First-principles-based calculations of the CaCO$_3$–MgCO$_3$ and CdCO$_3$–MgCO$_3$ subsolidus phase diagrams

Abstract Planewave pseudopotential calculations of supercell total energies were used as bases for first-principles calculations of the CaCO$_3$–MgCO$_3$ and CdCO$_3$–MgCO$_3$ phase diagrams. Calculated phase diagrams are in qualitative to semiquantitative agreement with experiment. Two unobserved phases, Cd$_3$Mg(CO$_3$)$_4$ and CdMg$_3$(CO$_3$)$_4$, are predicted. No new phases are predicted in the CaCO$_3$–MgCO$_3$ system, but a low-lying metastable Ca$_3$Mg(CO$_3$)$_4$ state, analogous to the Cd$_3$Mg(CO$_3$)$_4$ phase is predicted. All of the predicted lowest-lying metastable states, except for huntite CaMg$_3$(CO$_3$)$_4$, have dolomite-related structures, i.e. they are layer structures in which $A_mB_n$ cation layers lie perpendicular to the rhombohedral [111] vector.

Keywords First principles · Phase diagram calculation · Order–disorder · CaCO$_3$–MgCO$_3$ · CdCO$_3$–MgCO$_3$

Introduction

Experiments by Goldsmith and coworkers (Goldsmith and Heard 1961; Goldsmith 1972, 1983) elucidated phase relations in the systems calcite–magnesite, $X\cdot$CaCO$_3$–(1$-X$)·MgCO$_3$, and otavite–magnesite, $X\cdot$CdCO$_3$–(1$-X$)·MgCO$_3$ ($X =$ mol fraction MgCO$_3$) and established the characteristic phase diagram topology: a relatively narrow homogeneity range for an ordered dolomite structure phase that transforms by a second-order transition to a disordered calcite structure phase; broad calcite + dolomite two-phase fields flank the dolomite homogeneity range. Previous phase-diagram calculations (Navrotsky and Louks 1977; Burton and Kikuchi 1984; Burton 1987; Burton and Davidson 1988) for these and related systems (e.g. CaCO$_3$–FeCO$_3$, Davidson 1994) were based on empirically derived Hamiltonians (sets of energy parameters) and directed towards: (1) finding a minimal model that qualitatively reproduces phase-diagram topology and (2) fitting experimental phase equilibria and thermochemical data (Navrotsky and Capobianco 1987; Capobianco et al. 1987; Chai et al. 1995). This paper presents first-principles (FP) phase-diagram (FPPD) calculations in which cluster expansion (CE) Hamiltonians (Sanchez et al. 1984; McCormack and Burton 1997) are fit to sets of supercell total energies ($\{E_{Str}\}$, where $Str$ indicates the crystal structure) that were calculated with a plane wave pseudopotential code (Kresse and Hafner 1993).

The calcite crystal structure (calcite, otavite, magnesite) can be idealized as interpenetrating face-centered cubic (fcc) substructures of cations (Ca$^{2+}$, Cd$^{2+}$, Mg$^{2+}$), and planar CO$_3^-$ anion groups. One [111]$_{fcc}$ vector becomes the rhombohedral three fold axis $[\langle 111 \rangle_{fcc} = \langle 111 \rangle_{rhom} = \langle 0001 \rangle_{hex}]$ because the planes defined by CO$_3^-$ groups lie in the perpendicular (111) plane $[\langle 111 \rangle_{fcc} = \langle 111 \rangle_{rhom} = \langle 0001 \rangle_{hex}]$. In the dolomite structures [CaMg(CO$_3$)$_2$ and CdMg(CO$_3$)$_2$], alternating (111) planes are occupied by different cations (e.g. dolomite, Ca–Mg–Ca– etc.), which reduces space-group symmetry from $R3c$ in calcite to $R3$ in dolomite. In both calcite and dolomite, the CO$_3^-$ groups are ordered such that all groups in the same (111) plane have the same orientation, and groups on neighboring (111) planes are oriented in an opposite sense.

