

Synthesis and properties of the 2:4:7 superconductors $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ ($R = \text{Y, Eu, Gd, Dy, Ho, Er}$)

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(Received 20 July 1989)

Six high-temperature superconducting compounds $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ ($R = \text{Y, Eu, Gd, Dy, Ho, Er}$) are synthesized in oxygen at moderate pressures above 1 bar. Each 2:4:7 compound is stable only within a narrow range of oxygen pressures bounded by the stability regions of the 1:2:4 and 1:2:3 phases; the required $P(\text{O}_2)$ varies with temperature and R -ion radius. Our 2:4:7 compounds show low T_c 's (45–55 K) which vary inversely with ion size (as in 1:2:4). The basal plane areas are larger and orthorhombic distortions smaller than the corresponding 1:2:3 and 1:2:4, suggesting smaller oxygen content, lower hole concentration, and weaker bonding in the CuO_2 layers. The 2:4:7 phase has variable oxygen stoichiometry, and T_c decreases when oxygen is removed.

I. INTRODUCTION

Recently, new superconducting compounds $R\text{Ba}_2\text{Cu}_4\text{O}_8$, $R = \text{Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm}$ (abbreviated as 1:2:4), were synthesized in an environment of high-oxygen concentration.¹ Another phase $\text{Yb}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ (abbreviated as 2:4:7) was synthesized by oxidation of metallic precursors in 1-bar O_2 .² This 2:4:7 phase consists of alternating blocks of $\text{YbBa}_2\text{Cu}_4\text{O}_8$ (1:2:4) and $\text{YbBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (1:2:3) along the c axis. Isolated crystals of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ were subsequently found by Bordet *et al.* in a melt of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ that was subjected to 100-bar oxygen pressure.³

We report the preparation of the high-temperature superconductor $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ in bulk by the solid-state reaction method, as well as five analogous rare-earth compounds $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ ($R = \text{Eu, Gd, Dy, Ho, Er}$). Moderate oxygen pressures ranging from 11 to 35 bar were required. We have determined the oxygen pressure ranges within which each of the 2:4:7 compounds are thermodynamically stable, and find that the required $P(\text{O}_2)$ increases with rare-earth radius. The properties of the 2:4:7 compounds are interesting and are different from the 1:2:3 and 1:2:4 parent phases. The T_c of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ (55 K) is much lower than Y 1:2:3 (92 K) or Y 1:2:4 (81 K). Detailed comparison of structural parameters of the 2:4:7 phase with the 1:2:3 and 1:2:4 parent compounds may help elucidate the underlying mechanism responsible for high-temperature superconductivity. Comparisons among the R -substituted 1:2:3, 1:2:4, and 2:4:7 compounds may also prove fruitful for this purpose. The 2:4:7 phase shows variable oxygen stoichiometry, as one would expect since it contains blocks of 1:2:3. The effect on T_c of varying the oxygen content should provide information about the roles of the 1:2:4 and 1:2:3 blocks, and the coupling between the different layers.

II. SYNTHESIS EXPERIMENTS

The $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ compounds ($R = \text{Y, Eu, Gd, Dy, Ho, Er}$) were synthesized by solid-state reaction of a stoichiometric mixture of $R_2\text{O}_3 + \text{BaO} + \text{CuO}$ powders (all 99.9% or better) using a commercial high-pressure oxygen furnace.⁴ In the case of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$, reaction was carried out at 930 °C in oxygen at a pressure $P(\text{O}_2) = 18.6$ bar for 8 h. This was followed by slow cooling (5 °C min) to room temperature at the same pressure. The rare-earth-substituted compounds were prepared similarly, but a higher synthesis temperature (980 °C) was necessary for complete reaction of the lighter rare-earth compounds such as Eu 2:4:7. Differing synthesis pressures were used because the 2:4:7 stability region was found to vary with rare-earth radius (see Sec. V, Table I, and Fig. 2). In some cases, the pellets were ground and fired a second time under the same conditions to improve homogeneity and to ensure complete reaction.

