

Crystal structure of DyBa₂Cu₄O₈: A new 77 K bulk superconductor

Robert M. Hazen and Larry W. Finger

Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton Street NW,
Washington, DC 20008-3898

Donald E. Morris

Physics Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Single-crystal x-ray diffraction data from DyBa₂Cu₄O₈ are used to confirm the structure of R Ba₂Cu₄O₈ ($R = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, \text{ and } Tm$), all of which have been synthesized in bulk and display substantial Meissner diamagnetism. The structure is orthorhombic, space group $Ammm$, with $a = 3.846\ 3(3)$, $b = 3.872\ 6(3)$, and $c = 27.237(2)$ Å. Copper-oxygen layers parallel to (001) are dimpled as in the 1-2-3 structure. Unique copper-oxygen strips parallel to (100) have copper in distorted square-planar coordination. Magnitudes of oxygen anisotropic thermal vibrations are significantly less than in the 1-2-3 structure; thus the oxygen content of 1-2-4 is expected to be significantly more stable.

High-temperature superconductivity in layered copper oxides, first reported in materials possessing the K₂NiF₄¹ (2-1-4) and YBa₂Cu₃O₇² (1-2-3) structures, has now been documented in dozens of compounds with at least ten different structure types. Several of the recently discovered layered superconducting structures (those in the Bi-Ca-Sr-Cu-O³⁻⁶ and Tl-Ca-Ba-Cu-O⁷⁻¹² systems, for example) are closely related to each other, differing only in the number of adjacent copper-oxygen layers. Similar behavior has been observed in the Y-Ba-Cu-O system, in which the 1-2-3 structure may accommodate an extra copper layer, thus yielding compounds of stoichiometry 1-2-4¹³⁻¹⁶ and 2-4-7 (in which 1-2-3 and 1-2-4 layers alternate).¹⁷ Samples of YBa₂Cu₄O₈ have previously been produced only in thin-film form. Crystal structure analysis by Marsh *et al.*,¹⁵ was thus of necessity based on a limited data set. In this letter we describe x-ray diffraction analysis of a single crystal of DyBa₂Cu₄O₈, one of eight new 1-2-4-type superconductors synthesized in bulk by Morris *et al.*¹⁶ at high oxygen pressure. Our data confirm the results of Marsh *et al.*, while revealing important details of lattice distortions, atom positions, anisotropic atomic vibrations, and oxygen occupancies not evident from the thin-film work.

Morris *et al.*¹⁶ synthesized bulk 1-2-4 superconductors of composition R Ba₂Cu₄O₈ ($R = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, \text{ and } Tm$). Prior to that study 1-2-4 materials were only available in thin films. The DyBa₂Cu₄O₈ sample was prepared by grinding an oxide mix of 1-2-4 stoichiometry, pressing the powder into a pellet, and heating at 930 °C for 8 h at 102 atm oxygen pressure. After slow cooling for 8 h the pellet was reground, repressed, and the high-pressure heating and cooling treatment in oxygen was repeated. Diamagnetic measurements of the resulting black superconducting disk demonstrate a sharp onset at 78 K and a midpoint temperature of 73 K, as illustrated in Morris *et al.*¹⁶

X-ray powder diffraction of the bulk specimens revealed that the Dy sample was the most nearly pure 1-2-4 phase, and that sample was examined for suitable single crystals. A number of crystals with maximum dimensions up to 0.1 mm were observed; a single crystal of size 0.01 × 0.05 × 0.05 mm³ was selected for diffraction studies on a Rigaku four-circle

diffractometer equipped with rotating-anode generator. Unit-cell parameters were calculated from the measured positions of 20 reflections corrected for crystal centering errors. Resulting orthorhombic cell parameters ($a = 3.842 \pm 0.002$; $b = 3.867 \pm 0.002$; $c = 27.21 \pm 0.02$ Å) are consistent with, although less precise than, values obtained by Rietveld refinement of x-ray powder diffraction data of the same sample.¹⁶ The axial ratio b/a , which is a measure of the distortion from ideal tetragonal dimensionality, is 1.007—a value significantly smaller than the 1.017 ratio of fully ordered 1-2-3.

A complete sphere of diffracted intensities was measured with Mo $K\alpha$ radiation to a maximum 2θ of 60°. Systematic absences were consistent with space group $Ammm$ as reported by Marsh *et al.*¹⁵; however, there was a significant fraction of the crystal associated with a twin operation rotated by 90° about the c axis. The ω step-scan data were manually integrated to remove as much of the scattering due to the twin component, and the resulting intensities were corrected for absorption ($\mu_t = 290.7\ \text{cm}^{-1}$) using Gaussian integration.¹⁸ Calculated transmission factors ranged from 0.27 to 0.70. Corrected structure factors were averaged (internal agreement = 4.6%) to yield a total of 393 data, of which a total of 346 had intensities greater than $2\sigma_I$.

