SYNTHESIS OF OXIDE SUPERCONDUCTORS

Defects and thermodynamic instability play a major role in oxide superconductors. Understanding these issues is one important step to optimal synthesis of high-T_c superconductors.

Arthur W. Sleight

From the discovery of oxide superconductors in 1964, there were frequent indications that these materials are metastable. This lack of thermodynamic stability has now become one of the predominant issues in the synthesis of the high-temperature superconductors. Once prepared, metastable superconductors possess sufficient kinetic stability that we generally need have no concern that they will decompose into more stable phases that are not superconducting. Nonetheless, our understanding of the issues relating to the stability of the known superconductors greatly influences our approaches to synthesizing them. Furthermore, understanding the relationship between instabilities and the mechanism of high-T_c superconductivity could be the key to the synthesis of superconductors with even higher critical temperatures.

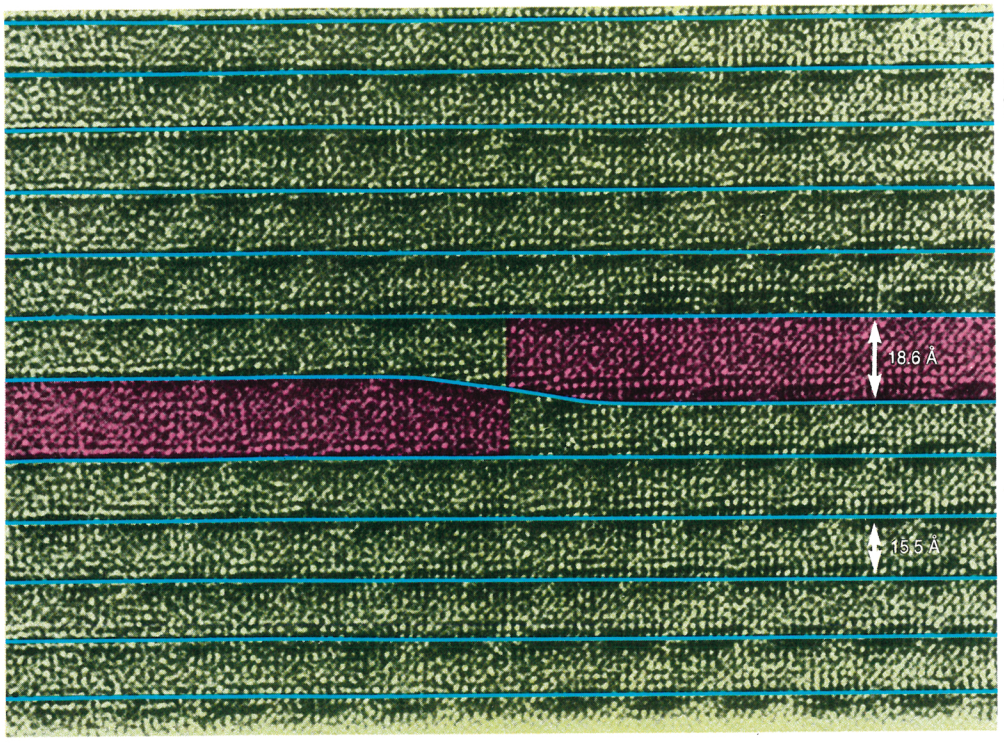
Oxides containing several cations are generally prepared by heating intimate mixtures of solid reactants to temperatures where solid-state diffusion becomes sufficiently rapid for there to be reasonable reaction rates. The reactants may be either oxides or salts that decompose on heating to give oxides. A variation on this approach is to mix appropriate amounts of the cations in solution. On evaporation of the solvent, a very intimate mixture of the reactants may result. In some cases heating this precursor can lead to product formation at lower temperature.

The synthesis of oxide superconductors usually requires some special considerations not required for most other oxides. For example, low-temperature syntheses from solution precursors have not been particularly useful in the synthesis of high-temperature superconductors. This problem is apparently related to a lack of thermodynamic stability at low temperatures. There are also other complications. In the synthesis of $YBa_2Cu_3O_7$ and other "1-2-3" compounds (so called because of the stoichiometry of their metal components), solution precursor methods generally lead to the formation of $BaCO_3$, which is unreactive except at high temperatures. This problem can be circumvented by using special solution methods that do not allow $BaCO_3$ formation.[1]

Most oxide superconductors exist over rather broad ranges of composition and therefore are frequently regarded as solid solutions. Thus we will use the word "phase" instead of "compound" to emphasize this variable composition whenever it is prevalent. The oxide superconductors with T_c's below 15 K are listed in the table on page 27. Most of these were discovered in the period 1964–75. The syntheses of these materials have not been considered greatly unusual, but there are interesting features in some cases. For example, superconductors of the type Ag_7O_8X (where X is NO_3, HF_2, ClO_4 or BF_4) have only been produced through electrodeposition. These materials have the same mixed-valency feature as the high-T_c cuprates: Both Ag^{II} and Ag^{III} are present in the former, both Cu^{II} and Cu^{III} in the latter. However, the T_c's for the Ag_7O_8X phases are only about 1 K. There has been a complete failure to prepare highly oxidized silver compounds by the more common synthesis techniques, even when high-pressure oxygen is used. Furthermore, recent efforts to produce new highly oxidized silver compounds by electrolysis have not met with success.