III. T_c AND DIAMAGNETISM

Bulk superconductivity in all samples was demonstrated by substantial Meissner diamagnetism (see Table I and Fig. 1), using a Quantum Design SQUID magnetometer. The critical temperatures of the 2:4:7 compounds were much lower than those of the corresponding 1:2:3 and 1:2:4 compounds. T_c 's range from 45 to 55 K and vary with rare-earth radius, as do the lattice parameters (see Figs. 3 and 4). This suggests the possibility of a large pressure dependence of T_c in the $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ phase, as reported for $\text{YBa}_2\text{Cu}_4\text{O}_8$.⁵ This range of T_c 's is consistent with the T_c of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ reported in Ref. 3, but not with $T_c \sim 86$ K for $\text{Yb}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ given in Ref. 2. Our samples showed no substantial diamagnetism

TABLE I. Superconducting and structural parameters of $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ compounds.

R = ion	Superconducting parameters ^a				Lattice parameters of 2:4:7 phase					Synthesis conditions	
	radius	T_c (K)	$\chi_{20\text{K}}^b$	$4\pi\rho\chi_{20\text{K}}^c$	a (Å)	b (Å)	c (Å)	V (Å ³)	b/a	T (°C)	$P(\text{O}_2)$
Eu ^d	1.066	45	-10	8%	3.879(2)	3.886(1)	50.39(3)	759.6	1.0018	980	35
Gd ^d	1.053	45	-13	10%	3.872(1)	3.879(1)	50.36(2)	756.4	1.0018	930	35
Dy	1.027	50	-8	6% 1	3.864(1)	3.879(1)	50.39(1)	755.3	1.0038	980	30
Y	1.019	55	-40	32%	3.854(1)	3.874(1)	50.40(1)	752.5	1.0052	980	20
Ho	1.015	55	-18	14%	3.857(1)	3.879(1)	50.40(1)	754.0	1.0057	930	15
Er	1.004	55	-15	12%	3.847(1)	3.873(1)	50.44(1)	751.5	1.0068	980	14

^aBy observation of flux expulsion. Note that the T_c 's of the different compounds are significantly different and are correlated with lattice parameters a and b , and with orthorhombic distortion which is larger for the heavier (smaller) rare-earth ions.

^bFlux expulsion on cooling to 20 K in a constant 6-Oe field, in units of 10^{-4} emu/g.

^cDiamagnetic volume fraction. The density ρ is calculated from the measured unit cell volume. The superconducting fraction may be larger, because some expelled flux will be trapped in the pores of these ceramic samples.

^dSample contained 1:2:4 as impurity phase. Lattice parameters were obtained by simultaneous Rietveld refinements of both phases.

above the onsets in the 45–55-K range, except for Gd which contained some 1:2:4 phase (Fig. 1).

IV. CHARACTERIZATION BY X-RAY DIFFRACTION

All grains in the polycrystalline samples appear black and optically opaque, with average grain sizes $\leq 2 \mu\text{m}$. X-ray powder diffraction was performed on a Scintag automated powder diffractometer using Cu $K\alpha$ radiation. Diffraction patterns of the samples were examined for evidence of the superconducting phases 2:4:7, 1:2:4, and 1:2:3, as indicated by the presence of low-angle peaks at d spacings of approximately 12.5, 13.6, and 11.7 Å, respectively. For each sample that showed the 2:4:7 structure as

the major phase, full scans were taken and cell parameters were refined by the Rietveld method, assuming space group $Ammm$ and the model structure reported in Ref. 3. Our preliminary Rietveld studies indicate that the atomic structure of our 2:4:7 compounds is consistent with that given in Ref. 3. Our lattice parameters are given in Table I. In the case of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$, we find $a = 3.854(1)$ Å, $b = 3.874(1)$ Å, and $c = 50.40(1)$ Å, in general agreement with Ref. 3 but with higher precision. The powder-diffraction pattern for $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ showed minor amounts of CuO and an unidentified phase (peaks at 3.09 and 3.00 Å), but no characteristic peaks of 1:2:4 or 1:2:3 compounds were seen. We conclude that the $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ compound is the predominant bulk superconductor in this sample. This low-angle x-ray method is less sensitive for Y compounds than for rare-earth-substituted samples, where the stronger low-angle peaks¹ permit the easy identification by powder diffraction of minor quantities of 1:2:4 and 1:2:3.

