Research News

Symmetry Reduction in Solid Solutions: A New Method for Materials Design

Since 1808 Proust's Law of Definite Proportions has played a key role in the development of modern chemistry, but by focussing attention on "pure" substances it has subtly tended to discourage chemists from studying solid solutions. Recently they are rediscovering what metallurgists have long known, that solid solutions offer exceptional opportunities for tailoring the physical and chemical properties of materials.

Most chemists would probably view a molecular solid solution as the analogue of a fluid solution, envisioning a lattice of host molecules replaced at random by guest molecules. For a more detailed understanding of the system's properties they would probably consult its phase diagram. This vision suffers from two serious errors which illustrate the maxim that casual application of valid concepts can be more misleading than simple ignorance.

The first error is to assume equilibrium. Most crystals are kinetic, not thermodynamic, phenomena. The distribution of solute molecules, like a crystal's overall shape, is controlled more by the dynamics of crystal growth than by the system's equilibrium stability. Once a molecule is built into the lattice, it is usually slow to change position or orientation. Local equilibration at the solid-fluid interface is probably faster than in the bulk, but even crystal surfaces rarely display the equilibrated, symmetrical form in which the shape and area of each facet is adjusted to minimize surface free energy. The failure of crystals to equilibrate has long been recognized as important both in theory and in technology. A key factor in increasing the sensitivity of photographic emulsions was learning to influence the dynamics of silver halide crystallization so as to obtain a tabular crystal habit.

The presence of a second error in the naive view of solid solutions was recognized only quite recently. Its recognition has fundamental implications both for technology and for our understanding of crystallization. This error is the assumption that guest molecules are randomly oriented, that is, that unit cell sites which are related to one another by symmetry operations of the host's crystal space group should have equal probabilities of occupancy by guest molecules. If occupancy were random, a guest molecule would disturb local symmetry in its immediate vicinity, but the average guest population for each type of lattice site would still reflect the overall symmetry of the host. Thus bulk properties of macroscopic crystal fragments would display the same symmetry as the pure host.

Such retention of symmetry makes good thermodynamic sense, but crystals are not equilibrium systems. Twenty years ago *Kitaigorodsky* cautioned that "Formally speaking, (retention of symmetry) does not necessarily occur."[1] Nonetheless he asserted on intuitive and empirical grounds, "If a substitution of A molecules for B is possible in which the B crystal retains its symmetry, we shall find that this is the substitution that actually occurs." This point of view seemed so natural that few scientists took seriously his "formal" warning that selective substitution might destroy crystal symmetry.

In a series of publications that began last summer *Lahav* and *Leiserowitz* of the Weizmann Institute and their collaborators have challenged the assumption of symmetrical substitution.[2] On the basis of this and other recent work,[3,4] it now seems that solid solutions should routinely show lower symmetry than the pure host, and that this reduction will provide a new level of control over solid-state properties.

The Weizmann studies began with efforts to control crystal growth by inhibiting molecular deposition on particular facets through selective adsorption of additives. Additive molecules were designed so that the portion in contact with the crystal facet closely resembled the host molecule, while the portion away from the crystal surface differed in structure. Thus the additive would adsorb strongly to a chosen crystal face, become trapped within the surface layer, and by protruding prevent deposition of further layers of host molecules on that face. Deposition would continue unhindered on faces to which the additive did not adhere.

To visualize this process, consider the packing of "ducks" in Figure 1. The guest ducks have a projection be-

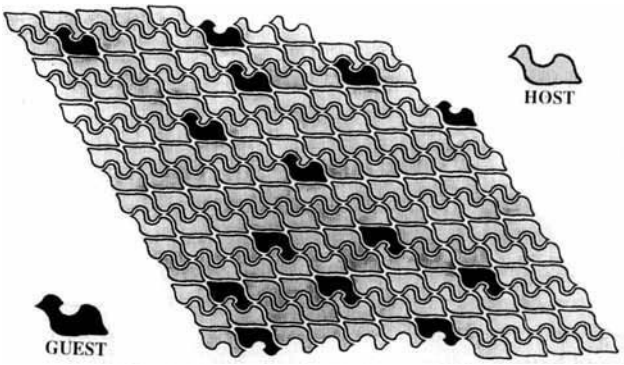

Fig. 1. Schematic solid solution of ducks with pointed heads in a $P2$ lattice of ducks with rounded heads. Note how diagonals of the crystal divide it into sectors with different symmetry properties. This shows that crystal growth nucleated at the center.

hind their heads which makes it difficult to continue deposition of host molecules in the top and bottom rows. Ultimately the head of a host duck may deform enough for it to occupy the unfavorable site where a guest's head protrudes, but the addition will be slower than normal because more energy is required.