In the CaCO$_3$–MgCO$_3$ system, some additional ordered superstructures have been predicted as possible equilibrium phases (Burton 1987), or reported as metastable phases in natural samples of magnesian calcite, calcian dolomite, or ankerite [Ca(Fe,Ca,Mg)(CO$_3$)$_2$ with dolomite structure; Van Tendeloo et al. 1985; Wenk and Zhang 1985; Meike et al. 1988; Reksten 1990a,b,c)].
Several superstructures can be described in terms of analogous Fcc-based ordered alloy structures (Burton and Davidson 1988; Wenk et al. 1991; Table 1). Huntite [\( \eta' \), CaMg\(_3\)(CO\(_3\))\(_4\); Graf and Bradley 1962] occurs in nature, and it exhibits CuAu\(_1\)-type ordering of both cations (as in \( \mu' \)) and CO\(_3\) anion groups. Unlike calcite, dolomite, or other superstructures considered here, the CO\(_3\) groups in huntite are orientationally ordered both between and within (111) anion layers. There are also dolomite-related layer structures that consist of various sequences of Ca- and Mg-rich layers perpendicular to [111] (Table 2).

Two factors that significantly affect carbonate phase relations are ignored in this study: (1) CO\(_3\) group orientational order disorder; (2) quasiteritary cation substitutions. The former is known to occur in CaCO\(_3\) (and cations (as in Ca- and Mg-rich layers perpendicular to [111] anion layers. There are also dolomite-related layer structures that consist of various sequences of Ca- and Mg-rich layers perpendicular to [111] (Table 2).

Table 1 Fcc-related crystal structures

<table>
<thead>
<tr>
<th>Name(^a)</th>
<th>Symbol(^b)</th>
<th>( X )</th>
<th>Space group(^c)</th>
<th>FCC-related prototype</th>
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<td>( \gamma )</td>
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<td>( C2/c )</td>
<td>Al(_2)Ti</td>
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<tr>
<td>( \mu )</td>
<td>( \times )</td>
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<td>( R3c )</td>
<td>CuMg</td>
</tr>
<tr>
<td>( \nu )</td>
<td>( \circ )</td>
<td>( \frac{1}{4} )</td>
<td>( C2/c )</td>
<td>CuMg</td>
</tr>
<tr>
<td>( \beta )</td>
<td>( \blacksquare )</td>
<td>( \frac{1}{2} )</td>
<td>( R3 )</td>
<td>CuMg dolomite</td>
</tr>
<tr>
<td>( \mathcal{H}' )</td>
<td>( \checkmark )</td>
<td>( \frac{1}{2} )</td>
<td>( R32 )</td>
<td>CuMg(_1) huntite(^d)</td>
</tr>
</tbody>
</table>

\( X = \frac{1}{2} \) for Ca\(_3\)Mg\(_3\)(CO\(_3\))\(_4\) (Table 2), \( X = \frac{1}{2} \) for CaMg\(_3\)(CO\(_3\))\(_4\) (Table 2)

\( \mathcal{H}' \) Huntite has CuMg\(_1\)-type cation order as in \( \mu' \), but its CO\(_3\) groups are orientationally ordered between and within (111) anion layers. There are also dolomite-related layer structures that consist of various sequences of Ca- and Mg-rich layers perpendicular to [111] (Table 2).

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Table 2 Dolomite-related layer structures

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<td>( [111]_{C,M} )</td>
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<td>( \square )</td>
<td>( \frac{1}{2} )</td>
<td>( R3 )</td>
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<td>( [111]_{C,M} )</td>
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<td>( [111]_{CM} )</td>
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<td>( C^1-M^1-C^1 )</td>
<td>( [111]_{CM} )</td>
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\( M = \) Mg layer

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Table 3: Calculated formation energies for \( \text{Ca}_m\text{Mg}_n(\text{CO}_3)_{(m+n)} \) and \( \text{Cd}_m\text{Mg}_n(\text{CO}_3)_{(m+n)} \) supercells; all energies are in kJ mol\(^{-1}\).