V. PHASE DIAGRAMS

Portions of the phase diagrams for the 1:2:3-1:2:4-2:4:7 systems with $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ ($R = \text{Y, Eu, Gd, Dy, Ho, and Er}$) are given in Fig. 2. Each point represents a different synthesis experiment. Samples which showed only a single low-angle x-ray diffraction (XRD) peak are marked with the symbol for the corresponding phase. For mixed-phase samples, both symbols are shown. The fractions of the different phases were estimated from the relative heights of the low-angle XRD peaks. The phase diagrams of the Y-Ba-Cu-O and Dy-Ba-Cu-O system show that at 930 °C the 2:4:7 phase is stable only in a small range of oxygen pressure between about 12 and 30 bar. This 2:4:7 region lies between the stability regions of the 1:2:4 and 1:2:3 phases. The required $P(\text{O}_2)$ increases with temperature;⁶ at 980 °C the 2:4:7 phase is found only between 20 and 60 bar (see Fig. 2). When lighter (larger) rare-earth elements are substituted for Y or Dy the region of stability of 2:4:7 appears to shift to higher pressure. This shift with R -ion size may explain the successful synthesis at 1-bar oxygen pressure of $\text{Yb}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ by oxidation of a metallic precursor,² and of $\text{ErBa}_2\text{Cu}_4\text{O}_8$ and of $\text{HoBa}_2\text{Cu}_4\text{O}_8$ by solid-state reaction starting with

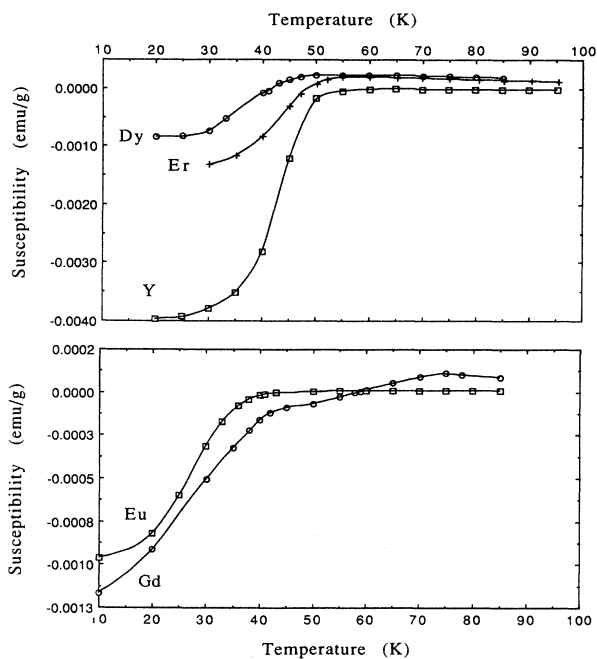


FIG. 1. Meissner susceptibility curves of superconducting compounds $R_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ ($R = \text{Y, Eu, Gd, Dy, Er}$) prepared under conditions given in Fig. 2. The transitions are strong and sharp. All samples are single phase except for Gd. T_c 's vary from 45 to 55 K and correlate with ion size (see Fig. 4).