One might imagine that the same problem would retard completion of the column at the right border of Figure 1. Here, however, the retardation would be modest, because the guest will soon leave the surface spontaneously, removing the obstacle to column growth. On the top and bottom surfaces the offending guests are locked in by a row of hosts. Many hosts would have to depart in order to allow the guest to escape, and this would take time under conditions of supersaturation. One would expect duck crystals grown in the presence of these guests to be wider than normal in comparison to their height.

In practice, appropriately chosen additives have proven useful for controlling the shape of individual crystals. They have also allowed resolution of racemic mixtures by selectively inhibiting the growth of one of the two enantiomeric crystal forms.[2e] Naturally, additives that were particularly effective in preventing crystal growth were not easily found beneath the crystal surface. Although guest molecules could sometimes be detected by spectroscopic or chromatographic techniques, their concentration was usually too low for diffraction studies that would reveal their orientation. This made it difficult to confirm a clear prediction of the proposed mechanism of growth inhibition, namely, that adsorption of additive molecules should be selective not only for certain faces, but also for certain additive orientations on those faces.

As host molecules deposit on a given face, they must assume all the symmetry-related orientations of the unit cell. At the crystal surface most bulk symmetry operations do not apply, so usually each "symmetry-related" orientation shows a different type of contact with any one crystal surface. This poses no problem for new host molecules, but for the additives some orientations will not fit to the surface. Thus only certain orientations of additive should be included through a given face, and the position of the crystal resulting from growth through that face should have lower symmetry than the pure host lattice.

In the case of Figure 1 hosts must be able to add to the top surface both head-up and head-down, but guests may add only head-up. This results in a division of the crystal into four triangular sectors, separated by diagonal lines which intersect in the region where growth began. The right and left sectors consist of molecules which were deposited through lateral faces as the crystal grew. They contain no guests, except for the one on the right border that will be rejected as the crystal continues to grow. Both top and bottom sectors include guests, but in opposite orientations. In the top all guests are oriented head-up; in the bottom, head-down. Although the crystal as a whole retains a statistical two-fold symmetry axis through its center, the top and bottom sectors considered individually have lost the axial symmetry of pure host.

Two types of diffraction studies now confirm these predictions. In both cases the additives were designed to favor high levels of incorporation and to maximize diffraction contrast. In one case, cinnamamide/thienylacrylamide, the additive differed from host only by replacement of a phenyl ring by a thienyl ring, whose sulfur provided good X-ray contrast.[2a] In the other, asparagine/aspartic acid, an NH_2 group of the host was replaced by OH, and neutron diffraction contrast was supplied by deuterating the guest molecule.[2a,b] Despite the similarity of guests to hosts, individual sectors from both solid solutions show reduction of symmetry ($P2_1/c$ to $P1$ and $P2_12_12_1$ to $P2_1$, respectively) and substantial differences in guest population among "symmetrically equivalent" sites (as much as 15% vs. 2%).

In the 99:1 cinnamamide/cinnamic acid system where low contrast and low additive incorporation made diffraction useless, symmetry reduction through selective incorporation was demonstrated by photochemistry.[2a,c] Although pure cinnamamide is centrosymmetric and thus achiral, unsymmetric incorporation of cinnamic acid makes opposite ends of a solid-solution crystal enantiomeric. Photocycloadducts between host and guest from one end of a crystal were optically active with enantiomeric excesses near 50% in the predicted direction. Cycloadducts from the other end of the same crystal showed the opposite stereochemistry, as expected.

Nonlinear optics may represent the most important application of symmetry lowering in solid solutions. These properties depend both on molecular features and on crystal packing. Crystals of many promising molecules have proven unsuitable because their symmetry pairs molecules in offsetting, antiparallel orientations. Cancellation can be avoided by replacing molecules in one of the orientations by additives, or by including the candidate molecule selectively as a guest in a centrosymmetric host. Second harmonic generation has now been used to demonstrate symmetry lowering in solid solutions containing as little as 0.01% guest.[2d] Solid solutions should provide a much greater number and variety of materials displaying second harmonic generation and other phenomena which require crystal polarity, such as piezo- or pyroelectricity.

Bertman and *McBride* have demonstrated another manifestation of symmetry lowering in solid solutions.[3] Host crystals of fatty acid diacyl peroxides viewed along their nominal tetragonal symmetry axes were birefringent, when they were grown so as to incorporate 5-15% of an additive. Diffraction studies on crystal segments showed complete loss of symmetry ($P4_12_12$ to $P1$). Using a polarizing microscope it was possible to trace the growth history of each crystal through differing interference colors in adjacent crystal sectors. These differences resulted from differing orientation of the polarizability tensors of guest molecules.

