THERMODYNAMICS OF TWIN COMPLEXIONS IN SPINEL: DEDUCING THE LOCI of TEMPERATURE and PRESSURE OF DEFORMATION PROCESSES WITHIN THE SOLAR PROTOPLANETARY DISK. V.R. Manga1,2, T. J. Zega1,2, K. Muralidharan1,2. 1Lunar and Planetary Laboratory, 2Dept. of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA. (manga@email.arizona.edu).

Introduction: Atomic-scale faults in materials offer unique evidence on their thermal and deformational histories. For example, planar faults such as twin boundaries and its associated complexions in the mineral phases not only reveal the process that caused them but also contain information on their subsequent thermal histories [1-4]. In our work, we aim to understand nebular processes by investigating twin complexions in spinel within calcium-aluminium-rich inclusions (CAIs) in meteoritic samples.

Twinning in particular can be caused by several phenomena and they are named accordingly: 1. growth twins that can occur during the condensation and growth of a mineral phase; 2. phase transformation twins that occur during displacive phase transformations; and 3. deformation twins that are caused by the plastic deformation of the crystalline mineral phase. Further, depending on the thermochemistry of the phase, these planar faults evolve in terms of their associated local atomic disorder, strain, and chemistry. Otherwise referred to as a ‘complexion’ such information can reveal the temperature and pressure under which they formed.

Mineral phases such as spinel and perovskite, nominally MgAl2O4 and CaTiO3 respectively in planetary materials, can experience twinning [5,6]. More recently, we have reported [111] twins in spinel inclusions within perovskite within a CA in the Allende CV3 chondrite. V occurs in the twin boundary as a single atomic plane along [111]. Motivated by these observations, as well as the abundance of twins in the refractory phases of CAI assemblages [1,4,5], we have undertaken a thermodynamic analysis of the twin complexions in spinel. Here we report on a first-principles quantum-mechanics investigation of the origins of twins in meteoritic spinel. This work is part of a broader effort on the chemistry and structure of CAI materials from the micrometer scale down to the atomic level and what this information tells us about their origins and histories.

First-Principles calculations and methods: Twin structures were investigated with first-principles calculations, which are carried out by using Vienna Ab initio Simulation Package (VASP) employing projector augmented wave (PAW) method [7]. The exchange correlation functional as described by the Perdew-Burke-Ernzerhof (PBE) is used in the calculations. A plane wave cutoff energy of 520 eV is used in the calculations. The thermodynamic driving force for inversion near the twin is expressed as the change in twin formation energy due to the inversion at the twin plane. In addition, to investigate the stable cation configurations at finite temperatures, the entropic contributions to the Gibbs free energies are predicted using Debye-Gruneneisen (DG) approach [8].

Results: The atomic structure of (111) twins in spinel can be described as a local hexagonal close packing (hcp) of oxygen atoms (CAC stacking) within an otherwise cubic-close-packed (ccp) sublattice of oxygen (ABCABC…)[9]. The twin plane contains mirror symmetry with respect to the O-sublattice but not with respect to the Al and Mg-sublattices. As shown in the Figure 1, with a pure Al-layer, which exhibits a Kagome (tri-hexagonal packing) lattice on one side and with a mixed Al-Mg-layer on the other side, the cation layers on each side of the (111) plane are not perfect mirror images of each other.

Polyhedral distortions occur as a result of twinning. Such distortions can be quantified via ∆d = 1/\( n \sum_{i=1}^{n} \frac{R-R}{R} \) (where R is the individual M-O bond length in (MO)n polyhedron and R is the mean M-O bond length in (MO)n polyhedron) in the vicinity of the twin and are also asymmetric about the twin plane. ∆d0 is the octahedral distortion parameter with ‘n’ is equal to 6 and ∆dt is the tetrahedral distortion parameter with ‘n’ is equal to 4. The mixed-cation layer (Figure 1) exhibits the highest strain and distortion in terms of the ∆d0 and ∆dt parameters and R. The ∆d0 in the layer with a value of 3.1x10^-4 is nearly the peak distortion on the AlO6-octahedra while the ∆dt with a value of 8.9x10^-4 is the highest distortion on the MgO4-tetrahedra. The Kagome layer within the hcp region exhibits the peak ∆d0 of 4.6x10^-4. Further, the polyhedral strain is not isotropic in the direction perpendicular to the twin plane.

Driven by polyhedral distortions, the mixed-cation layer in the twinned region (CAC stacking) exhibits a stronger driving force for the cation-inversion than any other cation-layers in the vicinity of the twin. The Gibbs free energy of inversion near the twin, within the mixed-cation layer is calculated by including the vibrational and configurational entropies, following the equation, ∆Ginv(T) = ∆Hinv(T) - T(∆Svib(T) + ∆Sconf(T)), where ∆Hinv and ∆Svib are the changes in enthalpy and entropy due to the inversion near the twin, and ∆Sconf is configurational entropy due to cation-disorder on the mixed-cation layer. Both the vibrational and configurational contributions to the entropy are positive at finite temperatures and favor the inversion.
At 1000 K, $\Delta G_{\text{inv}}^{\text{111}}$ at 100% inversion on the mixed-cation layer is 0.144 mJ/m$^2$/K. As shown in the Figure 2, the $\Delta G_{\text{inv}}^{\text{111}}(T)$ is negative in the entire range of temperature for all degrees of inversion on the mixed-cation layer while it is more favorable for complete inversion with $\Delta H_{\text{inv}}^{\text{111}}$ and $\Delta S^{\text{111}}(T)$ scaling favorably with the extent of inversion.

The V-segregation at the (111) twin also exhibits anisotropy about the twin plane. On the Al-site, V lowers the twin formation energy by 22 and 94 mJ/m$^2$ within the Kagome and mixed-cation layers, respectively. In comparison if V-substitutes on the Mg-site it lowers the twin energy by 54 mJ/m$^2$. The (111) twin formation energy in pure spinel is 946 mJ/m$^2$.

**Discussion:** Our results show that, in contrast to the pristine regions, cation inversion on the mixed-cation layer near the [111] spinel twins is thermodynamically favored in the entire range of temperature. However, in spite of the fact that a complete inversion is favored, kinetics (depending on the temperature at which twinning occurred) dictates the extent of cation-inversion. If twinning occurs at low temperatures, where the kinetics of inversion are sluggish, the developing twins could be metastable with no inversion. An approximation based on the kinetics of cation-ordering [10], indicates that the twinning at $T< 500$ K retains metastable ordering, whereas twins that formed at higher temperatures experience stable cation-inversion. Hence, twins with partial or no inversion in their vicinity point to low-temperature origins due to deformation processes. In other words, if experimental TEM characterization can reveal precisely the extent of cation-inversion near a twin boundary, it is possible to infer the temperature of twinning. Thus, our measured V-complexation of (111) twin [2] and the calculated thermodynamic driving force indicates a high temperature origin for the twin.


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