Many of the compounds in the table do not appear to be thermodynamically stable at low temperatures. This is not surprising, considering the long association of instabilities with high-temperature superconductivity.[2] There are several ways to assess the thermodynamic stability of a phase. At low temperatures, where equilibrium is not readily achieved, examination of the structure is frequently the best approach. At high temperatures, where we may expect to attain equilibrium, phase equilibrium studies may be employed. At intermediate temperatures, calorimetric studies are generally the best approach, if the entropy contribution to the free energy of formation can be estimated.

Arthur Sleight is the Milton Harris Professor of Materials Science in the department of chemistry at Oregon State University, in Corvallis, Oregon.



PRATIBHA L. GAI

Dislocation defect in a $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ composition that is predominantly the $n = 2$ structure (green). Regions with $n = 4$ (red) are present as stacking-fault defects. The dislocation defect occurs where the two $n = 4$ regions meet. **Figure 1**

Assessing metastability from structure

High defect concentrations are common in oxide superconductors, especially those with the highest T_c's. (See James D. Jorgensen's article on page 34.) Figure 1 illustrates a typical example of an extended defect typically found in high-temperature superconductors based on $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$. At high temperatures, defects may be thermodynamically stable due to their entropy contribution to the overall free energy of the phase. These defects will be eliminated at low temperatures if equilibrium is achieved. In the case of a solid solution, the defects may be eliminated simply by phase separation to give the end-member compounds (for example, $BaPbO_3$ and $BaBiO_3$ in figure 2). Alternatively, the defects may become ordered. This effectively eliminates them, because "ordered defects" are not defects at all; instead, they are part of a regular lattice. Thus broad ranges of solid solution may be thermodynamically stable at high temperatures. At equilibrium at low temperatures, however, solid solubility is eliminated, and only the end-member compounds and possibly intermediate compounds of fixed composition remain.

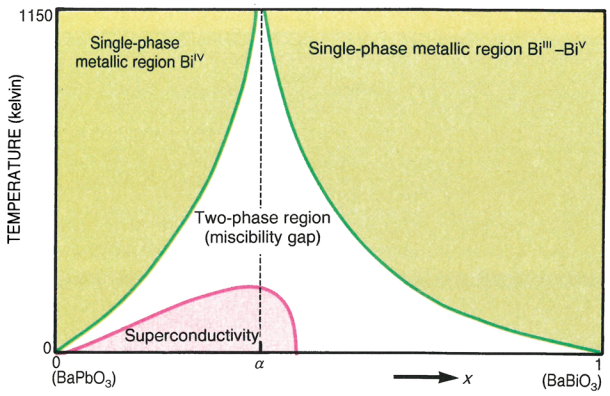
A defect mechanism is necessary to account for the continuous range of compositions found in superconductors. The defects in high-temperature superconductors are only poorly characterized, but there generally seem to be several important types in every system examined. Whatever the defects are, they cannot be stable at low temperatures. This might seem to be a trivial aspect of metastability. After all, carrier concentration tends to be a key variable influencing T_c (see Jorgensen's article and Bertram Batlogg's article on page 44), and in the absence of variable composition with inherent defects at most compositions, we would have no way to vary carrier concentration. However, these defects clearly affect properties in ways unrelated to carrier concentration. It is possible that the disorder associated with defects plays a significant role in allowing the existence of the high-temperature superconducting state.

A few of the compounds listed in the table may be thermodynamically stable at low temperatures. This group includes the Ag_7O_8X phases. For NbO there is a significant range of compositions, but this range includes stoichiometric NbO, which is presumably thermodynamically stable at low temperatures. On the other hand, "TiO" is grossly defect ridden at all compositions. These defects remain present at low temperatures to give a superconductor that is clearly not at equilibrium.

Most of the phases listed in the table may be regarded as solid solutions with variable composition. Frequently, superconductivity exists only for certain ranges within these solid solutions. The defect that makes the solubility possible is generally known. Superconductivity is introduced into insulating $SrTiO_3$ only by incorporation of defects such as oxygen vacancies. The phases of the type $Li_xMo_6O_{17}$, Li_xNbO_2 and A_xMO_3 (where A is Na, Ca, Sr, Ba, In, Tl, K, Rb, Cs or Li; and M is W, Mo or Re) all have their A cations partially occupying crystallographic sites in a disordered fashion. Both $Li_{1+x}Ti_{2-x}O_4$ and $BaBi_{1-x}Pb_xO_3$ are solid solutions with inherent disorder. In the high-temperature superconductors, the defect situation is generally more pronounced and complex.

