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COMMENTARY

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Lattice engineering via rational ordering for crystal growth and functions of materials

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Crystalline materials pack constituent atoms or molecules to form long range ordering atomic lattice, which also include the "lattice" composed of charge, spin and orbital orders at quantum degrees of freedom (Figure 1A).[1] These degrees of freedom are coupled together and determine the overall responses to stimuli, which appear as materials' electrical, magnetic, optical, thermal, and mechanical properties.[1] General crystal materials always have ordering lattice with a certain extent at different scale and degrees of freedom. In other words, defects often exist in all crystal, i.e., point defect, cation/anion disorder, dislocations, twinning, and impurities, etc. In multicomponent compounds, cations or anions should be arranged with specific order, which are called cation-ordered or anion-ordered materials, droved by balance between entropy of disordering and enthalpy of ordering. Lattice ordering or disordering have resulted in emergent properties and functions in materials science and condensed physics. A trigonal halide Li_3MCl_6 [M= Y or Er] superionic conductor has been designed by regulating cation order-disorder, in which metal ions served as both a diffusion inhibitor and pillar for maintaining interlayer distance.[2] The existence of chemical order in the medium- and high-entropy alloys have been found in experimental observation.[3] In this

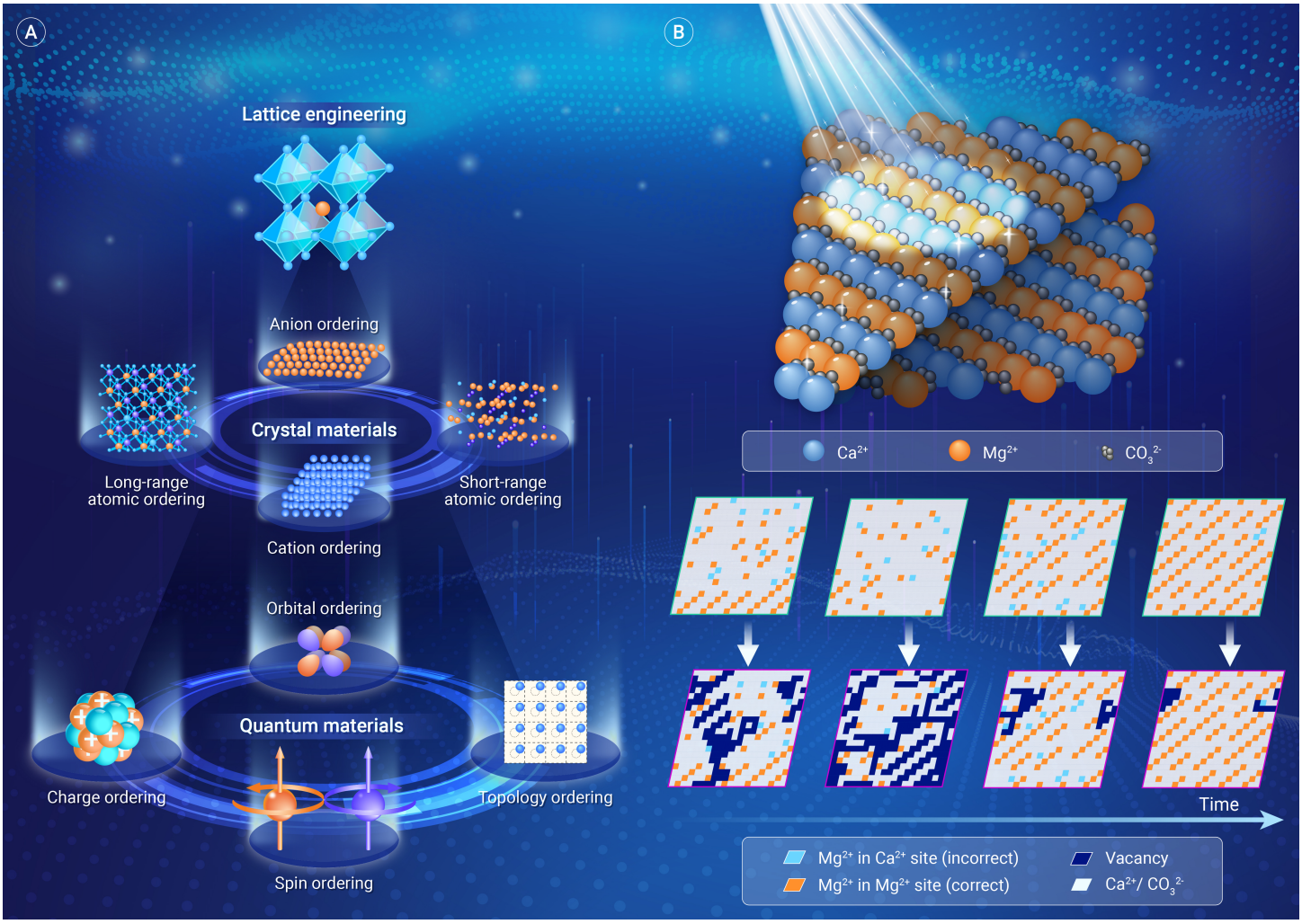

Figure 1. Lattice engineering via rational ordering (A) Lattice engineering with degrees of freedom of lattice, charge, spin, orbital, topology ordering at different scales, which affect crystal growth and magnetism-mechanics-thermal-electricity-light properties and functions of crystal and quantum materials. (B) Supersaturation fluctuations in accelerating dissolution-reprecipitation processes in dolomite ordering.[4] (Top) Dolomite step-growth and ordering in close-packed $(10\bar{1}4)$ surface. Ca^{2+} and Mg^{2+} have alternating order along $[\bar{4}41]$ step edge. (Bottom) Kinetic Monte Carlo simulations showing snapshots of surface structures from time-regulated supersaturation fluctuations at $\sigma = -1.5$.

case, twinning structure was formed in the medium-entropy-alloy nanoparticles.

For crystal growth and materials synthesis, the control of lattice ordering is also important. Large size single crystals with long-range ordering lattice, such as $LiNbO_3$, lutetium-yttrium oxyorthosilicate (LYSO), potassium dihydrogen phosphate (KDP) etc., were grown in undercooled melts or supersaturated solutions.[5] The crystal-liquid interface in melts and solutions often disturb the formation of perfect long-range lattice ordering structure due to

the fluctuation of undercooling and supersaturation degree at growth interface. In some serious instances, cation-disordered growth often induced high strains, and inhibit further atom deposition. Crystal growth process includes the chemical bond breaking and bond forming at crystal-liquid interface. Chemical bonds breaking between atoms of a material needs a kind of equivalence between heat energy and strain energy to break bonds with a constant maximum storage of both energy forms. In order to maintain ordering lattice, the method with coupling of force-thermal-electrical- magnetic-optical fields is necessary to balance strain and heat energy. Therefore, annealing, recrystallization processes are often used after crystal growth and crystal manufacturing.