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² T-matrix: Mg, M = 0
³ ΔE₈₀/ΔE₄₈: Energy difference
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$^a$ Matrix $T$ defines supercell lattice constants, relative to rhombohedral calcite [R3c cell constants: $a$ and $\tau$; Ca: (0, 0, 0); C: (1/4, 1/4, 1/4); O: $(x, 1/2 - x, 1/4)$, $x = 0.507$] (Megaw 1973). Such that the inverse of the transpose of $T$, $t \equiv [T^T]^{-1}$, transforms listed cation coordinates (column 3) into fractional supercell coordinates, e.g. for $\delta$ phase:

$$T = \begin{pmatrix} -1 & 1 & 0 \\ 0 & 1 & -1 \\ -1 & -1 & -1 \end{pmatrix} \Rightarrow [T^T]^{-1} \cdot 0 = \begin{pmatrix} -1 \\ 0 \end{pmatrix}$$

$^b$ $\Delta E_{\delta}$ is the formation energy for a Ca$_{\text{Mg}}$Mg$_n$ CO$_3$ supercell, and $\Delta E_{\delta'}$ is for the complimentary Ca$_{\text{Mg}}$Mg$_n$ CO$_3$ supercell; $\Delta E = -1.65$ kJ mol$^{-1}$ for Ca$_{\text{Mg}}$Mg$_n$ CO$_3$ and $\Delta E = 1.92$ kJ mol$^{-1}$ for Ca$_{\text{Mg}}$Mg$_n$ CO$_3$.

$^c$ Huntite, $H' = \text{CaMg}_3(\text{CO}_3)_4$, and $\zeta$ exhibit CuAu$_3$-type ordering of CO$_3$ groups in addition to CuAu$_3$-type cation ordering in $H''$, and Al$_2$Ti$_2$-type cation ordering in $\eta^Y$. The $Y$ (Yes) superscript is attached to each $\Delta E_{\delta}$ and $\Delta E_{\delta'}$ that was used to fit the effective cluster interactions (ECIs).

**First-principles phase-diagram calculations**

Fitting the cluster expansion

The cluster expansion (CE: Sanchez et al. 1984) is a compact representation of the alloy’s configurational total energy. In the quasibinary systems studied here, the alloy configuration is described by pseudospin occupation variables $\sigma_i$, which take values $-1$ or $+1$ depending upon which cation occupies site $i$; $\sigma_i = -1$ for Ca or Cd, $\sigma_i = +1$ for Mg.

The CE parametrizes the configurational energy (per exchangeable atom; Ca, Mg, Cd) as a polynomial in pseudospin occupation variables:

$$E(\sigma) = \sum_\ell m_\ell J_\ell \left( \prod_{i \in \ell} \sigma_i \right),$$

where $\ell$ is the cluster defined by the set of sites $\{i\}$. The sum is taken over all clusters $\ell$ that are not symmetrically equivalent in the parent structure space group, and the average is taken over all clusters $\ell'$ that are sym-
Dotted line connects calcite with the lowest-energy measurement for dolomite; * with error bars is data of Chai et al. (1995) for their most disordered dolomite sample; the dashed line is the FPPD calculated total energy for a random solid solution, $\Delta E_{\text{Rand}}(X)$; the solid line connects predicted ground-state structures: $\alpha$ calcite; $\beta$ dolomite; $\gamma$ magnesite.

The end result of this procedure is a set of ECI, $\{J_{(r,t)}\}$, which define the interactions associated with $r$-body clusters of types $t$. Fitted ECI sets for CaCO$_3$–MgCO$_3$ and CdCO$_3$–MgCO$_3$ are listed in Table 4, and the products of effective pair interactions [EPI; $J_{(2,t)}$] and their multiplicities, $m_{(r,t)}$, are plotted in Fig. 3.

Ground-state analysis

Ground-state (GS) analyses were performed by brute force enumeration of all ordered configurations with 60

Ground-state analysis

Ground-state analysis was performed by brute force enumeration of all ordered configurations with 60
or fewer atoms per supercell (12 or fewer cation sites). These analyses did not predict any new GS configurations besides those shown in Figs. 1 and 2. In addition, Monte Carlo (MC) simulations described below revealed no other GS, strongly suggesting that our GS search is exhaustive.

Monte Carlo phase diagram calculations

The MAPS package includes a companion MC code (described in A. Van de Walle and M. Asta) that was used to calculate the $\text{CaCO}_3$–$\text{MgCO}_3$ and $\text{CdCO}_3$–$\text{MgCO}_3$ phase diagrams (Figs. 4, 5). This code implements semigrand canonical MC simulations, in which the total number of atoms is fixed and the chemical concentration varies in response to a fixed difference in the chemical potentials of the two cation species.

