

## Introduction

### *What makes “Solid State Chemistry” an important and distinct subdiscipline of chemistry?*

(1) The densities of condensed matter, i.e., solids and liquids, exceed those of gases by factors of  $10^2$ – $10^4$  g/mL: at room temperature and pressure, the densities of solids and liquids are  $\sim 0.1$ – $10$  g/mL whereas they are  $\sim 0.001$  g/mL for gases. Therefore, the distances between different atomic or molecular components of a gas are much larger than the sizes of these entities so that most of the internal energy of a gas is translational kinetic energy. On the other hand, interatomic distances in solids and liquids are similar to atomic sizes, so translational motion of atoms in condensed matter is more restricted.

The chemical and physical behavior of solids involves the cooperative actions of atoms or molecules over length scales that are much larger than the sizes of atoms. Atomic radii range from  $\sim 0.3$  Å for He to  $\sim 3.0$  Å for Cs with an average of  $\sim 1.6$  Å over all elements. As a result, types of matter can be differentiated by the following length scales and numbers of atoms per fundamental building unit or domain:

Matter Type	Length Scale (1 nm = 10 Å)	Numbers of Atoms
<i>Molecular</i>	0.2–1.0 nm	$10^0$ – $10^2$
<i>Nanosopic</i>	10–100 nm	$10^4$ – $10^8$
<i>Microscopic</i>	1–100 $\mu$ m	$10^{10}$ – $10^{17}$
<i>Macroscopic</i>	1 mm – 10 m	$10^{20}$ – $10^{28}$

Macroscopic samples of matter can even reach geological scales as observed for some naturally occurring crystals, such as selenite (a variety of gypsum;  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), calcite ( $\text{CaCO}_3$ ), quartz ( $\text{SiO}_2$ ), and galena ( $\text{PbS}$ ).

Molecular scale behavior occurs in gases and dilute liquid solutions, whereas microscale and macroscale phenomena are intrinsic to solids and liquids. *Mesoscopic* phenomena, which cover nanoscopic to microscopic scales, are becoming increasingly apparent due to ongoing advances in electron microscopy and nanoscale chemistry. Although both mesoscopic and macroscopic substances contain a large number of atoms, differences in their respective properties are significantly influenced by their length scales. The average properties of a macroscopic substance often obey classical physical laws because the material is treated as either a continuum or bulk volume with a negligible surface area. As a result, surface effects can be ignored. On the other hand, the properties of mesoscopic materials exhibit effects of quantum confinement, which leads to noticeable fluctuations or deviations from the bulk properties of the macroscopic substance. Therefore, the length and number scales of solid-state phenomena contribute to the significance and distinction of solid-state chemistry as a sub-discipline.

Research in solid state chemistry involves four primary and mutually interwoven activities: (i) developing reaction strategies that effectively influence product stoichiometry; (ii) utilizing structural chemical principles to assess atomic arrangements and coordination environments in solids; (iii) elucidating electronic structure to derive important chemical bonding features; and (iv) analyzing measurable properties. Certain important considerations for each of these research emphases include:

**REACTIONS and COMPOSITIONS:** Temperature, pressure, and reaction containers are important factors to consider when designing and carrying out a solid-state reaction. High temperatures allow atoms in condensed phases to diffuse over time and length scales so as to achieve equilibrium in reasonable times. Moreover, temperature controls the values of Gibbs free energies, which dictate the reaction components that will dominate at equilibrium. However, at elevated temperatures, it is important to consider whether the container material will or will not react with any chemical constituents of a reaction. Furthermore, if gases are generated or used as reactants, then attention to safety demands recognizing how the container responds to changing pressure. Improvements in high pressure technology, such as the diamond-anvil cell, have led to increasing focus on solid-state reactions at high pressures.

The morphology of solids and the differences between their *bulk* and *surface* properties are important because they can influence reaction kinetics. In particular, as crystals nucleate, low-energy surfaces grow preferentially as compared to high-energy surfaces, a result that affects crystalline shapes. Another example is the different oxidation behavior for the metals Al and Fe.  $\text{Al}_2\text{O}_3$  forms a thin protective scale on the surfaces of aluminum and prevents diffusion of  $\text{O}_2$  molecules or O atoms to further oxidize the bulk metallic aluminum.<sup>1</sup> On the other hand, an oxide coating like  $\text{Fe}_2\text{O}_3$  does not form on the surface of iron so that bulk Fe remains vulnerable to oxidation. In addition to surface effects for crystalline morphologies and chemistry, the *interfaces* (grain boundaries) at which different solid domains (grains) meet each other in a bulk specimen can affect not only the kinetics of solid-state reactions but also the outcomes of property measurements.

