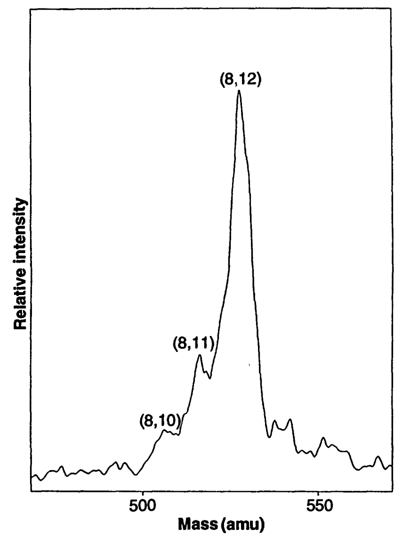

Fig. 3. Expanded view of Ti_8C_{12} spectrum shown in Fig. 2, top. The shoulders on the dominant Ti_8C_{12} peak are assignable as the fragments Ti_8C_{11} and Ti_8C_{10} produced during the desorption.

Aesar)–graphite composite electrodes and analyzed it in the same manner (Fig. 2, bottom spectrum). There is an obvious mass spectral shift of 24 amu from 528 to 552 amu, establishing the presence of the vanadium analog of V_8C_{12} in the sample. Moreover, we can assign the 540- and 564-amu species to V_8C_{11} and V_8C_{13}, respectively. These species are also observed in molecular beam studies of the vanadium derivatives of the Met-Cars (*3*, *10*).

These Met-Car–containing soot samples are stable in air. This finding is an important clue to the electronic nature of these clusters as well as an affirmation of their predicted stability. These soot samples are inhomogeneous and C_{60}, and to a lesser extent C_{70}, are, not surprisingly, commonly present in our soot. Because our soot samples are inhomogeneous, and oxidation of the soot does also sometimes occur, we do not detect Met-Cars in every sample analyzed from the same run. However, under favorable circumstances we can estimate our Met-Car abundance from the mass spectral data to be approximately 1%.

In considering the results of our analyses, we are aware that laser desorption can generate a range of products depending on the sample. However, we establish through the following arguments that we are actually desorbing Met-Cars from the raw soot. First, it is highly unlikely that we are producing M_8C_{12} (M = Ti, V) molecules within the sample with one laser pulse and desorbing them with subsequent pulses. The Met-Car signal is observed immediately (<ten laser shots) and the signal intensity thereafter decreases with time, neither of which would be expected if we produced Met-Cars in the soot sample with the desorption laser. Second, if the Met-Cars were generated during desorption via gas phase growth processes, we would expect to see their characteristic building pattern as is observed in the molecular beam experiments (*3*, *10*) and in the mass distribution of the laser desorption experiments of pure graphite samples in which fullerenes are produced (*11*). We see no evidence of these processes occurring during desorption. Additionally, as there are comparatively few collisions above the surface relative to the number of collisions in the plasma of either the laser vaporization source used in the gas phase experiments (*1–6*, *8*, *10*) or of the arc discharge used to produce the species in the present work. If either of these scenarios were the case, we would expect to see M_8C_{12} from a mixed sample of pure metal and graphite powders studied over a wide range of desorption laser powers; we have not seen any masses corresponding to Met-Cars in these test experiments. Similar tests were performed with baked titanium carbide with no indication that Met-Cars are formed by the desorption process. Third, we are certain that we are not merely fragmenting C_{60} to smaller fullerenes which have mass coincidences with Ti_8C_{12} (C_{44}) and V_8C_{12} (C_{46}). Besides the fact that no other fragments are observed, it is highly unlikely that C_{44} would be the most abundant fragment from the Ti/C soot with C_{46} then being the most abundant in the V/C soot. Finally, we observe the significant diminution of Met-Car abundance upon baking the soot samples, which is further evidence of their existence in the soot rather than being a product of the desorption process.

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Metastability of Superconducting Compounds in the Y-Ba-Cu-O System

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Precision isothermal solution calorimetry was used to determine the standard-state enthalpy of formation of a number of phases in the Y-Ba-Cu-O system. An analysis of the data indicates that $YBa_2Cu_4O_8$ is thermodynamically metastable under ambient conditions. Taken together with the results from previous investigations, these data show that all of the superconducting compounds in the Y-Ba-Cu-O system are thermodynamically metastable at low temperatures.

