Protonation of $[B_5H_8]^-$ gives nearly quantative yields of $B_5H_9$.[13]

Protonation of $K_2[B_5H_9]$ or $Cs_2[B_5H_9]$ with hydrogen chloride or hydrogen bromide provides a convenient route to pentaborane(11), $B_5H_{11}$ (eq 2). The protonation of $K_2[B_5H_9]$ with

$$M_2[B_5H_9] + 2HX \rightarrow B_5H_{11} + 2MX \qquad (2)$$

$$M = K, Cs; X = Cl, Br$$

HCl in butane at −78 °C has provided $B_5H_{11}$ in 38% yield based upon the $B_5H_9$ starting material. The product was isolated by trap to trap fractionation on the vacuum line through traps held at −111 and −196 °C. Pentaborane(11) was collected in the −111 °C trap and identified by its characteristic IR and $^{11}B$ NMR spectra[14,15] and by its vapor pressure at 0 °C of 52 mm.[16] This represents the simplist, most convenient, and safest preparative method to date for $B_5H_{11}$.[11,17-22] The starting material is commercially available.[23] Butane was chosen because it is chemically inert toward the boron hydrides and because its low boiling point allows easy separation of the $B_5H_{11}$ product on the vacuum line fractionation train.

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## Superconductivity at 91 K in the Magnetic Oxide $HoBa_2Cu_3O_{6+x}$

*Sir:*

A remarkable increase in $T_c$ (superconducting transition temperature) to temperatures near 90 K has been reported[1,2] recently for a phase of the Y–Ba–Cu–O system, variously identified as $YBa_2Cu_3O_{9-\delta}$ ($\delta = 2.1$),[3] $YBa_2Cu_3O_{6+x}$ ($x = 0.5$),[4] and $YBa_2Cu_3O_{6.81}$.[5] Relatively sharp superconducting transitions occur for this material with onset $T_c$'s at 93–98 K, with zero resistance at 80–94 K, and with substantial Meissner effects measured at temperatures not far below zero resistance. This superconducting oxide is a compound similar in metal stoichiometry to $Y_2Cu_2O_5$[6] on the basis of the total noncopper metal-to-copper atomic ratios. It is well documented that, in addition to Y, the lanthanide ions, $Ln^{3+}$, with more than seven 4f electrons form similar compounds, $Ln_2Cu_2O_5$.[6,7] Consequently, one speculates that superconducting oxides with $T_c$'s near 90 K might also occur for compositions $LnBa_2Cu_3O_{6+x}$, where $Ln^{3+}$ is any one of the heavier lanthanide ions. An interesting question in this case is the effect of the magnetic moment on superconductivity. Normally, the presence of the moment decreases $T_c$ through exchange interactions and, if magnetic ordering occurs, may lead to the coexistence of superconductivity and magnetism, or reentrant superconductivity (reentrant means return to the normal state). We have chosen to explore the synthesis and superconducting properties of $HoBa_2Cu_3O_{6+x}$ because $Ho^{3+}$ has the same radius as nonmagnetic $Y^{3+}$ (0.89 Å)[8] and, along with $Dy^{3+}$, has the largest magnetic moment (10.4 $\mu_B$)[9] of the $Ln^{3+}$ ions. In the course of this work, conflicting reports have appeared which indicate that an uncharacterized phase (or phases) of the Ho–Ba–Cu–O system is superconducting with $T_c$'s of ~46,[10] 70,[11] or 93 K.[12,13] In this communication we report on bulk superconductivity near 91 K without reentrant behavior down to 0.55 K for $HoBa_2Cu_3O_{6+x}$.

**Synthesis.** Ceramic oxides of both the Y and Ho compounds of initial composition $MBa_2Cu_3O_{6+y}$ (M = Y or Ho) were prepared to provide a comparison of the properties of the Ho-based material with the superconducting properties of the Y-based material. These were synthesized by adding stoichiometric amounts of $Y_2O_3$ or $Ho_2O_3$ to CuO and $BaCO_3$ (all dry, reagent grade powders). The components were intimately mixed and ground by the use of a ball mill, placed in a Pt crucible, and calcined in air at 950 °C in a muffle furnace. After 24 h, the samples were removed and allowed to cool to room temperature in air. The calcined products were reground with a mortar and pestle and pressed into pellets. The pellets, contained in a Pt boat, were placed in a fused silica tube, which was heated in a tube furnace. Under an atmosphere of pure $O_2$ at a flow rate of 85 mL/m, the pellets were sintered at 950 °C for 16 h and then cooled to 200 °C over a period of 1 h. After this sintering, the pellets were removed from the furnace and further cooled in air.