Solids also broaden our perspectives about stoichiometry. If macroscopic domains of solids are considered to be “quasi-infinite molecules” because they contain  $\sim 10^{23}$  atoms, then empirical formulas for solids can be *nonstoichiometric*, i.e., the subscripts in chemical formulas need not be integers. Such compounds are called *berthollides*, whereas stoichiometric compounds are called *daltonides*. The empirical formulas of many solids do not have to follow Dalton’s laws involving integer compositions due to the presence of defects or vacancies in the bulk. In essence, what is the significance of an integer scale of chemical composition when there are  $\sim 10^{23}$  atoms in a single chemical domain?

Nonstoichiometry can be extremely important for properties. For example, the high- $T_C$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  relies on there being a small but measurable fraction of vacancies at certain O atom sites in its crystal structure ( $0.1 \leq \delta \leq 0.3$ ). Another example is the polymer polyacetylene  $(\text{CH})_\infty$ . When undoped,  $(\text{CH})_\infty$  is semiconducting, but when it is doped with small amounts of bromine,  $(\text{CH})\text{Br}_x$  ( $0 < x \leq 0.2$ ), the material obtains an electrical conductivity at room temperature that is  $\sim 10\%$  the conductivity of metallic copper. If the concentration of vacancies, dopants, or other defects becomes sufficiently large in the ideal bulk material, then the atomic structure and properties can be influenced by their arrangement in the bulk.

**(2) ATOMIC STRUCTURE:** This is the *central issue* of research in solid state chemistry because there are widely accepted interrelationships among atomic structure, chemical composition, chemical reactivity, and physical characteristics. Therefore, structure determination is a primary activity in the research efforts of solid-state chemists. For this, diffraction using single crystals or polycrystalline samples is the essential tool, but nuclear magnetic resonance spectroscopy and electron microscopy can also be effective. Diffraction relies on the presence of

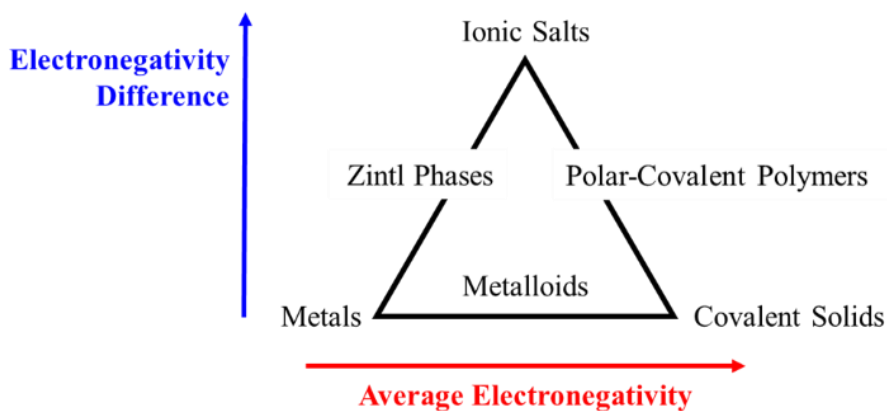
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<sup>1</sup> R. Prescott & M.J. Graham, *Oxid. Metals* **1992**, 38, 233-254.

long-range order of atoms. All solids display some degree of short-range order because atoms cannot be separated by arbitrarily short interatomic distances. Therefore, long-range order is a convenient and useful way to discriminate among different solid-state materials: (a) crystalline solids have the highest degree of long-range order; (b) quasicrystalline and other incommensurate structures exhibit intermediate long-range order; and (c) amorphous or glassy structures have essentially no long-range order. The type of long-range order exhibited by a solid sample significantly influences how effectively and conclusively its microscopic atomic structure can be characterized.

The stability of any solid-state compound is also intimately connected to its atomic structure and chemical composition. Characteristics such as valence electron concentrations (electron-to-atom ratios), derived from chemical compositions, and sphere packing efficiencies, which are evaluated by treating atoms or ions as spheres with specific radii, can provide some rationale for stability. However, and most importantly, atomic structures and compositions provide the essential information for calculating electronic, vibrational, and magnetic structures that are analyzed for structural stability and assessing modes of chemical bonding.

