

CHAPTER 5.

Conclusion.

Solid-state chemistry is moving beyond classical descriptive crystal chemistry to the study of the dynamic processes that inter-relate structural classifications. A dynamic view of solids is driven in part by the intellectual challenge and in part by practical applications, i.e., the development of "smart materials" that can be used in devices with sensing, processing and actuating functions to respond their environment. As solid-state chemistry moves toward the rational synthesis of designed materials, understanding solid-state reaction mechanisms becomes increasingly important in gaining synthetic control over composition and morphology. The research presented in this dissertation emphasizes the dynamic interplay between structure and properties under optical excitation, thermal stress and chemical stress and considers the mechanisms of the responses to these external stresses by CuAlCl_4 .

In terms of designing optical materials, one may recognize how the choice of building blocks for the three dimensional framework of $\alpha\text{-CuAlCl}_4$ has led to its brilliant, room temperature, blue luminescence. The $\text{CuCl}_{4/2}$ corner-sharing tetrahedral building units are well isolated by $\text{AlCl}_{4/2}$ tetrahedra in the framework structure. These isolated copper (I) centers serve as intrinsic activators giving rise to a brilliant blue luminescence. The heavy ion substitution in the solid solution $\text{CuAlBr}_x\text{Cl}_{4-x}$ results in the quenching of luminescence that is directly proportional to the statistical distribution of Br throughout the lattice. The flexibility of the metal halide structure is responsible for the reversible binding of small molecules by $\alpha\text{-CuAlCl}_4$. The coupling of photoluminescence and gas sorptive properties leads to a useful probe of the chemistry of the system.

In contrast to the optical properties, which focus on the dynamics of charge transfer in CuAlCl_4 , the phase transformation from $\beta\text{-}$ to $\alpha\text{-CuAlCl}_4$ represents a

dynamic process of framework reconstruction in which atoms are re-arranged. Using *in situ* time-resolved ^{63}Cu MAS NMR and synchrotron PXRD, kinetic and activation parameters for the phase transformation from β - to α - CuAlCl_4 have been determined which provide the basis for an atomistic description of reaction mechanism. The MAS NMR parameters were successfully simulated and demonstrate the sensitivity of the ^{63}Cu nucleus to subtle changes in its environment. Time-resolved ^{63}Cu MAS NMR kinetic data for the phase transformation have been shown to obey a first-order Avrami-Erofe'ev rate law. The results of variable temperature time-resolved powder X-ray diffraction experiments show that the transformation of pseudo-hexagonal close-packed β - CuAlCl_4 into pseudo-cubic close-packed α - CuAlCl_4 is a first-order phase transition with no intermediate phase. A shearing mechanism and a mechanism involving random motion and reordering seem to be unlikely, rather these data suggest an ordered one-dimensional growth mechanism. The one dimensional growth occurs in the direction perpendicular to the close packed layers and involves a combination of Cu^+ self-diffusion and a translational reorganization of the close-packed anion layers imposed by periodic rotations of AlCl_4^- tetrahedra. This atomic re-ordering appears to be directed by the rotational and translational degrees of freedom allowed by the symmetry constraints of the crystalline lattice. This mechanistic study highlights the importance of considering the lattice symmetry in the understanding of first-order phase transitions and shows how simple arguments based on the energetics of individual molecular-type sub-units are useful for evaluating different transformation mechanisms. Furthermore, the symmetry breaking events of the lattice reconstruction only become possible when the amplitude of the symmetry-allowed librations exceeds some threshold determined by the phase

boundary. Finally, this mechanistic understanding suggests that degeneracy of the symmetry-allowed lattice librations may impact whether or not a given metastable phase can be isolated. More mechanistic examples are clearly required to explore the generality of some of these ideas, however, this latter suggestion in particular may represent a step towards the goal of rationally designing metastable materials.