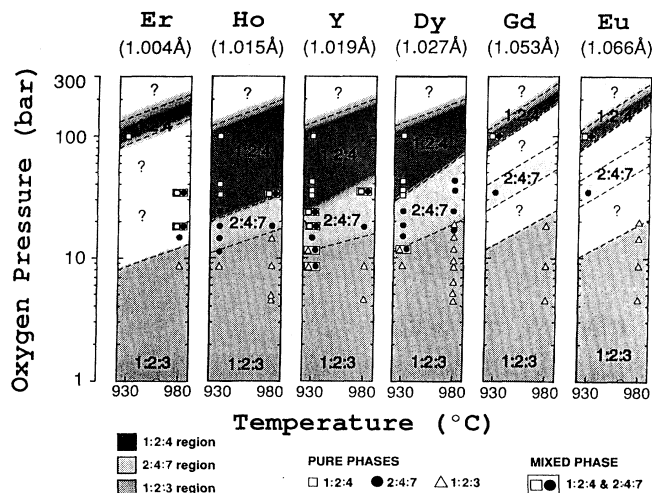


FIG. 2. Partial P - T - x diagrams of superconducting phases in several rare-earth R -Ba-Cu-O systems. The rare-earth-ionic radii (Ref. 12) are indicated. Each data point represents a different synthesis experiment. The phase content in each case was determined by low-angle XRD patterns. Shaded areas represent estimated stability regions for the different phases; 2:4:7 is between 1:2:3 and 1:2:4.

nitrate.⁷ Based on the data for Dy and Y in Fig. 2, the pressure range of stability of 2:4:7 appears to become narrower as the synthesis temperature is decreased from 980°C to 930°C. At still lower temperatures, the 2:4:7 region may pinch off for ions larger than Yb, leaving only the 1:2:4 and 1:2:3 phases at 1-bar oxygen pressure.

VI. VARIABLE OXYGEN STOICHIOMETRY OF 2:4:7

Oxygen variation provides an additional tool for studying superconductivity in the 2:4:7 compounds, and may possibly vary the anisotropy of normal-state transport and superconducting parameters. Preliminary oxygen content studies were performed on $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ using a Perkin-Elmer TGA-7 thermogravimetric analyzer. Samples were heated in 1-bar O_2 and in N_2 and rapid oxygen loss was observed above $\sim 400^\circ\text{C}$, which was reversible in O_2 . As expected, T_c shifts downward with decreased oxygen content. Details will be published elsewhere.

VII. CORRELATION OF STRUCTURAL PARAMETERS OF 2:4:7-1:2:4-1:2:3 WITH T_c

It is interesting to compare the differences in lattice parameters of 2:4:7, 1:2:4, and 1:2:3, since some of these differences may be related to the large disparity in T_c 's. In fully oxygenated 2:4:7 compounds the formal average copper valence (FACV) would be 2.28, intermediate between 1:2:4 (FACV = 2.25) and 1:2:3 (FACV = 2.33), so one might expect an intermediate hole concentration and T_c . The observed T_c 's of 2:4:7 are much lower than those of the corresponding 1:2:4 and 1:2:3 compounds. If the reduced T_c of 2:4:7 is due to lower oxygen content and hole concentration, the antibonding Cu-O orbitals will be more filled resulting in longer bonds in the CuO_2 planes, which may be reflected in the lattice parameters. In fact,

several structural parameters of our 2:4:7 compounds are *not* intermediate between those of the corresponding 1:2:3 and 1:2:4 compounds. These include the a and c lattice parameters, the orthorhombic distortion, and the basal-plane area.

For all the 2:4:7 compounds, the c axis is shorter than the sum of the c axes of the corresponding 1:2:4 and 1:2:3 compounds (see Fig. 3), possibly indicating shorter apical oxygen distance. This, and the larger ab area, suggest smaller hole concentration in the CuO_2 planes. Measurement of the oxygen content and of the mobile-hole concentration (by Hall effect) may clarify this. Differences in atomic positions and unit-cell size can also change the Madelung energy, and thereby change the degree of carrier delocalization,⁸ but based on the atomic positions in Y 2:4:7 from Ref. 3, the differences between the calculated ΔV_M in CuO_2 sheets of 2:4:7, 1:2:3, and 1:2:4 are negligible.⁸

