Equation of state of spinel ($MgAl_2O_4$): Constraints on self-consistent thermodynamic parameters and implication for mineral and fluid inclusion geobarometry

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Spinel is ubiquitous in a variety of geological environments from the crust to the uppermost mantle, and recent evidence suggests that its distribution extends close to the mantle transition zone. Due to its high stiffness and approximately isotropic elastic behavior, spinel serves as an ideal capsule for inclusions trapped under such high-pressure and -temperature (*P-T*) conditions and is therefore expected to be one of the best host minerals (and in some cases also as inclusions) for elastic geobarometry, which is used to estimate trapped *P-T* conditions for inclusions (Angel et al., 2014; 2017; Mazzucchelli et al., 2019). The accurate equation of state (EoS) of spinel is essential to obtain reliable trapping pressures by applying elastic geobarometry to a host-inclusion system containing spinel, but even the end member $MgAl_2O_4$, for which there are much more thermoelastic data than for other spinels, various EoS have been reported by previous studies, which makes it difficult to apply elastic geobarometry using spinel. Here, we have determined the accurate EoS of $MgAl_2O_4$, which is effective from the low to high *P-T* conditions and discuss the application of elastic geobarometry to spinel inclusion in olivine and CO_2 inclusion in spinel.

There are five major problems with the procedure used by previous studies to constrain the EoS of $MgAl_2O_4$: 1) all available volume (*V*), elasticity (*K*), and heat capacity (C_P) data are not reviewed, 2) volume-temperature (*V-T*) data reported in previous studies are highly variable, but there is no discussion of which data are consistent with other thermoelastic data, 3) pressure estimated from the original quartz EoS have not been corrected using the renewed EoS (Angel et al., 1997; Scheidl et al., 2016), 4) the fitting was performed using the EoS, which contains assumptions that do not hold for $MgAl_2O_4$, and 5) the effectiveness of the EoS above the order-disorder transition temperature, where the inversion degree changes significantly, is not discussed. To overcome these problems, all the available thermoelastic data have been subjected to appropriate normalization, correction, and scaling. Then, self-consistent *VT* data with other thermoelastic data were determined with the help of C_P-EoS, which uses isobaric heat capacity in addition to *P-V-T-K* data. As a result of fitting the selected self-consistent datasets with various types of EoS, we found that the thermal pressure EoS, which is a combination of the third-order Birch-Murnaghan EoS and the Mie-Grüneisen-Debye EoS, can explain the thermoelastic data of $MgAl_2O_4$ well. To exclude the effect of changes in inversion degree on the EoS, the fitting was performed using only data below 800 K, which is sufficiently lower than the order-disorder transition temperature (Suzuki et al., 2000), and then the EoS above 800 K was shown to be valid up to about 1400 K with appropriate correction.

The determination of the EoS parameters to fit the *P-V-T-K* data for $MgAl_2O_4$ was performed using the EosFit7c program (Angel et al. 2014) following the approach of Milani et al. (2017) where elasticity and volume data are fitted simultaneously. Finally, using the EoS of $MgAl_2O_4$ obtained in this study and the EoS of olivine (Angel et al., 2018) and CO_2 (Pitzer and Sterner, 1994), we calculate the entrapment isomeke of spinel inclusion in olivine and CO_2 inclusion in spinel, and discuss the applicability of elastic geobarometry to these systems.

References

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