Phase boundaries at a given temperature were found by scanning a range of imposed chemical potential values while monitoring the concentration in the simulation cell. Phase transitions were located by identifying discontinuities in the concentration. Values of the concentration just before and just after the discontinuity bracketed the equilibrium concentrations of coexisting phases at the transition.

Convergence with respect to system size was tested by calculating $T_c$ for the $\text{CaCO}_3$–$\text{MgCO}_3$ system in $\text{CaCO}_3$–$\text{MgCO}_3$ supercells (3465 cation sites) was selected for all MC calculations. Thermodynamic functions of interest, such as concentration, were obtained by averaging over 1500 MC passes for each value of chemical potential and temperature. Temperature and chemical potential were scanned in increments of 5 K and 0.01 eV atom$^{-1}$, respectively. After each detected phase transition, the system was reequilibrated for 1500 MC passes before the

---

**Table 4** Effective cluster interactions in kJ mol$^{-1}$

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<th>Rhombohedral cluster coordinates minus (0,0,0)</th>
<th>( m(r, t) )</th>
<th>Multiplicity</th>
<th>$\text{CaCO}_3$–$\text{MgCO}_3$</th>
<th>$\text{CdCO}_3$–$\text{MgCO}_3$</th>
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Fig. 3 Effective pair interactions, \( J_{(2,1)} \), multiplied by their multiplicities, \( m_{(r,t)} \), for $\bullet \text{CaCO}_3$–$\text{MgCO}_3$ and $\square \text{CdCO}_3$–$\text{MgCO}_3$. The sign convention is: \( J_{(2,1)} > 0 \) implies that interlayer ordering is energetically favorable; \( J_{(2,2)} < 0 \) implies that intralayer ordering is energetically unfavorable (as postulated by Burton and Kikuchi 1984).

Fig. 4 Calculated $\text{CaCO}_3$–$\text{MgCO}_3$ phase diagram (solid and dashed lines through small open circles). Experimental phase boundary data are from Goldsmith (1983) and references therein.
process of locating the phase boundary at the next temperature was initiated.

**Discussion**

Equilibrium phase relations: comparison with experiment

Qualitatively, there are no discrepancies between calculated and experimental phase diagrams. The unobserved \( \epsilon \) and \( \epsilon' \) phases in \( \text{CdCO}_3–\text{MgCO}_3 \) were investigated experimentally. Predicted values for the critical temperatures of \( \beta \rightarrow \alpha \) order–disorder transitions at \( X = 0.5 \) are: \( T_C(\text{Predicted})/T_C \approx 1.16 \pm 0.03 \) for \( \text{CaCO}_3–\text{MgCO}_3 \), and \( T_C(\text{Predicted})/T_C \approx 1.04 \pm 0.02 \) for \( \text{CdCO}_3–\text{MgCO}_3 \). Typically, FPPD calculations overestimate transition temperatures especially when, as here, vibrational effects are ignored; e.g. \( T_C(\text{Predicted})/T_C \approx 1.32 \) for the compound \( \text{CdMg} \) (Asta et al. 1993).

Solubilities of \( \text{Ca} \) or \( \text{Cd} \) in the dolomite structure phases are significantly overestimated. In addition, the predicted \( \text{CaCO}_3–\text{MgCO}_3 \) homogeneity range for \( \alpha' \) is enhanced, and the field for two \( \text{Mg} \)-rich disordered phases is reduced, relative to the experimental diagram.

