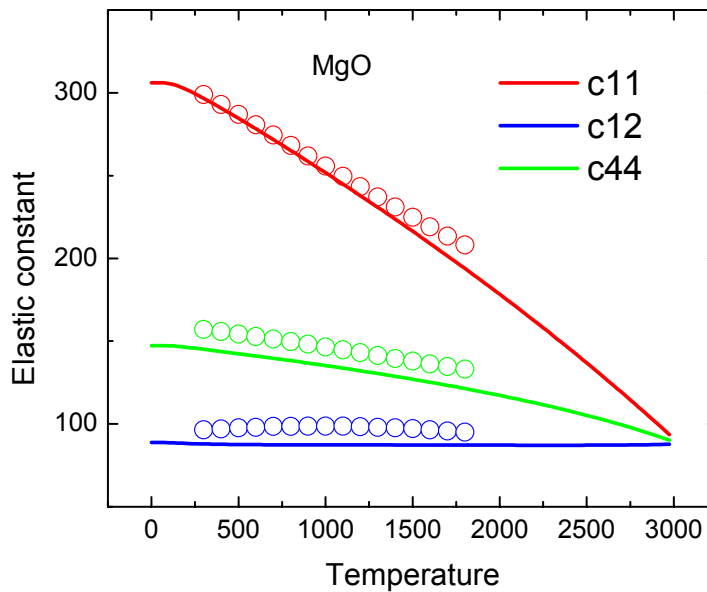


Fig.3 The temperature dependence of elastic constants at zero pressure is well consistent with experiment data denoted by open circle.

method to get thermal elastic constant. Obviously, our method can reduce more than one order of computation time for not having to calculate the DOS of strain structure. The thermal elastic constant of MgO obtained by using our method is in excellent consistent with the experimental data and previous result we got with calculating DOS of strain structure, indicating that our method keeps the accuracy (see fig.3).

Past research

Before joining Professor Wenzcovitch's group, I concentrated my research in ferroelectric ultrathin film. It is commonly believed that the ferroelectric nanostructure such as ultrathin film will have some physical properties distinctly different from those of bulk material since both long-range dipole and short-range covalent interactions and their balance are varied in regard to those in the bulk. Our investigations on $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ultrathin film with Monte Carlo simulations on the basis of a first-principles-derived Hamiltonian really disclosed some unusual phenomena:

Ferroelectricity critical thickness and nano stripe domain (see fig. 4)

It is found that there exists a critical thickness of about three unit cells ($\approx 1.2\text{nm}$) below which the ferroelectricity disappears. Above the critical thickness, the periodic 180° stripe domains with out-of-plane polarizations are formed. The 180° stripe domain period is determined by film thickness and almost unchanged with temperature and compressive strain, which make the ferroelectric film potentially useful for the quasi-phase matching.

Domain structure evolvement under the electric field (see fig. 5)

We observe two transformations of domain structure, which indicates a domain evolution completely different from that of bulk material. Firstly, the straight stripes transform into the concentric loop stripes at the field region. Then with increasing field, the concentric stripes further transform into the nanodomain lattice. The characteristic size of domain structure can be conveniently adjusted by controlling

the film thickness and the external field, which is very attractive in many aspects such as nonlinear photonic crystal and the assembly of nanostructure.

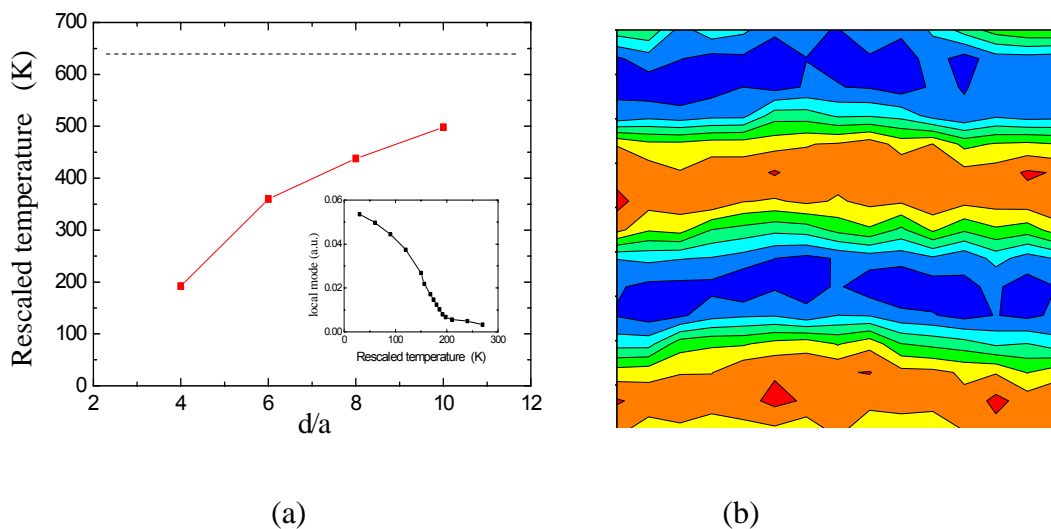


Fig.4. (a) Ferroelectric phase transition temperature with film thickness and (b) stripe domain

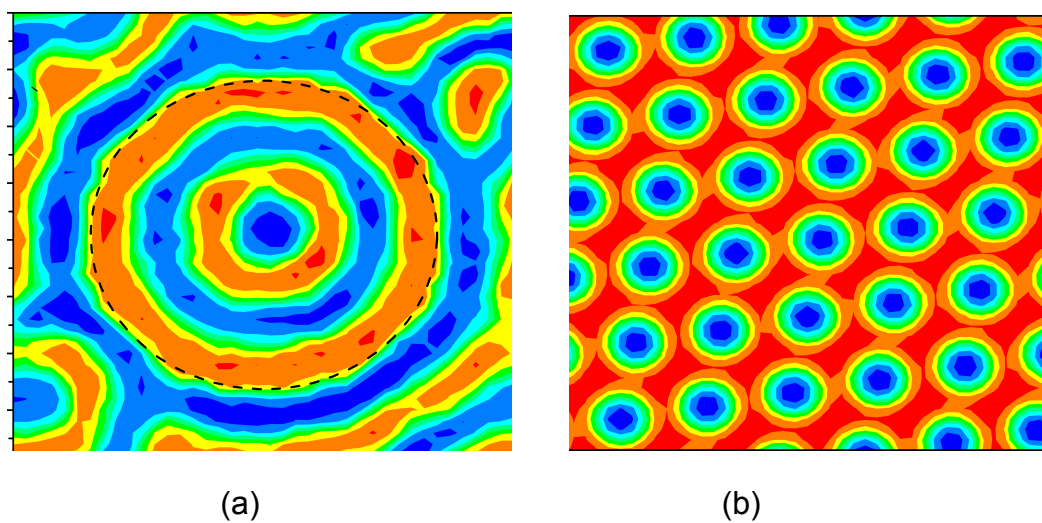


Fig. 5 Domain structure evolution under the electric field (a) $3 \cdot 10^7 \text{ V/m}$, and (b) $20 \cdot 10^7 \text{ V/m}$. Polarization in red regions are along the field.