**CHEMICAL BONDING:** The forces holding atoms together to give extended structures involve a combination of short-range and long-range interactions that are typically identified as metallic, ionic, or covalent bonding. They are also used to distinguish different classes of compounds, such as on a van Arkel-Ketelaar triangle,<sup>2</sup> which is an example of a structure map:



In this diagram, which is designed essentially for binary compounds, every substance receives two coordinates. The  $x$ -coordinate is the average electronegativity value of the two atomic components. Atomic electronegativities can be assigned using different definitions, but effective values for this diagram are *absolute (Mulliken) electronegativities*,<sup>3</sup> which are evaluated as the averages of the first ionization energies and the electron affinities of the elements. The  $y$ -coordinate is the corresponding electronegativity difference between the two atomic components. In this map, the base of the triangle is the sequence of elements going from most electropositive (Cs) to most electronegative (F), and the apex is the most ionic compound (CsF). All binary compounds, then, find a position inside the triangle, but the scales of the two axes do not have to be linear. As a result, the van Arkel-Ketelaar diagram is a qualitative structure map that

<sup>2</sup> L.C. Allen, et al., *J. Molecular Struct.*, **1993**, 300, 647-655; W.B. Jensen, *Bull. Hist. Chem.* **1992**, 13/14, 47-59; and W.B. Jensen, *J. Chem. Educ.* **1995**, 72, 395-398.

<sup>3</sup> R.G. Pearson, *Inorganic Chemistry*, **1988**, 27, 734-740.

emphasizes the quasi-continuous relationships among the different bonding types. Furthermore, various structure maps using other types of coordinates can be useful in solid-state sciences not only for classifying substances but also for predicting properties.<sup>4</sup>

**(3) PROPERTIES:** Unlike discrete molecules, solids can show *collective* or *cooperative* phenomena. To understand what this means, as a gedanken experiment, consider one mole of H atoms in the gas phase. Each H atom has one unpaired electron that creates a local magnetic moment. In the gas, the motions of these H atoms are uncorrelated translations, and the total magnetization of the gas is zero arising from a *random superposition* of the local magnetic moments at the H atoms. If the gas condenses into an ordered solid and there are sufficiently strong exchange interactions between neighboring H atoms, then the total magnetization of the solid can take on nonzero values because the superposition of local moments is no longer random throughout the solid. As a result, magnetization arising from ordering of local magnetic moments in a solid is a collective phenomenon that involves all magnetically active sites. Some important cooperative properties that are intrinsic to the solid state include: (1) superconductivity; (2) topotactic reactions, which are collective and synchronous shifts of layers of atoms during a chemical reaction to create new structures, such as by intercalation; and (3) magnetic ordering phenomena like ferromagnetism and antiferromagnetism.

The *electronic properties* of solids are closely tied to chemical bonding and are often couched in whether the bonding modes involve “delocalized” or “localized” electrons, although electrons in molecules can also be classified as localized or delocalized. Nonetheless, metallic bonding is often synonymous with delocalized electrons, whereas covalent and ionic bonding involve electrons localized either in bonds or at ions. Regardless of many of the philosophical and scientific arguments behind the definitions of electronic localization and delocalization, atomic structure greatly influences the electronic properties arising from “delocalized” and “localized” bonding. For example, consider similarities and differences between the chemical bonding features of the benzene molecule and sodium metal. In benzene, three pairs of  $\pi$ -bonding electrons contribute to a ring current via their delocalization around the ring, but the six-membered ring is structurally rigid due, in large part, to the six pairs of localized  $\sigma$ -bonding electrons. On the other hand, each sodium atom has just one valence electron but four low-energy valence atomic orbitals, which overlap with orbitals on adjacent Na atoms in the solid to form partially occupied electronic bands that extend throughout the structure. However, this model of electronic structure also exists in gas-phase clusters of sodium atoms. Therefore, how many sodium atoms are necessary to agglomerate before the structure shows “metallic” characteristics?<sup>5</sup>

Many properties in solids are *linear* responses to external forces. These responses can be *equilibrium properties*, which lower the total internal energy of the system, or *transport properties*, which represent small departures from equilibrium and are treated by steady-state conditions. A linear response  $Y$  is related to an applied force  $X$  by an effect  $K$  via the constitutive relation:  $Y = KX$ . Effects are characterized as either principal or cross terms. Principal effects relate conjugate forces and responses; cross effects relate nonconjugate forces and responses. Some examples of linear responses and their principal effects are:

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<sup>4</sup> D.G. Pettifor, *J. Phys. C* **1986**, C19, 285-313; K.M. Rabe, J.C. Phillips, P. Villars, I.D. Brown, *Phys. Rev. B*, **1992**, B45, 7650-7676.

<sup>5</sup> B.K. Teo and H. Zhang in *Metal Nanoparticles: Synthesis, Characterization, and Applications*, Eds. D.L. Feldheim, C.A. Foss, Jr., Marcel Dekker, Inc., New York, 2002, pp. 55-88.