**Analysis.** X-ray powder diffraction patterns of the Y-based ceramic pellet indicated the existence of two phases. These could be identified as the superconducting phase $YBa_2Cu_3O_{6+x}$ and the semiconducting[3] phase $Y_2BaCuO_5$.[14] Chemical analysis of the metal constituents gave ~70% for the molar concentration of the superconducting phase. The Ho-based ceramic also showed the existence of two phases by X-ray powder diffraction analysis. The major phase could be indexed by use of an orthorhombic unit cell with $a = 12.178$ (3) Å, $b = 5.660$ (2) Å, and $c = 7.127$ (2) Å, in excellent agreement with the parameters reported for $Ho_2BaCuO_5$.[14] The second phase was indexed by use of an orthorhombic unit cell with $a = 3.825$ (3) Å, $b = 3.894$ (4) Å, and $c = 11.682$ (11) Å. These dimensions are close to those reported for the $YBa_2Cu_3O_{6+x}$ superconducting phase,[3-5] and since $Ho^{3+}$ and $Y^{3+}$ have essentially identical radii, we conclude that the second phase is $HoBa_2Cu_3O_{6+x}$.

Measurements of the atomic ratios of metal constituents in the ceramic pellets were carried out by the method of inductively coupled plasma/atomic emission spectroscopy. Since the X-ray diffraction patterns indicate the presence of only two phases,

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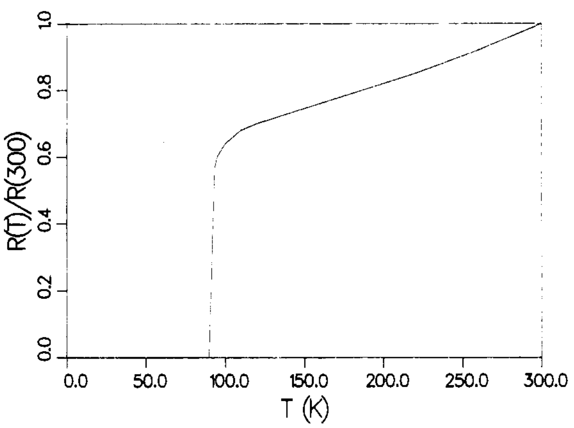

**Figure 1.** Relative resistivity as a function of temperature for a ceramic sample of $HoBa_2Cu_3O_{6+x}$. $T_c$ (midpoint) $\simeq$ 90.8 K.

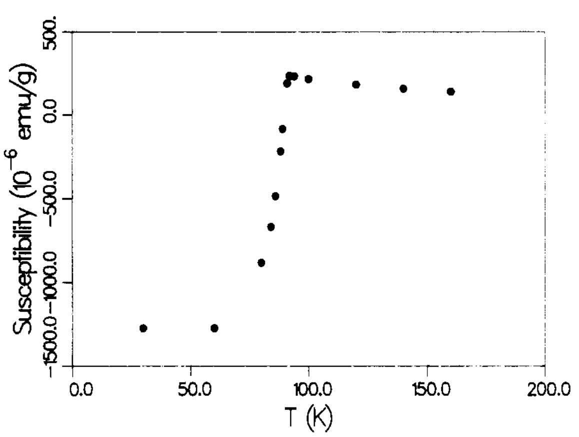

**Figure 2.** Dc susceptibility in a field of 53 Oe for a powdered sample of $HoBa_2Cu_3O_{6+x}$. $T_c$ onset is 91.5 K, and the Meissner effect at 30 K is ~30%, indicating bulk superconductivity.

$MBa_2Cu_3O_{6+x}$ and $M_2BaCuO_5$ (M = Y or Ho), these ratios could be used to derive the percentage composition of each phase. For the Ho-based ceramic specimen, the Ho:Ba:Cu ratios were found to be 1:0.81 (±0.16):1.4 (±0.3), where the errors are ranges in the metal:Ho ratios based on a ±10% error in the percentage weight of each metal relative to the total weight of the analyzed sample. These ratios give a molar percentage composition for $HoBa_2Cu_3O_{6+x}$ of ~50 ± 10% based on the Cu:Ho ratio and ~30 ± 10% based on the Ba:Ho ratio, or an average of ~40%. This is consistent with the X-ray powder diffraction results. We are presently varying the preparative conditions in order to produce single-phase superconducting material.