Metastable phase relations: magnesian calcite and calcian dolomite

Assuming that cation ordering is the only relevant process, the \( \Delta E_{\text{Str}} \) results plus the \( \Delta E_{\text{Rand}}(X) \) curve (dashed line, Fig. 4) provide a substantially improved basis for interpreting metastable phase relations in magnesian calcite and calcian dolomite (Wenk et al. 1991). Metastable ordered phases have a driving force for formation only if their free energies are lower than that of the disordered solution from which they might form; i.e. \( F_{\text{Ord}} < F_{\text{Rand}} \) is a necessary, but not sufficient, condition for metastable formation. Because the random state has greater configurational entropy than any ordered configuration (or a disordered phase with short-range order), it will therefore have lower free energy than any ordered state of equal or higher formation energy, at finite temperature. It follows that:

\[
\Delta E_{\text{Ord}} > \Delta E_{\text{Rand}} \Rightarrow F_{\text{Ord}} > F_{\text{Rand}},
\]

which implies that \( \Delta E_{\text{Ord}} < \Delta E_{\text{Rand}} \) is a necessary condition for an ordered phase to be a candidate for metastable formation. Thus, all phases with \( \Delta E_{\text{Ord}} > \Delta E_{\text{Rand}}(X) (\mu, \nu, \zeta) \), or \( \Delta E_{\text{Str}} \approx \Delta E_{\text{Rand}}(X), (\gamma) \) are poor candidates for metastable formation. These results clearly contradict all proposed models of ordering in magnesian calcite with \( X \approx \frac{1}{3} \). (1) the proposal of Wenk et al. (1991) that \( \epsilon \) reflections in magnesian calcite might be caused by \( \nu \)-type ordering; (2) predictions of Burton (1987) and Burton and Davidson (1988) that a \( \mu \)- or \( \zeta \)-type ordering, or a combination of the two, might actually be associated with a stable or metastable low-temperature phase. Except for huntite (see below) the lowest-energy metastable states are all dolomite-related layer structures: \( \delta, [\text{111}]_{\text{CMC3M}}; \epsilon, [\text{111}]_{\text{CM}}; \eta, [\text{111}]_{\text{CM}} \) (Table 1). From an energetic perspective, it is surprising that \( \epsilon \)-type ordering has not been reported in magnesian calcite; \( \epsilon \) is predicted to be very nearly stable, and it is substantially more stable than any of the previously predicted candidates.

Predictions of Burton (1987) “that \( \text{Ca}_3\text{Mg}((\text{CO}_3)_4 \) is probably stable at low temperature,” meaning that a phase with \( \mu \)- or \( \zeta \)-type cation order, or a combination of the two (Burton and Davidson 1988), are apparently wrong. This prediction was based on a cluster variation method (CVM: Kikuchi 1951) calculation in the tetrahedron approximation (TA), that could only include the first two EPI \( J_{(2,1)} \) and \( J_{(2,2)} \); \( nn \) interlayer and intra-layer pair interactions, plus one three-body term. The Hamiltonian fit by MAPS, however, includes the first seven EPI plus two three-body terms. Clearly, the CVM TA is not sufficient for this system because the largest clusters it includes are too small, and this demonstrates the advantage of using MC simulation for FPPD calculations; MC calculations easily handle relatively long-range interactions, whereas CVM expansions typically become intractable when interaction range exceeds third or fourth \( nn \).

Wenk et al. (1991) used a concentration wave (CW) analysis (Khachaturyan 1978; Khachaturyan and Porskhovski 1985; Khachaturyan et al. 1988) as a basis for discussing metastable phase relations between \( \alpha, \beta, \gamma, \delta, \mu, \) and \( \nu \), phases (ignoring \( \epsilon \) and \( \zeta \)). The CW criterion for a plausible transition between two phases (e.g. \( \beta \rightarrow \gamma \)) is that the two crystal structures are sufficiently similar to be related by a “simple instability;” i.e. by an infinites-
imal perturbation in the amplitude of one ordering CW which reduces the free energy of the system. This criterion combines two concepts: (1) structural similarity; (2) instability with respect to a change in ordering. Instability implies a negative second derivative of the free energy with respect to at least one order parameter, i.e., one CW. The CW analysis, however, provides no Hamiltonian with which to evaluate formation energies, free energies, or instabilities, and these are severe limitations. Also, the \( \alpha \rightarrow \epsilon \) reaction is associated with a “simple instability,” \( k_{\text{inst}} = \frac{2\pi}{\alpha} \frac{1}{2} (111)^{\text{c15}} \) in the notation of Wenk et al. (1991), and because its energy is so low, one would expect it to form readily. However, \( \epsilon \) is associated only with unobserved \( d \) reflections \( (hkl : -h + k + l \neq 3n) \), Table 2 in Van Tendeloo et al. (1985) rather than the observed \( c \) reflections.