Since the discovery of the phenomenon of superconductivity in mercury at 4 K, by Onnes in 1911, researchers have attempted to synthesize superconducting materials with higher transition temperatures. Superconductivity in the temperature range from 1 to 23 K is observed in more than 1000 metal-metalloid compounds (*1*, *2*). However, superconductivity above the boiling point of liquid nitrogen (~77 K) is a recent observation and has been found in only a very small class of cuprate-based oxide superconductors. The

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search for materials with high superconducting transition temperatures (T_c) has not been easy because these materials are often difficult to prepare and are synthesized only in a relatively small region of the phase diagram. Recently, the possible implication of local structural instabilities in the mechanism of high-temperature superconductivity has become increasingly recognized. Both neutron diffraction (*3, 4*) and x-ray absorption (*5, 6*) local-structure probes have suggested that lattice instabilities are associated with the onset of superconductivity in the cuprate phases. The macroscopic thermodynamic manifestation of such phenomena is likely to be metastability or marginal stability in phases with high critical temperatures. Several investigators (*7–9*) have pointed out that most high-T_c phases appear to be metastable at low temperatures, a fact that also has severe consequences for the synthetic route that must be used (*7*). It has been known for some time that $YBa_2Cu_3O_{7-x}$ is metastable at low temperatures (*10–14*), but the stability of $YBa_2Cu_4O_8$ has been a matter of speculation (*7, 15*). We present here calorimetric data that show unambiguously that all of the known superconductors in the Y-Ba-Cu-O system are metastable at room temperature.

The Y-Ba-Cu-O quaternary system contains three superconducting phases: $YBa_2Cu_3O_{7-x}$, $YBa_2Cu_{3.5}O_{7.5-x}$, and $YBa_2Cu_4O_8$. The low-temperature metastability of the oxidized superconducting variants of the $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_{3.5}O_{7.5-x}$ phases was demonstrated by a number of researchers (*10–14, 16*). Under conditions of a partial pressure of oxygen $P(O_2)$ of 1 atm and low temperature, the $YBa_2Cu_3O_{7-x}$ phase was reported as being unstable with respect to a mixture of the $YBa_2Cu_4O_8$ and nonsuperconducting Y_2BaCuO_5 and $BaCuO_2$ phases. Similarly, coulometric titration experiments by Beyers and Ahn (*16*) indicated that the $YBa_2Cu_{3.5}O_{7.5-x}$ superconductor is unstable below 600°C and is replaced by the $YBa_2Cu_4O_8$ phase. Therefore, the stability of the $YBa_2Cu_4O_8$ phase is of great interest because it appears to be the most stable superconductor at low temperature (*10–16*).

Brosha *et al.* (*15*) demonstrated that highly reactive, carbon-free precursors derived from ultrasonically prepared, freeze-dried Y-Ba-Cu-nitrate precursors were ideally suited to the study of the low-temperature phase stabilities in this system. In particular, they showed that, under 1 atm $P(O_2)$, none of the ternary cuprate superconductors could be stabilized below 675°C. For example, samples with a bulk composition of $YBa_2Cu_4O_8$ yielded a three-phase mixture of the nonconducting phases $Ba_2Cu_3O_{6-x}$, CuO, and Y_2O_3; the $YBa_2Cu_4O_8$ cuprate superconductor could only be formed between 675° and 825°C. The absence of any stable superconducting phases in a pure oxygen environment below this temperature is apparently the result of the dominant stability of the highly oxidized barium cuprate, $Ba_2Cu_3O_{6-x}$. Although this phase has been reported in the literature, its existence has not been widely recognized by many researchers (*17, 18*) and complete determination of its apparently modulated structure has not been accomplished. To confirm that the apparent metastability of the cuprate superconductors is attributable to thermodynamic rather than kinetic effects, we report here on a calorimetric determination of the enthalpy of formation of $Ba_2Cu_3O_6$ and resultant calculations of the thermodynamic stabilities of the oxidized cuprate superconductors.

Single-phase $Ba_2Cu_3O_6$ was prepared from a nitrate precursor at 620°C and 1 atm $P(O_2)$. The precursor was placed in a platinum boat and plunged into a heated furnace under flowing oxygen. Although freeze-dried nitrate precursor reactions generally occur within minutes, the sample was annealed for 120 hours to enhance grain growth. The sample was then quenched under oxygen. We determined the oxygen content by performing a thermogravimetric analysis under flowing, forming gas (a mixture of 15% H_2 and Ar, 50 cm^3/min), with a Dupont 951 thermogravimetric analyzer. The preparation of single-phase $YBa_2Cu_4O_8$ at 800°C and 1 atm $P(O_2)$ is presented in detail in (*15*).

