

Modeling of lattice thermal expansion close to phase transitions: a DEA model extension

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While polynomial coefficients cannot explain the physical parameters associated, the Debye-Einstein-Anharmonicity (DEA) model [1, 2] adequately describes the temperature-dependent vibrational energy in the Grüneisen first-order approximation for lattice thermal expansion of a crystalline solid. In the DEA model, the Grüneisen parameter accounts for the isothermal and the anharmonicity parameter for the isochoric anharmonicity. Beside such advantages in DEA that concomitantly holds both quasi-harmonic and low-perturbed anharmonic [3] terms, this model is limited to explain metric thermal expansions close to phase transitions. For instance, framework material $[\text{Na}_8\text{I}_2][\text{AlSiO}_4]_6$ sodalite [4] shows Landau-type tri-critical phase transition at 1080(6) K driven by tilt mechanism. The DEA model strikingly departs from the evolution of lattice parameters from 820(10) K up to the T_c . The kentrolite-type $\text{Pb}_2\text{In}_2\text{Si}_2\text{O}_9$ exhibits a second order phase transition at 778(5) K due to group-subgroup driven coordinate changes; again, the thermal expansion between 580(10) K and T_c cannot be modeled using DEA. Starting from the Landau theory for phase transitions [5-7], we propose a model that considers additional energy contributions integrated into the DEA, leading to metric parameter calculations close to phase transition. Adding the gliding (G) function to the temperature-dependent changes of internal energy essentially extends the general description as DEA+G. Thus, for the temperature-dependent metric parameter ($M_i(T)$) the Grüneisen first-order approximation can be expressed as:

$$M_i(T) = M_{0,i} + M_i^{\text{DEA}}(T) + M_i^{\text{G}}(T) \quad (1)$$

with $M_{0,i}$ as the zero-point metric parameter of the i^{th} phase and $M_i^{\text{DEA}}(T)$ be the contributed by DEA energy. $M_i^{\text{G}}(T)$ is expressed as:

$$M_i^{\text{G}}(T) = k_G U_G = a_G \kappa_G 3N k_B T e^{-\lambda(T_c - T)^n} \quad (2)$$

where N is the number of atoms, κ_G ($1/K_0$) the compressibility, a_G the isochoric anharmonicity parameter, k_B the Boltzmann constant, T_c the phase-transition temperature, λ the purview parameter, and n the transition exponent. While κ_G could be calculated from the bulk moduli associated with the Debye- and Einstein-thermoelastic terms, the only variable parameter is the isochoric anharmonicity in the range of $a_G \sim 10^{-5} \text{ K}^{-1}$ [3]. The function $U_i^{\text{G}}(T)$ keeps the properties that describe the abrupt change of the metric parameters of a given material close to phase transition. The new approach (DEA+G) shows excellent fits for thermal expansion of both $[\text{Na}_8\text{I}_2][\text{AlSiO}_4]_6$ and $\text{Pb}_2\text{In}_2\text{Si}_2\text{O}_9$ (Figure 1), and the model can be further justified using more relevant cases.

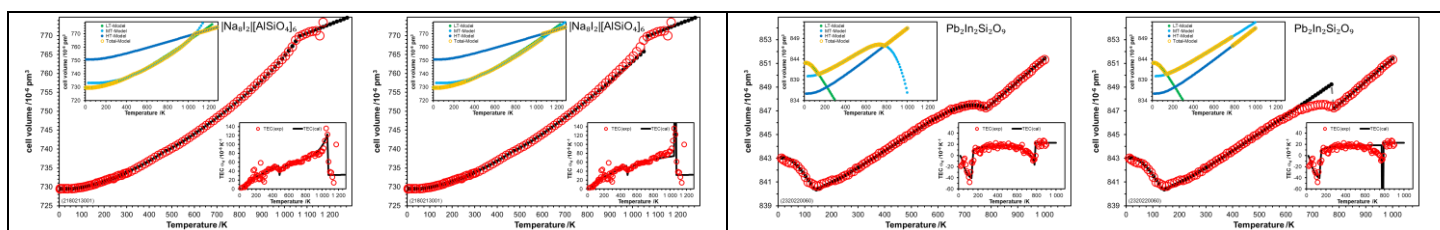


Figure 1. Thermal expansion modelling for $[\text{Na}_8\text{I}_2][\text{AlSiO}_4]_6$ sodalite and $\text{Pb}_2\text{In}_2\text{Si}_2\text{O}_9$ kentrolite. For each phase, the DEA+G (each left) and the DEA only (each right) modellings are shown for the room-temperature thermodynamically stable phases.

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