Routes to metastable materials

The overwhelming majority of compounds that chemists prepare are not thermodynamically stable over a broad range of conditions under which these compounds are studied. Some compounds that are metastable at ambient conditions are stable at some other temperature and pressure. In this case, the usual approach is to synthesize the compound under conditions where it is thermodynamically stable. Then if the compound possesses sufficient kinetic stability, it may be studied and used at conditions where it is metastable. We shall refer to this general approach to synthesis as route 1. Thus most, but not all, solid solutions are prepared at temperatures high enough that entropy stabilizes the defects



Instability and optimum T_c are linked in this schematic phase diagram for the $BaPb_{1-x}Bi_xO_3$ solid solution. The most unstable mixture (α) requires the highest temperature to achieve a stable single phase (green regions) and coincides with the superconducting phase possessing the highest T_c. The miscibility gap is not normally observed because equilibrium is easily suppressed at lower temperatures, allowing metastable single phases (red region) such as the superconducting phases to lie within the miscibility gap without segregating on a microscopic scale. They may be synthesized by cooling from single phases that are stable above 1150 K ("route 1"). **Figure 2**

inherent to the solid solution.

In the $BaPbO_3$–$BaBiO_3$ system, entropy allows essentially complete solid solubility at temperatures higher than about 1150 K. On cooling, a two-phase region appears. Not surprisingly, this phase separation begins right at the boundary between semiconducting and insulating regions in the phase diagram. As can be seen from figure 2, the superconducting phase having the highest T_c requires the greatest entropy contribution to achieve thermodynamic stability. Many systems show no superconductivity except in phases that have been quenched from high pressure. Examples include the high-pressure forms of GeP, GeAs, SnP and InTe.

Another common approach to metastable phases—route 2—is through insertion of ions (intercalation) and related reactions such as ion exchange. These syntheses have two or more steps. In the first step, the basic structure is formed, usually under equilibrium conditions. Successive steps are carried out under conditions where the basic structure is kinetically stable, so that formation of metastable products is possible. Examples of these syntheses are $x\mathrm{Li} + \mathrm{TiS_2} \rightarrow \mathrm{Li}_x\mathrm{TiS_2}$ and $\mathrm{NaAlSiO_4} + \mathrm{KCl} \rightarrow \mathrm{KAlSiO_4} + \mathrm{NaCl}$. The products are metastable and cannot be produced at any temperature or pressure by direct reaction of the elements.

Instead of adding ions to a structure, we can also remove them to form a metastable compound (deintercalation). An example of this[13] is the synthesis of superconducting $\mathrm{Li}_x\mathrm{NbO_2}$ phases from insulating $\mathrm{LiNbO_2}$. In the case of $A_x\mathrm{WO_3}$ superconductors, where A is an alkali, it was found that decreasing x in a second step[9] increased T_c while it presumably decreased stability.

A third route to metastable phases avoids equilibrium at all stages of the synthesis. Diamond films have been grown at conditions far from equilibrium. We may say such "route 3" syntheses are controlled by kinetics rather than by thermodynamics. It is commonplace in chemistry for there to be several intermediates between reactants and thermodynamically stable products. If we can isolate an intermediate, we have isolated a metastable phase. For such syntheses to be successful a significant activation barrier to the thermodynamic equilibrium products is generally needed.

Simple cuprate superconductors

The simplest formula for rare earth cuprates that can be doped to become superconducting is $R_2\mathrm{CuO_4}$, where R represents a trivalent rare earth cation. Such phases contain entirely divalent copper and are antiferromagnetic insulators. Three different structures, referred to as T, T′, and T*, are found for this formula. With the T and T* structures, doping to produce hole carriers leads to superconductivity, whereas with the T′ structure, doping to produce electron carriers leads to superconductivity. In addition to doping on the R site, there may be oxygen vacancies or interstitial oxygen atoms. Thus the general formula is given as $R_{2-x}A_x\mathrm{CuO}_{4\pm y}$, where A is chosen to either oxidize the $\mathrm{CuO_2}$ sheets (for example, Sr^{2+}) or reduce the $\mathrm{CuO_2}$ sheets (for example, Ce^{4+}). When doped, these phases with T, T′ or T* structure possess defects that cause them to be metastable at superconducting temperatures. The electron superconductors actually appear to be metastable at all temperatures and pressures.

Phases of the type $\mathrm{La}_{2-x}A_x\mathrm{CuO}_{4-y}$ (where A is Ba, Sr, Ca, K or Na) have the T structure and variable composition. The defects associated with nonzero x and y are not known to become well ordered at any composition. An extended defect associated with nonzero values of y has been identified by Pratibha L. Gai.[17] This defect, which may be characterized as a screw dislocation bounding a stacking fault, is well ordered in two dimensions but is disordered in the third dimension. It would appear that all superconducting samples of the $\mathrm{La}_{2-x}A_x\mathrm{CuO}_{4-y}$ type have nonzero y and substantial quantities of this extended defect. The random occupancy of A cations on R cation sites is another defect contribution to the low-temperature metastability of these phases and of the T′ and T* phases.

The defect situation for T′ phases is still only poorly understood, but synthesis requirements suggest that they are metastable materials achieved through route 2. The first step in the synthesis produces an $R_{2-x}A_x\mathrm{CuO}_{4+y}$ phase, where y is small and positive. Presumably these oxygen-rich phases form under equilibrium conditions. However, these phases are not superconducting unless oxygen is extracted from the lattice in a second, nonequilibrium step. Attempts to synthesize the superconducting $R_{2-x}A_x\mathrm{CuO}_{4-y}$ phases in one step at reduced oxygen pressure have not been successful.