From one point of view this simple technique uses the additives as "indicators" to provide a new means for studying crystal growth. From another, it provides a new way to study molecular recognition by showing whether the growth site on a crystal surface can distinguish certain structural features of the additive. For example, a particular surface was shown to distinguish chlorine from iodine, but not from bromine.

If symmetry lowering in solid solutions is so general, it seems surprising that it was not recognized long ago, particularly in optical mineralogy, where solid solutions have been studied so extensively. Over the years anomalies have indeed been noted in which high symmetry minerals show division into sectors with lowered symmetry, but this phenomenon was usually attributed to strain fields or gross chemical segregation. By careful optical and X-ray studies *Allen* and *Buseck* recently established that sectoring in optically anisotropic grossular garnets is due to differing ratios of $Al^{3\oplus}$ to $Fe^{3\oplus}$ in octahedral sites which are nominally related by symmetry.[4] To explain this desymmetrization they independently postulated the type of selection during crystal growth that was proposed by *Lahav, Leiserowitz,* and their collaborators.

For all its aesthetic appeal, crystal symmetry can become a liability for designing new materials, e.g. for nonlinear optics, when it results in cancellation of desired properties between symmetry-related molecules. The generality of symmetry lowering during crystallization of solid solutions provides a promising new approach for circumventing this obstacle.

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[1] A. I. Kitaigorodskii: *Organic Chemical Crystallography*, Consultants Bureau, New York 1961, p. 233.

[2] a) M. Vaida, L. J. W. Shimon, Y. Weisinger-Lewin, F. Frolow, M. Lahav, L. Leiserowitz, R. K. McMullan, *Science (Washington D.C.) 241* (1988) 1475-1479; b) Y. Weisinger-Lewin, F. Frolow, R. M. McMullan, T. F. Koetzle, M. Lahav, L. Leiserowitz, *J. Am. Chem. Soc. 111* (1989) 1035; c) M. Vaida, L. J. W. Shimon, J. van Mil, K. Ernst-Cabrera, L. Addadi, L. Leiserowitz, M. Lahav, *ibid. 111* (1989) 1029; d) I. Weissbuch, M. Lahav, L. Leiserowitz, G. R. Meredith, H. Vanherzeele, *Chem. Mater. 1* (1989) 114; e) L. Addadi, Z. Berkovitch-Yellin, I. Weissbuch, M. Lahav, L. Leiserowitz, *Top. Stereochem. 16* (1986) 1-85.

[3] J. M. McBride, S. B. Bertman, *Angew. Chem. 101* (1989) 342 *Angew. Chem. Int. Ed. Engl. 28* (1989) 330.

[4] F. M. Allen, P. R. Buseck, *Am. Mineral. 73* (1988) 568-584.

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Ferroelectricity and Superconductivity

Some time ago the editor of this journal asked one of us *(H. B.)* to give, every now and then, comments on recent research news, of course, mainly concerned with materials science. Since most of the materials described in this journal are by far too complicated for basic theoretical investigations I wondered, being a theoretical physicist, what the editors really want to see in my comments. I decided that they probably want to have some founded speculations, some educated guesses, and perhaps a personal view on basic problems and ideas. Here is a first try; it is written under the impression that progress in modern materials science is mainly achieved under a broad view of various mechanical, electromagnetic or thermal properties of complex materials.

As an example, I want to discuss some theoretical considerations of the relationship between ferroelectricity and high-temperature superconductivity. This first comment is somewhat courageous as up to now there are many open questions since the pioneering ideas of *B. T. Matthias*[1] who suggested that there must be a mutual exclusion of these two properties. I don't want to give a full account of the historical aspects of the following discussion but would like to point to another paper discussing the coexistence of both effects.[2] (Experimentally, for example, it is very difficult to measure a reversable polarization in good conductors, but it seems to have been established that the superconductor GeTe is also ferroelectric.) Today we know that ferroelectricity is inherently related to the local electron-phonon coupling resulting in a soft-mode behavior for displacive ferroelectrics.[3] In recent years the late *H. Bilz* and his coworkers suggested a shell-model description of the lattice-dynamics of ferroelectrics where the main nonlinearity is locally centered at the lattice site of the chalcogen-ion (preferably oxygen) of representative ferroelectric materials.[4] The microscopic origin of the lattice instability is the nonlinear polarizability of the electron cloud around the oxygen ion, resulting in a dynamic hybridization of the corresponding p-orbitals with the orbitals of the metal-ion ("dynamic covalency").

Recently (but before the discovery of the new high-temperature superconductors), discussion of a possible connection of both phenomena was taken up again. Within the shell-model the point was stressed that a dynamic covalency induces phonon anomalies.[5] That might be thought of as the origin of both, ferroelectricity and superconductivity. Contrary to this, it was argued that pure static polar-