The reversible reconstructive sorption of ethylene by α -CuAlCl₄, at modest pressures, also demonstrates the ability of a metal halide framework to undergo a dynamic, and in this case reversible, reconstruction. The degree to which this reconstruction occurs has been related to the Cu(I)-olefin bond that is characterized by both σ -donation into the Cu *4s* and π -donation from the Cu *3d* orbitals. The tuning of the binding strength of ethylene and other olefins to Cu(I), based on the σ -donor strength of the ancillary ligands in the complex, is seen in the structural trend of Cu-*et* distances and the ¹³C MAS NMR chemical shifts. In addition to the ancillary ligands, structural considerations are identified that influence the reactivity of Cu(I) ethylene, vis-à-vis the pseudo-tetrahedral and pseudo-trigonal planar coordination geometries adopted by the adducts. The coordinative unsaturation of (C₂H₄)₂CuAlCl₄, opens up a high lying filled Cu(I) *3d* orbital, and a low lying empty Cu(I) *4p* orbital, creating a reactive center on the face of the trigonal plane of the (C₂H₄)₂CuCl fragment. By analogy with a proposed mechanism for the structural analog Ni(C₂H₄)₃, the di-ethylene compound provides a model for the catalytic species in previously known dimerization and trimerization of ethylene. Structural considerations also lead to the understanding that the similar chemical and physical properties of the two mono-ethylene adduct phases are rooted in their common pseudo-tetrahedral coordination of the copper(I). The differentiation of the

β - and α -(C_2H_4)CuAlCl₄ phases is shown to be based on crystal packing considerations of common structural elements.

The dynamics of the reconstructive sorption of ethylene are explained in terms of three limiting processes: (1) the direct formation of (C_2H_4)₂CuAlCl₄ from α -CuAlCl₄, (2) the direct formation of (C_2H_4)CuAlCl₄ from α -CuAlCl₄ and (3) the formation of (C_2H_4)₂CuAlCl₄ from (C_2H_4)CuAlCl₄. Experimental results are explained in terms of these three processes and a classical picture of solid-state diffusion of ethylene through the forming adduct phases, combined with nucleation and growth at solid-solid phase boundaries. Crystal-packing considerations are invoked to differentiate the rapid diffusion of ethylene through solid (C_2H_4)₂CuAlCl₄, as compared to diffusion through solid (C_2H_4)CuAlCl₄. The recognition of common structural elements shared by the parent metal halide framework and the crystal structures of the adduct phases leads to a mechanistic description of phase inter-conversion within the phase boundary. The importance of the van der Waal's channels in directing the excision of structural elements from the parent α -CuAlCl₄ phase to form the adduct phases becomes apparent in this mechanistic model.

It is noteworthy that different structure-property relationships emphasize different structural elements and that it has been useful to be flexible in the choice of structural sub-units defined for the same structure, depending on the property being probed. For example, in the optical study the CuCl₄³⁻ fragment was emphasized, but in the β - to α -CuAlCl₄ phase transformation it was useful to focus on the AlCl₄⁻ fragment and consider the Cu⁺ as an independent unit able to hop between interstices. The 2x2 chains of metal centered polyhedra, observed as common structural elements in the ternary halide and

both mono- and di-ethylene adducts, indicate the significance of recognizing more complex structural features. The role of unit-cell symmetry in determining the properties of crystalline solids is well known, however it is also useful sometimes to think, “out-of-the-box”. Recognition of the close-packed layers as the structural feature guiding the dynamic process of the symmetry-breaking event in the β - to α -CuAlCl₄ phase transformation is an example of this. Similarly, the van der Waal’s channels in α -CuAlCl₄ act as the structural feature guiding the dynamic process in the sorptive reconstruction that occurs upon exposure to ethylene. The initial impetus of this work, to wed the well known crystal chemistry of metal oxides to the reactivity of metal halides, in the design of corner-shared tetrahedral frameworks, has led to a rich chemistry that has enhanced our understanding of dynamic solid-state processes.