1-2-3 type superconductors

The synthesis of $R\mathrm{Ba_2Cu_3O_7}$ (1-2-3) superconductors is a

Oxide superconductors with T_c below 15 K*

Compound	T_c (K)	Synthesis method	Reference
NbO	1.4–1.6	Normal	3
TiO	0.7–1.1	Normal	3
$SrTiO_{3-x}$	0–0.5	Normal	4
$Na_{0.3}WO_3$ (tetragonal)	0.5	Normal, electrodeposition	5
$Na_{0.2}WO_3$ (tetragonal)	3.0	Normal, electrodeposition	6
$Ca_{0.1}WO_3$ (hexagonal)	3.4	Normal	7
$Sr_{0.08}WO_3$ (hexagonal)	4.0	Normal	7
$Ba_{0.14}WO_3$ (hexagonal)	2.2	Normal	7
$In_{0.11}WO_3$ (hexagonal)	2.8	Normal	7
$Tl_{0.30}WO_3$ (hexagonal)	2.1	Normal	7
$K_{0.30}WO_3$ (hexagonal)	5.7	Deintercalation	8,9
$Rb_{0.30}WO_3$ (hexagonal)	6.6	Deintercalation	8,9
$Cs_{0.30}WO_3$ (hexagonal)	4.8	Deintercalation	8,9
$Li_{0.30}WO_3$ (hexagonal)	2.2	Normal	10
Na_xWO_3 (hexagonal)	5.4	Normal	10
$(NH_4)_{0.33}WO_3$(hexagonal)	3.2	Normal	10
K_xMoO_3 (tetragonal)	4.2	High pressure	11
K_xReO_3 (hexagonal)	3.6	High pressure	11
$Li_{0.9}Mo_6O_{17}$	~2	Normal	12
$Li_{0.45}NbO_2$	5.5	Deintercalation	13
Ag_7O_8X ($X = NO_3$, HF_2, ClO_4, BF_4)	1.4	Electrodeposition	14
$LiTi_2O_4$	13.7	Normal	15
$BaBi_{1-x}Pb_xO_3$	13	Normal	16

*Superconductors with an oxygen-to-metal ratio of less than 1 are not listed.

classic example of route 2. One first synthesizes phases of the type $R Ba_2Cu_3O_{6+x}$, where x is less than 1. As a second step, one oxidizes this structure to $R Ba_2Cu_3O_7$ to obtain optimal superconducting properties. Increasing the oxygen pressure during the first synthesis step does not lead to the formation of $R Ba_2Cu_3O_7$ phases; instead, one fails to synthesize the $R Ba_2Cu_3O_{6+x}$ type structure.[18]

The $R Ba_2Cu_3O_{6+x}$ phases can exist at any value of x from 1 to 0 (figure 3). Such phases are best prepared by equilibration (relaxation toward equilibrium) at a fixed oxygen pressure and temperature. For a given x the highest T_c is generally found for samples annealed so that the interstitial oxygen is well ordered. It appears that the carrier concentration in the CuO_2 sheets increases as the interstitial oxygen becomes ordered. Thus T_c increases according to the usual relationship between T_c and carrier concentration. Such samples, although prepared by "equilibration" with oxygen of fixed pressure, are not necessarily at equilibrium. Oxygen uptake or removal is very fast, whereas complete destruction of the $R Ba_2Cu_3O_{6+x}$ structure is slow due to the large activation energy required. Furthermore, many defects remain after the interstitial oxygen becomes well ordered.

Examination of the structure of $R Ba_2Cu_3O_7$ phases shows the lack of thermodynamic stability at low temperatures. The copper–oxygen chains are not straight but zigzagged, and the oxygen displacements associated with this distortion are not ordered in three dimensions. The reasons for this lack of order are not clear. Ordering should lower the energy, and there does not seem to be a significant barrier to such ordering. It is likely that the lack of an ordered zigzag distortion is related to another kind of disorder present in this chain. If the two oxidation states of copper, Cu^{II} and Cu^{III}, are themselves not ordered along the chain, then ordering of the oxygen displacements associated with the zigzag might well be frustrated.

Recent calorimetry results of Fernando H. Garzon and Ian D. Raistrick[19] have confirmed that the $YBa_2Cu_3O_{6+x}$ phases are not thermodynamically stable over a wide range of x. For example, at $x = 0.75$, the reaction $4\ YBa_2Cu_3O_{6.75} \rightarrow 2\ YBa_2Cu_4O_8 + Y_2BaCuO_5 + 3\ BaCuO_2$ is favored, and it is unlikely that any temperature or pressure would favor the reverse reaction. The actual decomposition products of course depend on oxygen pressure and x. For $x = 0.5$, the reaction $2\ YBa_2Cu_3O_{6.5} \rightarrow Y_2BaCuO_5 + 3\ BaCuO_2 + 2\ CuO$ becomes favorable[20] below 1073 K.