It should be pointed out, however, that estimates of changes in bond lengths from changes in a , b , and c do not take into account possible changes in bond angles such as those resulting from the "puckering" of the CuO_2 layers. It is known⁹ that the average Cu-O-Cu bond angle in the CuO_2 planes of 1:2:4 is 165.7° , somewhat larger than in 1:2:3 (163.8°). If the bond angle increases to 168.8° in 2:4:7, the larger basal-plane area of 2:4:7 can be accounted for without an increase in bond lengths. Precise atomic

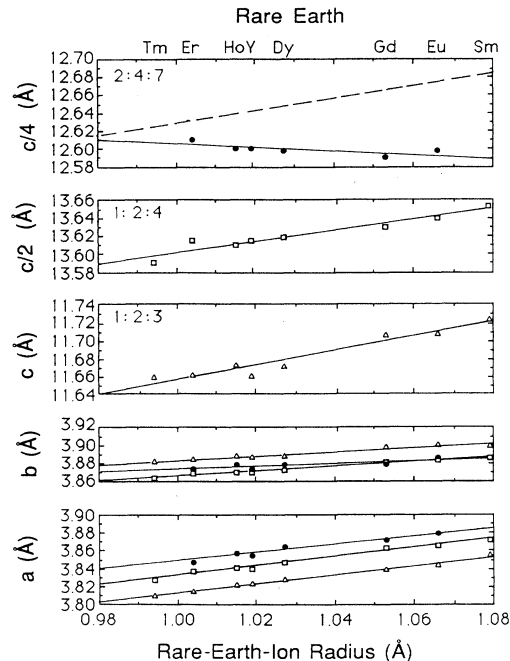


FIG. 3. Dependence of a , b , and c lattice parameters of 2:4:7, 1:2:4, and 1:2:3 superconductors on rare-earth-ion radius. The 2:4:7 parameters are shown by filled circles, and 1:2:3 and 1:2:4 are shown by open triangles and squares, respectively. The lattice parameter values for the 1:2:4 and 1:2:3 were taken from Ref. 1 and Ref. 13, respectively, and rare-earth radii were taken from Ref. 12. For ease of comparison we plot the sizes of a single R - R block (c for 1:2:3, $c/2$ for 1:2:4, and $c/4$ for 2:4:7) using the same scale. The dashed line in the 2:4:7 plot gives the sum of the 1:2:3 and 1:2:4 values.

positions, necessary to determine bond lengths and angles, can be obtained by neutron diffraction.

The orthorhombic distortion found in 2:4:7 is much less than that in the corresponding 1:2:4 compound. This suggests that the 1:2:3 blocks in our 2:4:7 samples are of the tetragonal type without ordered Cu-O chains. The oxygen content of our Y2:4:7 samples was 14.6–14.7 by chemical determination (idometric). Though our 2:4:7 compounds were processed in pressurized oxygen, they contain less than 15 oxygens. Bordet³ also found low Cu-O layer oxygen (O1) site occupation (~ 0.2 in their 2:4:7 crystals) by Rietveld refinement of single-crystal x-ray data.

The basal-plane areas ab of each 2:4:7 compound is considerably larger ($\sim 0.6\%$) than in the corresponding 1:2:4 or orthorhombic 1:2:3 compound (see Fig. 4). We may compare this with the change of basal plane area of 1:2:3 when oxygen is removed. From Fig. 2 of Ref. 10, the change in ab is only about 0.2% when x is varied from 6.9 to 6.05 in $\text{YBa}_2\text{Cu}_3\text{O}_x$. Even with this large change in oxygen content, which reduces T_c from 92 K to zero, the increase of ab is only $\frac{1}{3}$ as large as the difference between the ab of 2:4:7 and of 1:2:4. It seems difficult to account for the enlarged ab of 2:4:7 only by differences in oxygen stoichiometry.