**Superconductivity.** Measurements of the electrical resistance of small sections cut from the ceramic pellets were carried out by use of the four-lead technique at temperatures from 300 K down to 15 K for the Y-based material and down to 0.55 K for the Ho-based material. The $YBa_2Cu_3O_{6+x}$ samples showed an approximately linear decrease in resistance with decreasing temperatures from 300 K to below 100 K and a sharp drop in the resistance to the superconducting state near 90 K. The superconducting onset temperature (defined by the intersection of lines extrapolated from the normal-state resistance and from the sharp, linear drop in resistance) occurred at 93 K. Zero resistance below instrument resolution occurred at 89.7 K. The midpoint of the transition was 91.7 K, and the 10%–90% transition width was ~1 K. These parameters compare favorably with those previously reported for the pure-phase $YBa_2Cu_3O_{6.9}$ superconductor[3]. The room-temperature resistivity $\rho$(300 K) $\simeq$ 6000 $\mu\Omega$ cm and resistivity ratio $\rho(300\ K)/\rho(100\ K) \simeq 2$, however, indicate some degradation in sample quality. Measurements of the dc susceptibility of our $YBa_2Cu_3O_{6+x}$ sample by the use of a squid magnetometer yielded a sizable Meissner effect. The excluded flux as a fraction of that excluded by an ideal superconductor of the same volume is given by the formula $\Phi/\Phi_i = -4\pi\chi(1-n)$, where $\chi$ is the dimensionless volume susceptibility and $n$ is the demagnetizing factor. With $n = 0$ (no demagnetizing correction) the susceptibility measured at 30 K in a field of 53 Oe gave a susceptibility equivalent to a 79% Meissner effect, proving bulk superconductivity.

Figure 1 illustrates the temperature dependence of the resistivity of the $HoBa_2Cu_3O_{6+x}$ sample. The resistive superconducting onset occurs at 93.5 K, and the resistance becomes zero below instrument resolution at 89.2 K and remains zero down to 0.55 K. The transition midpoint is 90.8 K with a 10%–90% width of ~1.5 K. Some loss in sample quality is indicated by the relatively large room-temperature resistivity and low resistivity ratio, $\rho$(300 K) $\simeq$ 10 000 $\mu\Omega$ cm and $\rho(300\ K)/\rho(100\ K) \simeq 2$. Figure 2 shows the dc susceptibility as a function of temperature in a field of 53 Oe for the $HoBa_2Cu_3O_{6+x}$ sample. One observes paramagnetic behavior followed by a sharp drop in the susceptibility where diamagnetism first appears. The onset of the inductive superconducting transition occurs at 91.5 K, which is between the onset and midpoint temperatures of the resistive superconducting transition. An analysis of the normal-state susceptibility ($1/\chi$ vs. $T$) shows Curie behavior. On the basis of the number of magnetic ions per unit volume, the densities, and the weight fractions of each phase, we estimate that about 75% of the experimental mass susceptibility in the normal state is due to the susceptibility of the impurity phase. The impurity phase also gives a paramagnetic contribution to the total susceptibility below $T_c$. From a Curie law extrapolation of this paramagnetic contribution and from an apportionment of the experimental susceptibility according to the weight fraction of each phase, we can estimate the diamagnetic susceptibility of the superconducting phase. From this we obtain for superconducting $HoBa_2Cu_3O_{6+x}$ at 30 K a Meissner effect ($n = 0$) of ~30%, indicating bulk superconductivity.

In summary, we have synthesized a ceramic oxide composition of the Ho–Ba–Cu–O system that exhibits bulk superconductivity with transitions essentially identical with those reported for superconducting $YBa_2Cu_3O_{6+x}$ ($T_c \simeq 90$ K). This material consists of $Ho_2BaCuO_5$, which we believe to be a semiconducting phase analogous to $Y_2BaCuO_5$, and a second phase, which is the superconducting phase $HoBa_2Cu_3O_{6+x}$, analogous to $YBa_2Cu_3O_{6+x}$. Despite the large magnetic moment of $Ho^{3+}$, $HoBa_2Cu_3O_{6+x}$ exhibits no reentrant behavior down to $T = 0.55$ K, implying that the exchange interactions between the local magnetic moments and conduction electrons are extremely small.

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