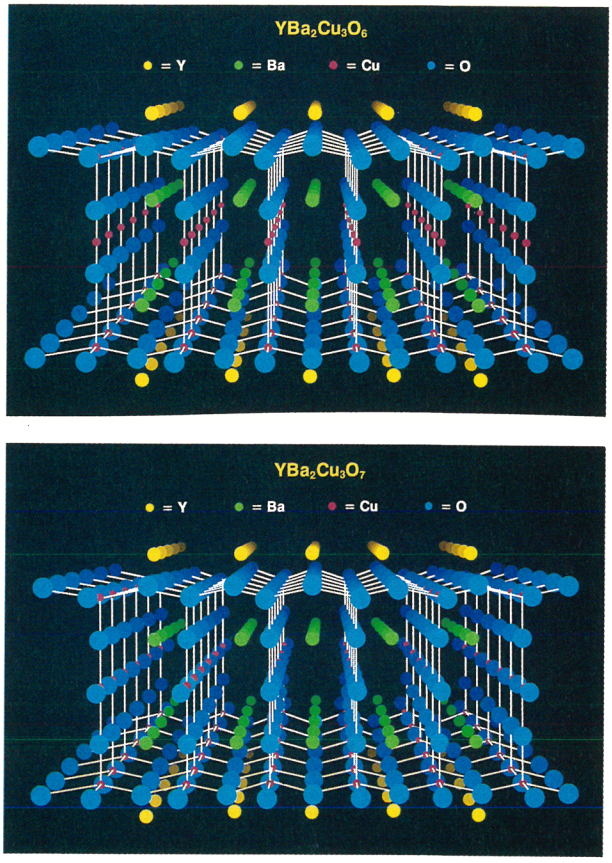
Although there are now adequate data for us to conclude that $R Ba_2Cu_3O_7$ superconductors are not thermodynamically stable at any temperature or pressure, the situation remains unclear for $R Ba_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14+x}$. Phase equilibrium studies suggest that these phases are thermodynamically stable at the conditions under which they form.[18] We may expect $Y_2Ba_4Cu_7O_{15}$ to be metastable at low temperatures due to the disorder associated with the Cu–O chains.

The $R Ba_2Cu_3O_{6+x}$ phase is most stable when $x = 0$. Thus low-temperature syntheses show the most success when the oxygen pressure is reduced to a level consistent with this value. This is true for bulk synthesis[1] as well as thin film synthesis.[21] However, even when working at $x = 0$, the synthesis temperature of $R Ba_2Cu_3O_{6+x}$ phases has not been reduced below about 900 K.

Complex cuprate superconductors

There is now a very large group of complex superconductors that may be represented as Tl,Pb,Bi/Ba,Sr,Ca/Cu/O. Some of these give us the highest T_c's observed to date. The structures as well as the compositions are complex and generally still not well determined. The synthesis of these high-T_c materials is difficult, for reasons that relate to a general theme of this article, thermodynamic instability.

One family of superconductors in this group may be represented by the ideal formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$. The ideal structure for these phases has n CuO_2 sheets stacked between each successive $Bi_2Sr_2O_4$ layer. Only the $n = 1$ (T_c up to 10 K) and $n = 2$ (T_c up to 95 K) phases are



Structures of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. The latter must be synthesized in a two-step process by oxidation of a $YBa_2Cu_3O_{6+x}$ phase. Attempts to synthesize it directly fail to give the structure shown, due to its thermodynamic instability. (From A. W. Sleight, *Science* **242**, 1519, 1988.) **Figure 3**

easily prepared. The $n = 3$ phase, which can have a T_c of about 110 K, is only prepared with great difficulty in the Bi/Sr/Ca/Cu/O system. The synthesis of this three-layer structure is greatly facilitated by addition of a sixth element, Pb. Synthesis of $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ phases with $n > 3$ has been achieved only by special thin film techniques where the structure is developed by deposition of the elements layer by layer.[22] From such experiments, it has been found that the T_c peaks at $n = 3$ and steadily decreases for larger n.

Each of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ phases has a considerable range of compositions—which apparently does not include the composition indicated by the ideal formula! The situation is analogous to that found for FeO_x. The ideal structure for FeO is that of sodium chloride. A range of compositions is found for FeO_x, but the ideal, one-to-one ratio does not exist at any temperature (see figure 4). It should be further noted that FeO_x disappears from the equilibrium phase diagram below about 560° C. Thus FeO_x is a simple example of an endothermic, or entropy-stabilized, compound. Our present evidence suggests that many of the Tl,Pb,Bi/Ba,Sr,Ca/Cu/O superconductors are also entropy stabilized. They can only be prepared at temperatures close to where melting behavior is observed. They have broad ranges of compositions that, at least in general, do not include the ideal composition.

It is natural to ask what instability of the ideal structures requires stabilization through entropy. The answer is the geometric misfit of the layers that stack one on another. The lattice dimensions within the CuO_2 sheets are basically fixed by the Cu–O distance, which is 1.9 ± 0.1 Å. For the ideal structures, this constraint gives unreasonably long Bi–O or Tl–O distances. Thus at low temperatures these structures are unstable and would not ordinarily form. At high temperatures the entropy term can make up for this size mismatch, and some phases can have a small window of thermodynamic stability. When these structures are cooled into the region where they are metastable, various complex distortions occur so as to achieve reasonable interatomic distances for all atoms (see figure 5).[23] (This is discussed further in Jorgensen's article.)