The FPPD results establish an energy hierarchy which rules out most proposed metastable ordering processes: e.g., \( \Delta \epsilon \approx \Delta \epsilon_{\text{Rand}} \), and \( \Delta \epsilon > \Delta \epsilon_{\text{d}} \), so \( \beta \rightarrow \gamma \) is a highly unlikely reaction, but \( \beta \rightarrow \delta \) is highly plausible. Some caveats related to \( \text{CO}_3 \)-group disorder and impure samples: (1) \( \text{CO}_3 \)-group disorder would increase the energy of disordered magnesian calcite, or metastable calcian dolomite, and this could make some high-energy states accessible as metastable reaction products. \( \text{CO}_3 \)-group disorder in magnesian calcite is plausible because the \( 1260-K \) order–disorder transition temperature (Dove and Powell 1989) implies energetics that are comparable to cation order–disorder; however, disordered natural samples with higher energy than \( \Delta \epsilon_{\text{Rand}} \) have not been reported. (2) Natural samples that exhibit sharp \( e \) reflections with streaking (Wenk et al. 1991) are very Fe-rich, \( \text{Ca}_{0.5} \text{Mg}_{0.5} \text{Fe}_{0.5} \text{CO}_3 \), which may have a significant effect on their energetics. Samples of composition \( \text{Ca}_{0.95} \text{Mg}_{0.05} \text{CO}_3 \) also exhibit \( e \) reflections, but they are more diffuse, and streaking is not observed.

Huntite, \( \text{CaMg}_3(\text{CO}_3)_4 \)

Huntite (\( \mathcal{H}' \), in Fig. 1) is observed in nature (Graf and Bradley 1962), and it exhibits \( \text{Cu}_3\text{Au} \)-type ordering of both cation and \( \text{CO}_3 \) anion-group orientations. Huntite’s \( \text{CaMg}_3(\text{CO}_3)_4 \) stoichiometry is in a region of the phase diagram in which dolomite- plus magnesite-based solid solutions coexist, so it is clearly metastable. This is consistent with the FP results; \( \Delta \epsilon_{\text{inst}} \) is lower than any other \( \Delta \epsilon_{\text{d}} \) at \( \text{CaMg}_3(\text{CO}_3)_4 \) stoichiometry (Fig. 1). Note, however, that the CE-based GS analysis does not include huntite, or any other structures with orientationally ordered anion groups. Therefore, the prediction that huntite is the lowest-energy metastable state at \( \text{CaMg}_3(\text{CO}_3)_4 \) stoichiometry is weaker than it would be if \( \text{CO}_3 \) group orientational order was included in the Hamiltonian and GS search. For completeness, the formation energy of huntite structure \( \text{Ca}_3\text{Mg}(\text{CO}_3)_4 \) was also calculated; \( \Delta \epsilon_{\mathcal{H}} = 44.73 \text{ kJ mol}^{-1} \) (Table 3).

Predicted phases in \( \text{CdCO}_3–\text{MgCO}_3 \)

In the \( \text{CdCO}_3–\text{MgCO}_3 \) system, both the \( \epsilon \) and \( \epsilon' \) phases are predicted to be stable, but neither has been observed experimentally. This does not contradict experiment however, because the highest temperature at which \( \epsilon' \) is predicted to be stable is \( \sim 650 \text{ K} \), which is \( \sim 40 \text{ K} \) below the lowest temperature experiments reported in Goldsmith and Heard (1972).

Conclusions

The results presented above demonstrate semiquantitative agreement between FPPD calculations and experimental phase equilibria and thermochemical data. They also provide an energetic hierarchy that can be used to evaluate the plausibilities of proposed metastable reaction paths. Specifically, the FP and FPPD results presented above appear to rule out the proposed metastable formation of \( \gamma \) or \( \nu \) in magnesian calcite, unless the magnesian calcite is disordered with respect to both cation ordering and \( \text{CO}_3 \)-group orientation. Low-temperature \( \epsilon \) and \( \epsilon' \) phases are predicted in the \( \text{CdCO}_3–\text{MgCO}_3 \) system.

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