

Anharmonic effect on equation of state of NaCl

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An equation of state (EoS) of NaCl-B1 is one of the representative pressure scales to about 25 GPa. Especially, Decker's EoS [1] based on a lattice dynamics and the quasi-harmonic Debye model have been frequently used over 30 years. However, Decker's EoS cannot reproduce the 0 pressure thermodynamical properties [e.g. thermal expansion coefficient $\alpha(0,T)$ and isobaric specific heat $C_p(0,T)$]. Later Brown [2] have reported an EoS that is consistent with experimental $\alpha(0,T)$, however inconsistency of $C_p(0,T)$ is significant. These two EoSs commonly assume the quasi-harmonic Debye model and the Gruneisen parameter (g) that depends only on molar volume, i.e., $g = g(V)$.

Spetzler et al. [3] have provided us with experimental support of the $g = g(V)$ model. They measured the ultrasonic velocity to 800 K and 0.8 GPa. Major thermodynamic quantities including g were calculated from the ultrasonic data combined with $\alpha(0,T)$ and $C_p(0,T)$. It is noted that Spetzler and Yoneda [4] have called it the complete travel-time equation of state, or CT-EoS. However, we have found that Spetzler et al. calculated the CT-EoS by using $C_p(0,T)$ based on a theoretical model [5]. The discrepancy between the model C_p and experimental one [6] is as large as 7% at 800 K. This discrepancy causes the significant influence for the calculation of g , because g is given as $g = \alpha V K_s / C_p$ (K_s : adiabatic bulk modulus).

In this study, the CT-EoS is recalculated with substituting the experimental $C_p(0,T)$ for the model one. The calculated g is significantly different from the result of Spetzler et al., and shows not only positive volume dependence but also negative temperature dependence. At high temperatures, the calculated specific heat at constant volume (C_v) is significantly smaller than that obtained by using a harmonic approximation model. Furthermore, C_v is expected to have positive volume dependence.

These features of g and C_v cannot be explained by harmonic or quasi-harmonic approximation. Therefore we develop a thermodynamic model which includes an anharmonic quartic term in the potential of the lattice vibration. The classical statistical mechanics for the anharmonic potential and the quantum effect in harmonic approximation are applied to C_v of anharmonic crystal. The model for temperature dependence of g is devised from a thermodynamic identity. We report that the present anharmonic model explains all the properties of g and C_v in the scheme of the CT-EoS.

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