While many of the Tl,Pb,Bi/Ba,Sr,Ca/Cu/O superconductors are metastable materials made through route 2, others appear to be made through route 3. This is a tentative conclusion based mainly on our inability to find any combination of temperature, pressure and composition where they will form at equilibrium. For superconductors based on Tl/*A*/Ca/Cu/O, such as "$Tl_2Ba_2Ca_2Cu_3O_{10}$," reaction time is one of the more important synthesis parameters. Particularly for superconductors with T_c's of about 125 K, the reaction time must be neither too short nor too long. It appears that these phases actually decompose at the same conditions under which they form. If this is really the case, they are blatant examples of route-3 metastable materials.

This conclusion is valid only if the reaction is studied in a closed system, that is, with a fixed composition of the solid phase and fixed partial pressure of the gases present. This condition is difficult to achieve for Tl/*A*/Ca/Cu/O superconductors. Thallium and oxygen are readily lost from the system. Many experiments have been carried out in sealed silica, gold or silver containers. However, these are not necessarily closed systems. Oxygen can readily diffuse through gold and silver, and Tl_2O vapors readily react with SiO_2. Thus, although closed-system experiments are in principle possible, they are difficult to achieve in practice. Nonetheless, current evidence suggests that the closed-system requirement has been fulfilled in some experiments,[24] and reaction time still remains a critical variable in the successful synthesis of the highest T_c phases of the Tl/*A*/Ca/Cu/O superconductors.

Metastable materials made by route 3 cannot generally be prepared as a single phase. It can be difficult to impossible to prepare a phase without impurity phases if the desired phase has virtually no region of true thermodynamic stability. Such a phase will always tend to be contaminated with reactants, more-stable products or both. Equilibration of such samples does not help; instead, it leads to complete destruction of the desired phase. This problem is commonplace in chemistry, where the desired product can frequently be isolated by methods such as fractional distillation. For mixtures of solid compounds, there are generally no convenient purification techniques.

The structures of the Tl,Pb,Bi/Ba,Sr,Ca/Cu/O superconductors also show the metastability in dramatic ways. The disordered atomic displacements related to geometric misfit have already been mentioned. Point defects also abound. Detailed structural determinations on $Bi_2Sr_2CaCu_2O_{8+y}$ *always* show pronounced evidence of point defects in the form of lattice vacancies, interstitial atoms and antisite disorder. (See also Jorgensen's article.)

It is commonly found that the composition and the defects vary from crystal to crystal of one reaction product. A precise evaluation of the defect situation, even for any one crystal, is impeded by the complex displacements of atoms, especially those of the Bi_2O_2 sheets. A determination on one crystal of "$Bi_2Sr_2CaCu_2O_8$" indicated[25] that the structural formula should be written as $[Bi_{1.75}]$-$[Sr_{1.58}Bi_{0.10}][Ca_{0.80}Sr_{0.14}Bi_{0.06}]Cu_2O_8$, where the groupings in the formula indicate the lattice sites occupied. This determination ignored defects associated with oxygen and assumed that Ca was on one site only. It has subsequently been found that some Ca can substitute for Sr in "$Bi_2Sr_2CuO_6$." Thus a more likely formula for this crystal of "$Bi_2Sr_2CaCu_2O_8$" would be $[Bi_{1.90}][Sr_{1.70}Ca_{0.10}Bi_{0.05}]$-$[Ca_{0.80}Sr_{0.14}Bi_{0.06}]Cu_2O_8$.

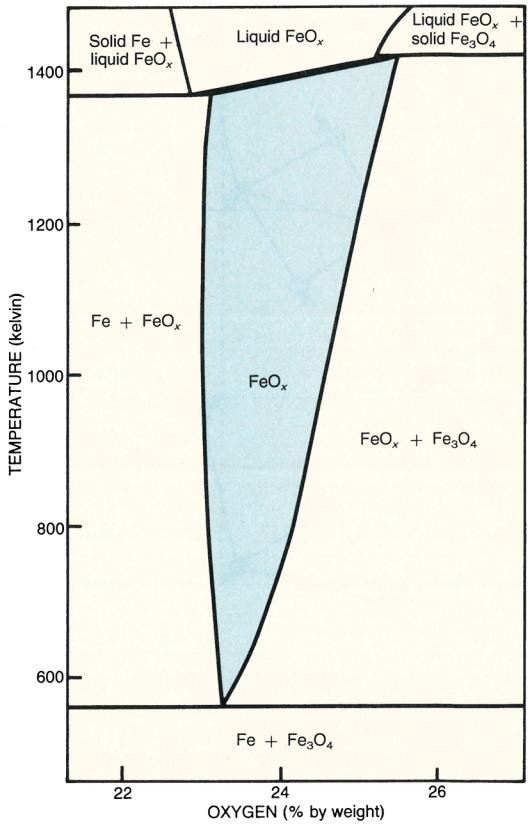
A similar situation exists for the Tl/*A*/Ca/Cu/O phases (where *A* is Bi, Pb, Ba, Sr and/or Ca). Again, complex and disordered displacements of atoms—here, those in the Tl_2O_2 sheets (figure 5)—impede our ability to obtain a complete description of the point defect situation. Researchers wishing to prepare the 125-K superconductor "$Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$" with $n = 3$ have frequently, and incorrectly, assumed it would be best to use reactant ratios in accord with this ideal formula. Some reactions using such reactant ratios have shown a product that was nearly single phase, but with n equal to 2 instead of 3. This result is easy to understand based on structural studies.[24] Multiplying the subscripts of the ideal "$Tl_2Ba_2Ca_2Cu_3O_x$" by $\frac{2}{3}$ gives $Tl_{1.6}Ba_{1.6}Ca_{1.6}Cu_2O_x$, which may be rearranged to $[Tl_{1.5}Ca_{0.3}][Ba_{1.6}Ca_{0.4}]$-$[Ca_{0.9}Tl_{0.1}]Cu_2O_x$. This formula agrees with structural studies that show Tl on the Ca site and reduced scattering power on the Tl and Ba sites.