Equilibrium Properties

Thermal:  $\Delta S = (C/T)\Delta T$  = measure of the ability to become disordered

$X = \Delta T$  = temperature change (Kelvin)       $Y = \Delta S$  = entropy change (Joule/Kelvin)

$K = C/T$  = heat capacity/temperature (Joule/Kelvin<sup>2</sup>)

Electrical:  $D = \epsilon E$  = measure of the ability to be polarized in an electric field

$X = E$  = electric field (Volt/meter)       $Y = D$  = electric displacement (Coulomb/meter<sup>2</sup>)

$K = \epsilon$  = dielectric permittivity (Coulomb/Volt·meter = Farad/meter)

Magnetic:  $B = \mu H$  = measure of the ability to be magnetized in a magnetic field

$X = H$  = magnetic field (Ampere/meter)       $Y = B$  = magnetic induction (Tesla)

$K = \mu$  = magnetic permeability (Tesla·meter/Ampere = Henry/meter)

Mechanical:  $\epsilon = s\sigma$  = measure of the deformation of a material under exertion of forces or pressure

$X = \sigma$  = stress (Newton/meter<sup>2</sup> = Pascal)       $Y = \epsilon$  = strain (no units)

$K = s$  = elastic compliance (meter<sup>2</sup>/Newton)

Transport Properties

Energy:  $\phi = \kappa \nabla T$  (Fourier's law of heat conduction)

$X = \nabla T$  = temperature gradient (Kelvin/meter)       $Y = \phi$  = thermal energy flux (Watt/meter<sup>2</sup>)

$K = \kappa$  = thermal conductivity (Watt/meter·Kelvin)

Charge:  $j = \sigma E$  (Ohm's law of electrical conductivity)

$X = E$  = electric potential gradient (Volt/meter)       $Y = j$  = current density (Ampere/meter<sup>2</sup>)

$K = \sigma$  = electrical conductivity (Ampere/Volt·meter = Siemens/meter)

Matter:  $J = -D \nabla c$  (Fick's law of matter diffusion)

$X = \nabla c$  = concentration gradient (mole/meter<sup>4</sup>)       $Y = J$  = matter flux (mole/meter<sup>2</sup>·second)

$K = D$  = diffusivity (meter<sup>2</sup>/second)

Specific characteristics of the force  $X$ , the corresponding response  $Y$ , and the solid sample place important constraints on the characteristics of the overall effect  $K$ . In particular, forces and responses can be scalar, vector, or tensor quantities:  $\Delta T$  and  $\Delta S$  are scalars;  $E$ ,  $D$ ,  $H$ ,  $B$ ,  $\nabla T$ ,  $\phi$ ,  $j$ ,  $\nabla c$ , and  $J$  are vectors; and  $\sigma$ ,  $\epsilon$  are tensors. For single domains of crystalline solids, the vector and tensor responses give distinct effect outcomes depending on the orientation of the atomic structure with respect to the applied force. For polycrystalline samples ("powders"), with randomly oriented crystalline domains, or noncrystalline solids, the anisotropic effect outcomes will be averaged.

The constitutive relation also introduces the possibility of cross or interaction effects, which relate nonconjugate forces and responses. Some examples of cross effects include:

Magnetocaloric effect:  $\Delta S = qH = \sum q_i H_i$  ( $i = 1,2,3$ ) (thermal with magnetic)

A change in magnetic entropy effected by an applied magnetic field. Although  $\Delta S$  is a scalar and  $H$  is a vector, which requires the effect  $q$  (Joule/Tesla·Kelvin) to be a vector, measurements are accomplished using polycrystalline samples, so that an averaged (scalar) outcome is measured.

Thermal expansion:  $\epsilon = \alpha \Delta T$ ;  $\epsilon_{ij} = \alpha_{ij} \Delta T$  ( $i, j = 1, 2, 3$ ) (mechanical with thermal)

A change in mechanical stress, which manifests as a relative volume change, by a change in temperature. Volumes of solids generally increase as temperatures increase, but there are some materials that show “negative thermal expansion” (NTE).

Piezoelectric:  $\mathbf{D} = d\boldsymbol{\sigma}$ ;  $D_i = \sum d_{ijk} \sigma_{jk}$  ( $i, j, k = 1, 2, 3$ ) (electrical with mechanical)

The ability to generate an electric charge or electric potential in response to a mechanical stress.

In summary, solid state chemistry is a broad discipline that both relies on and contributes to the physics and engineering of matter. Often, the first step is the preparation of a proper sample, followed by thorough structural characterization and chemical analysis. As the discipline has matured, these results are accompanied by quantum chemical calculations to assess chemical bonding and electronic structure and a variety of physical property measurements.