A detailed description of the calorimetric procedure is given elsewhere (*12*); only a summary is given here. A Tronac 558 isothermal solution calorimeter, specially modified for perchloric acid calorimetry, was used for our work. Samples were encapsulated in borosilicate glass ampoules and attached to the stirring rod of an isothermal vessel that contained 25 ml of 4.00 M $HClO_4$ (Baker Ultrex grade). The vessel was then submerged in a constant-temperature water bath (±0.001°C per week) and allowed to reach thermal equilibrium at 25°C. The sample ampoule was broken and the subsequent heat of dissolution was determined by automatic electrical compensation. The magnitude of the heat effects was measured directly. We performed electrical calibrations automatically, before and after ampoule breakage, by adding a known amount of Joule heat from a calibration resistor immersed within the vessel.

Table 1. Thermodynamic data for the Y-Ba-Cu-O system. Data for Y_2O_3 and CuO are from (*28*) and (*19*), respectively.

Compound	$\Delta H°_{298}$ (solution) (kJ/mol)	$\Delta H°_{298}$ (formation) (kJ/mol)
$YBa_2Cu_3O_{7-x}$ ($x < 0.06$)	−802.1 ± 3	−2713 ± 18
$YBa_2Cu_4O_8$	−847.5 ± 5	−2906.4 ± 25
Y_2BaCuO_5	−655.5 ± 19	−2686.9 ± 22
$BaCuO_2$	−249.1 ± 0.2	−822.3 ± 7.9
$Ba_2Cu_3O_6$	−555.2 ± 6	−1825 ± 24
Y_2O_3		−1905.6 ± 2
CuO		−155.2 ± 3

Because ΔH^0_f is a state function, one can calculate standard-state enthalpies of formation by forming appropriate thermodynamic cycles of various chemical reactions whose net summation yields the elemental formation reaction for the $Ba_2Cu_3O_6$ compound at standard-state conditions. For reactions involving only condensed phases, ΔH_{rx} is approximately equal to the Gibbs free energy of reaction, ΔG_{rx}. We constructed appropriate thermodynamic cycles using the data presented in (*12*). The enthalpies of formation of other phases in the Y-Ba-Cu-O system that we measured are listed in Table 1.

The standard-state heat of solution for $Ba_2Cu_3O_6$ was measured to be +555.22 ± 6.03 kJ/mol, and the standard-state heat of formation was calculated to be −1825 ± 24 kJ/mol. The decomposition of the $YBa_2Cu_4O_8$ phase can be represented by the following reaction:

$$1/2O_{2(g)} + 2YBa_2Cu_4O_{8(s)}$$

$$= Y_2O_{3(s)} + 2Ba_2Cu_3O_{6(s)} + 2CuO_{(s)} \quad (1)$$

The enthalpy of reaction, $\Delta H°_{rx}$, at 298 K and 1 atm $P(O_2)$ is −53 ± 8 kJ. The change in entropy of gaseous oxygen to lattice oxygen can be estimated to be 202.9 J/mol·deg (*19*). Thus, at 298 K, the entropy contribution to the overall reaction free energy, $-T\Delta S_{rx}$, is approximately +30 kJ/mol. At 298 K, the free energy change of reaction 1 is negative, indicating that $YBa_2Cu_4O_8$ is thermodynamically unstable. By using these data and ignoring the entropies of the solid phases and heat capacity changes, we find that reaction 1 would be in equilibrium at 250°C. Although this temperature is somewhat lower than that predicted from the experimental phase investigations, both studies confirm the metastable nature of the $YBa_2Cu_4O_8$ superconductor.