Optimal synthesis and outlook for higher T_c

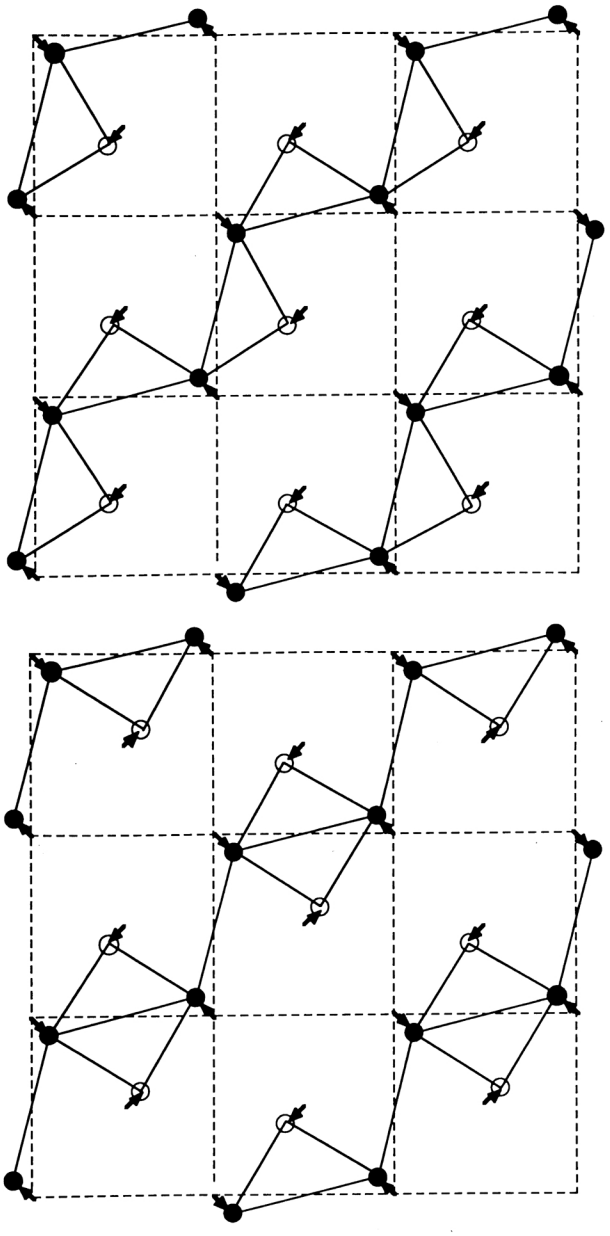
The ways in which metastability arises are very different for the various superconductors. Thus our approaches to the syntheses must be different. In the case of the $RBa_2Cu_3O_{6+x}$ phases, we have learned that achieving the ideal composition with x close to 1 and with well-ordered oxygen gives the highest T_c. There is a good window of thermodynamic stability for synthesis when $x \gtrsim 0.6$.

Learning about optimal synthesis of $RBa_2Cu_3O_{6+x}$ superconductors is, however, of little value in the synthesis of the higher-T_c Tl,Pb,Bi/Ba,Sr,Ca/Cu/O superconductors. For those superconductors, the ideal compositions and structures tend not to be found in actual samples, especially for the phases with the highest T_c's. Striving for ideal compositions and structures in syntheses can, in fact, lead one astray. Furthermore, it can be reasonably concluded that if $Bi_2Sr_2CaCu_2O_8$ could be prepared with its ideal composition and structure, it would not be superconducting or even metallic, because there would be no carriers for the CuO_2 sheets. Phase equilibrium studies for various Tl,Pb,Bi/Ba,Sr,Ca/Cu/O systems are giving us valuable information on optimal synthesis methods for those superconductors that can be prepared through route 2. However, such studies are of little value for the synthesis of metastable materials that can be made only through route 3, which is the route that appears to be generally required for the highest-T_c phases.