VIII. VARIATION OF LATTICE PARAMETERS AND T_c WITH RARE-EARTH SUBSTITUTION

The 2:4:7 compounds with lighter (larger) rare-earth elements showed decreased T_c 's [Fig. 4(a)]. This behavior is also found in 1:2:4,¹ but not in 1:2:3 where T_c is constant or increases slightly with ion size.¹¹ When rare-earth elements with larger radius¹² (Gd, Eu) are substituted for Y in the 2:4:7 structure, the a and b parameters increase with ion radius. The a parameter in 2:4:7 is larger than in 1:2:4 or 1:2:3 but increases at the same rate with R -ion size; b of 2:4:7 is intermediate between 1:2:3 and 1:2:4 but increases with R -ion size at a slower rate. Surprisingly, c of 2:4:7 decreases with increasing R -ion size, opposite to the trends of 1:2:3 and 1:2:4 (see Fig. 3). The decreasing c suggests progressively shorter apical oxygen distances in the 2:4:7 compounds with increasing R -ion size possibly indicating decreasing hole concentration in the CuO_2 planes of these compounds, whose T_c 's are found to progressively decrease [Fig. 4(a)].

The basal-plane area ab of 2:4:7 increases with R -ion size (as in 1:2:4 and 1:2:3) and in the samples we prepared, is consistently about 0.6% larger than in the 1:2:3 or 1:2:4 phases in all rare-earth systems [Fig. 4(c)]. In comparison, in the $\text{RBa}_2\text{Cu}_3\text{O}_x$ series, the difference in ab

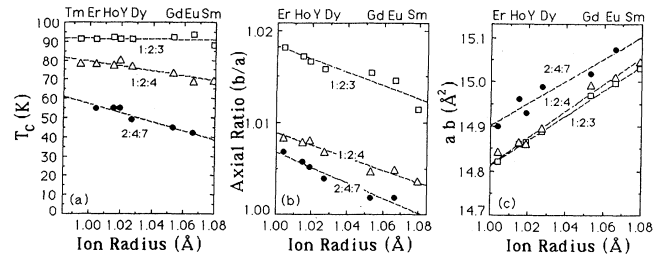


FIG. 4. (a) T_c vs rare-earth-ion radius. Symbols and references are the same as in Fig. 3. For 2:4:7 and 1:2:4, T_c decreases as ion size increases. (b) Orthorhombic distortion of the 1:2:3, 1:2:4, and 2:4:7 compounds vs rare-earth radius. For 2:4:7 the distortion approaches zero beyond Eu. (c) Basal plane areas ab vs rare-earth-ion radius. The 2:4:7 compounds prepared under conditions given in Fig. 2. All have larger ab than corresponding 1:2:3 and 1:2:4 compounds. This suggests longer and weaker bonds in the CuO_2 planes of 2:4:7 and reduced charge transfer.

between the orthorhombic and tetragonal phases increased with rare-earth radius, and ranged from 0.2% for Y, Er, and Tm, to 0.5% for Eu (from data in Table I of Ref. 10). This is a further indication that the increased ab in the 2:4:7 compounds is not simply a reflection of lower-oxygen content. The orthorhombic distortion of the 2:4:7 phase is small and decreases rapidly as rare-earth size increases [Fig. 4(b)]. The distortion reaches a very small value for Eu 2:4:7, and extrapolates to zero at Sm 2:4:7, which we were unable to synthesize.

In short, the low T_c 's of the 2:4:7 compounds are accompanied by large basal-plane areas and small orthorhombic distortions, compared to the values for the corresponding 1:2:3 and 1:2:4 compounds. The a and b lattice parameters of 2:4:7 increase with rare-earth size as expected, but c decreases. The 2:4:7, 1:2:4, and 1:2:3 phases offer three families of cuprate superconductors with incremental variation in structure and properties, which may be useful in testing theories of high-temperature superconductivity.

The authors thank Daphne Ross for assistance with x-ray diffraction, R. M. Hazen, J. Jorgenson, A. P. B. Sinha, and G. W. Smith for useful advice, M. T. Tran, N. A. Crocker, J. Chen, and G. Segre for laboratory assistance, and H. Nelson for general assistance. Work at the Geophysical Laboratory was supported by National Science Foundation Grants No. EAR8419982 and No. EAR8618602.

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