The $YBa_2Cu_3O_{7-x}$ phase is also unstable with respect to the $Ba_2Cu_3O_6$ phase and Y_2O_3. The decomposition reaction of the $YBa_2Cu_3O_{7-x}$ phase can be represented by

$$1/2O_{2(g)} + 2YBa_2Cu_3O_{7(s)} = Y_2O_{3(s)} + 2Ba_2Cu_3O_{6(s)} \quad (2)$$

The enthalpy of this decomposition reaction is −130 ± 24 kJ/mol. As in the decomposition of $YBa_2Cu_4O_8$, the decomposition reaction of $YBa_2Cu_3O_7$, with respect to $Ba_2Cu_3O_6$ and Y_2O_3, involves the transfer of a half mole of gaseous oxygen to the lattice, with an entropic $-T\Delta S_{rx}$ contribution of approximately +30 kJ/mol. We compared the free energies of decomposition of both $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_{7-x}$ with respect to $Ba_2Cu_3O_6$; our comparison reaffirms that $YBa_2Cu_4O_8$ is more stable at low temperatures than $YBa_2Cu_3O_{7-x}$.

As expected, the phase relations in this system appear to be controlled by the oxidation thermodynamics of the copper ion; as the temperature of the system is reduced, higher formal valence states for copper are stabilized in electropositive lattice environments (*8, 20*). For the perovskite-related cuprates, the oxidation of copper from a formal valence of 2^+ to 3^+ is exothermic, releasing ~200 kJ per mole of O_2 (*12, 21, 22*); this favorable contribution to the partial molar ΔG_{rx} is, of course, balanced by the decrease in entropy of the system from the transformation of oxygen from the gaseous state to the solid state.

In this Y-Ba-Cu-O system, the highest formal valence occurs in the binary compound $Ba_2Cu_3O_6$; the average copper valence in this compound is +2.66 compared to +2.33 in $YBa_2Cu_3O_7$. A complete understanding of why $Ba_2Cu_3O_6$ exhibits such high stability at low temperatures, and thus why the superconductors are metastable, will require knowledge of the $Ba_2Cu_3O_6$ structure (it has not been completely refined). Previous electron and x-ray diffraction studies (*17, 18*) suggest that the structure is closely related to that of the trivalent cuprate, $NaCuO_2$. This structure, in which infinite one-dimensional chains of edge-shared cuprate groups are linked by the larger electropositive cations, is adopted by several highly oxidized cuprates. For example, closely related $ACuO_2$ phases can be stabilized at low temperatures for A = K (*23*), Cs (*24*), and Rb (*25*). The same arrangement of cuprate chains is also found in the low-temperature form of calcium cuprate, $Ca_{1-x}CuO_2$ (x = 0.8 to 0.85) (*26*) and in several ternary calcium–rare earth (RE) compounds, such as $(Ca_{2-x}RE_{2+x})Cu_5O_{10}$ (RE = Y, Gd, Nd) (*27*). The reduced occupancy of the larger interchain cation sites in these cation-deficient compounds is accommodated by a modulation of the positions of the larger cations. It is these modulations, which can be commensurate or incommensurate, that have complicated the refinements of these compounds. However, the published models for $Ba_2Cu_3O_6$, or $Ba_{0.67}CuO_2$, indicate that this may be another example of a stable modulated $NaCuO_2$-type structure. Apparently the higher electropositive environment provided by this structure is particularly effective in increasing the stability of the trivalent state for copper.

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Electrostatic Screening of Charge and Dipole Interactions with the Helix Backbone

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Electrostatic interactions in proteins are potentially quite strong, but these interactions are mitigated by the screening effects of water, ions, and nearby protein atoms. The early work of Kirkwood and Westheimer on small organic molecules showed that the extent of the screening may depend on whether charged or dipolar groups are involved. The dielectric and ionic screening of the interactions between the dipolar backbone amide groups of monomeric α helices and either (i) solvent-exposed charges or (ii) solvent-exposed dipoles at the amino terminus was measured. The dielectric screening effects are an order of magnitude greater for the backbone-charge interactions than for the backbone-dipole interactions, and the ionic strength dependence is substantially different in the two cases. These results suggest that interactions that involve the dipolar groups of proteins may be relatively more important for stability and function than is generally thought.

The screening of electrostatic interactions results primarily from electronic polarization, reorientation of dipolar groups, and changes in the concentrations of charged species in the vicinity of charges and dipoles. These effects are well understood and can be accurately determined for interactions in isotropic, homogeneous media. However, in complex inhomogeneous environments such as those near the surface of proteins, dielectric and ionic screening is difficult to predict. In these cases, factors such as the shape and composition of the surface and whether the interactions involve charged or dipolar groups are expected to be especially important. Structurally well defined peptides provide good model systems in which to study screening effects on electrostatic interactions at protein surfaces.

We have measured previously the interaction between the backbone of short, stable monomeric α helices and a solvent-exposed

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