There have been many reports of superconductivity at temperatures significantly higher than 125 K. A large number of these results are clearly due to experimental artifacts. Other results appear to be genuine, but are difficult to verify because the superconducting component is very small and unstable. If there is indeed a direct correlation between instability and high T_c, we might well expect that as we continue to raise T_c the instabilities will become so pronounced that exceptional synthesis proce-



The Fe–O system shown in this phase diagram exhibits a rare example of an entropy-stabilized phase, FeO_x (blue region). The ideal composition, FeO, is not stable, and all neighboring regions are liquid or two-phase regions. FeO_x is not a superconductor, but its stability properties are analogous to those of the complex cuprate superconductors "$Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$" and "$Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$," which have not been found in their ideal compositions. **Figure 4**



Displacement of thallium (filled circles) and oxygen (open circles) from their ideal positions, caused by a geometric mismatch between the Tl_2O_2 and CuO_2 layers in $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$, can occur in the two configurations shown. A given sample is likely to have a random mixture of these configurations. (From ref. 23.) **Figure 5**

dures will be required to produce reasonable superconducting fractions of these phases. This is a considerable challenge for those attempting to raise T_c. A firm theoretical foundation that made a connection between instabilities and the mechanism of high-T_c superconductivity could be helpful in meeting this challenge.

References

1. H. S. Horowitz, S. J. McLain, A. W. Sleight, J. D. Druliner, P. L. Gai, M. J. Van Kavelaar, J. L. Wagner, B. D. Biggs, S. J. Poon, Science **243,** 66 (1989).
2. J. C. Phillips, Phys. Rev. Lett. **26,** 543 (1971). B. T. Matthias, E. Corenzwit, A. S. Cooper, L. D. Longinotti, Proc. Natl. Acad. Sci. USA **68**, 56 (1971).
3. A. M. Okay, P. H. Keeson, Phys. Rev. B **12,** 4917 (1975).
4. J. F. Schooley, H. P. R. Frederikse, W. R. Hostler, E. R. Pfeiffer, Phys. Rev. **159**, 301 (1967).
5. C. J. Raub, A. R. Sweedler, M. A. Jensen, S. Broadston, B. T. Matthias, Phys. Rev. Lett. **13**, 746 (1964).
6. H. R. Shanks, Solid State Commun. **15**, 753 (1974).
7. P. E. Bierstedt, T. A. Bither, F. J. Darnell, Solid State Commun. **4,** 25 (1966).
8. A. R. Sweedler, C. J. Raub, B. T. Matthias, Phys. Lett. **15**, 108 (1965).
9. J. P. Remeika, T. H. Geballe, B. T. Matthias, A. S. Cooper, G. W. Hall, E. M. Kelly, Phys. Rev. Lett. **24A**, 565 (1967).
10. T. E. Gier, D. C. Pease, A. W. Sleight, T. A. Bither, Inorg. Chem. **7**, 1646 (1968).
11. A. W. Sleight, T. A. Bither, P. E. Bierstedt, Solid State Commun. **7**, 299 (1969).
12. M. Greenblatt, W. H. McCarrol, R. Neifield, M. Craft, J. V. Waszczak, Solid State Commun. **51**, 671 (1984).
13. M. J. Geselbracht, T. J. Richardson, A. M. Stacy, Nature **345**, 324 (1990).
14. M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, D. B. McWhan, Phys. Rev. Lett. **17**, 917 (1966).
15. D. C. Johnston, H. Prabash, W. H. Zachariasen, R. Viswanattian, Mater. Res. Bull. **9**, 777 (1973).
16. A. W. Sleight, J. L. Gillson, P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).
17. P. L. Gai, E. M. McCarron, Science **247**, 553 (1990).
18. D. E. Morris, N. G. Asmar, J. H. Nickel, R. L. Sid, J. Y. T. Wei, J. E. Post, Physica C **159**, 287 (1989). J. Karpinski, S. Rusiecki, E. Kaldis, B. Bucher, E. Jilek, Physica C **160**, 449 (1989).
19. F. H. Garzon, I. D. Raistrick, in *Chemistry of Electronic Materials*, Proc. Int. Conf., Jackson, Wyo., 17–22 August 1990, Natl. Inst. Standards Technol. Spec. Publ. 804 (1991), p. 373.
20. V. B. Lazarev, K. S. Gavrichev, V. E. Gorbunov, J. H. Greenberg, P. Z. Slutskii, Ju. G. Nadtochii, I. S. Shaplygin, Thermochim. Acta **174**, 27 (1991).
21. R. Bormann, J. Nolting, Appl. Phys. Lett. **54**, 2148 (1989).
22. K. Ogawa, K. Nakamura, H. Hayakawa, H. Hattori, J. Sato, S. Ikeda, *Advances in Superconductivity II,* Proc. 2nd Int. Symp. on Superconductivity, Tsukuba, Japan, T. Ishigino, K. Kajimura, eds., Springer-Verlag, New York (1989), p. 27.
23. W. Dmowski, B. H. Toby, T. Egami, M. A. Subramanian, J. Gopalakrishnan, A. W. Sleight, Phys. Rev. Lett. **61**, 2608 (1988).
24. C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrisey, T. R. Askew, R. B. Flippen, U. Chowdhry, A. W. Sleight, Science **240**, 631 (1988).
25. P. Lee, Y. Gao, H. S. Sheu, V. Petricek, R. Restori, P. Coppens, A. Darovskikh, J. C. Phillips, A. W. Sleight, M. A. Subramanian, Science **244**, 62 (1989). ■