Very recently, Sun's group reported to solve the long-standing mystery known as the "dolomite problem" by the growth of dolomite ($Ca_{0.5}Mg_{0.5}CO_3$) under fluctuating cycling of supersaturation and undersaturation solution.[4] In ambient conditions, dolomite is failed to grow from constant supersaturated solutions. In contrary, the massive deposits of dolomite existed in natural environment. The fundamental science question is why a thermodynamically stable inorganic carbonate mineral cannot directly precipitate abiotically from supersaturated solutions. Dolomite exhibits alternating Ca^{2+} and Mg^{2+} layers perpendicular to the [0001] direction. The primary growth surface of rhombohedral carbonates is the close-packed $(10\bar{1}4)$ surface, and the primary step edges for growth and dissolution are along the symmetry-equivalent $[48\bar{1}]$ and $[\bar{4}41]$ directions (Figure 1B). In ordered dolomite, Ca^{2+} and Mg^{2+} alternate along these $[48\bar{1}]$ and $[\bar{4}41]$ step edges. Thus, under constant supersaturation, it needed ~10^7 years for dolomite step-edge growth and ordering in constant supersaturation.

Kim et al found supersaturation fluctuations can accelerate dolomite ordering by up to seven orders of magnitude.[4] If dolomite is initially precipitated in a disordered protodolomite form, this disordered structure will fundamentally be in a nonequilibrium state. On this disordered surface, the locally more-ordered regions are correspondingly more stable and therefore have lower solubility. Disordered regions will therefore dissolve faster than ordered ones, whereas ordered regions of the surface, once formed, will dissolve more slowly. Over time, dissolution-reprecipitation processes will gradually evolve a disordered dolomite surface toward an ordered surface, upon which subsequent dolomite layers can grow (Figure 1B). The dolomite step-edge growth easily formed a cation-disordered surface because that the entropy of cation disordering exceeds the enthalpy of ordering in the early stages of dolomite growth. The provided atomistic ordering mechanisms can extend to geological length scales. The growth and ripening of crystals with some disordered structures can be kinetically accelerated by deliberate periods of mild dissolution.

Except for crystal growth, rational ordering lattice can reshape materials' properties and functions. The ordering can exist at different degrees of freedom (lattice, charge, spin, and orbital) and different scales (from atomistic to microscopic scale), which may be dynamically intertwined to launch materials' mechanical, thermal, electrical, magnetic, and optical properties.[1] In this field, the following fundamental questions are need to be studied: What is the internal origin of order or disorder? How to characterize the correlated disorder or local order? What is the detailed correlation between ordering and materials properties? Disorder or local order structures have been characterized using special aberration corrected transmission electron microscope, atomic electron tomography, high-resolution synchrotron grazing incidence X-ray diffraction, femtosecond X-ray laser diffraction. This field still call for more fundamental study of rational ordering lattice engineering. In future, the controlling of ordering or disordered lattice of a crystal material with advanced technology maybe execute some specific "functions" in response to certain stimuli.

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AUTHOR CONTRIBUTIONS

K.C. wrote the manuscript with input from D.X. D.X. supervised the project. All authors contributed to the manuscript and approved the final version

DECLARATION OF INTERESTS

The authors declare no competing interests.