Least-squares refinement was carried out using program RFINES88, a development version of RFINES4,¹⁹ starting with the previous results.¹⁵ Complex scattering factors for neutral atoms were taken from International Tables.²⁰ After convergence with isotropic temperature factors, an isotropic extinction correction of type 1 with Lorentzian distribution,²¹ and a twin fraction parameter, the temperature factors were converted to anisotropic to yield the parameters shown in Table I. Oxygen occupancy factors were refined and the difference Fourier maps were searched in the vicinity of the defect sites. The occupancies of all four symmetrically distinct oxygens refined to within 5% of unity. Similarly, there were no features greater than 0.5 electrons per Å³ in the difference Fourier maps, which suggest no significant concentration of oxygen at the "vacant" positions near (0,0,0) and (0,0,0.2). The composition of this material is thus assumed to be stoichiometric DyBa₂Cu₄O₈. In the final

TABLE I. Crystallographic data for DyBa₂Cu₄O₈. Diffraction experiments with Rigaku AFC-5 diffractometer, rotating anode generator, Mo Kα₁ radiation, graphite monochromator, λ = 0.7093 Å, ω step scan, ambient temperature and pressure. a = 3.8463(3) Å, b = 3.8726(3) Å, c = 27.237(2) Å; V_{cell} = 405.70. Space group Ammm; Z = 2; molecular mass = 819.3; ρ_{calc} = 6.71 g cm⁻³. Crystal 10 × 50 × 50 μm³, μ_f = 290.7 cm⁻¹. Reflections = 393, observed = 346, R = 3.2%, R_w = 2.7%. Cell parameters from Ref. 16. B_{jj} = 4a_j²β_{jj}.

	x	y	z	B ₁₁	B ₂₂	B ₃₃	B _{eq}
Dy	½	½	0	0.54(3)	0.37(4)	0.48(3)	0.46(2)
Ba	½	½	0.134 96(3)	0.69(3)	0.44(3)	0.69(3)	0.61(2)
Cu1	0	0	0.213 12(5)	1.16(7)	0.39(6)	0.43(5)	0.66(3)
Cu2	0	0	0.061 80(6)	0.53(6)	0.30(5)	0.72(5)	0.52(3)
O1	0	0	0.145 8(3)	1.9(5)	0.7(4)	0.9(3)	1.2(2)
O2	½	0	0.052 6(3)	0.5(3)	0.6(4)	1.0(3)	0.7(2)
O3	0	½	0.053 2(3)	1.0(4)	0.5(4)	0.8(3)	0.8(2)
O4	0	½	0.218 6(3)	1.9(5)	0.8(4)	0.9(3)	1.2(2)

refinement, the twin fraction converged to 0.101(8). A table of calculated and observed structure factors, corrected for twinning, is available from the authors.

To examine oxygen stoichiometry, the occupancy factors for all oxygen atoms were refined to values of 1.05(4), 1.00(3), 1.04(3), and 0.92(4) for O1–O4, respectively. Although this calculation could be affected by inaccuracies in the absorption correction, it is improbable that the oxygen total is as low as 7.5, which is required for all Cu²⁺. We conclude that the oxygen is stoichiometric at 8 per formula unit.

Atomic coordinates of the converged structure (weighted R = 2.7%) confirm the proposed structure of Marsh *et al.*,¹⁵ who identified two symmetrically distinct types of copper atoms (Fig. 1). A principal structural feature, topologically identical to that of 1-2-3, is the pair of Cu2-O layers parallel to (001) with square-planar coordinated copper [average Cu2-O(2,3) distance is 1.945 Å; see Table II]. These planar features are separated by the rare-earth cations. As in 1-2-3, the copper-oxygen planes are “dimpled,” with oxygens displaced toward the rare earth. The average Cu2-O-Cu2 angle in 1-2-4 is 165.7°, compared to 163.8° in 1-2-3.²²

Each corner-lined Cu2-O(2,3) square plane is capped

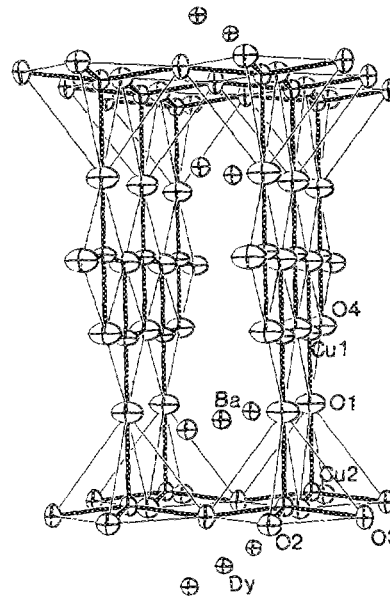


FIG. 1. Crystal structure of DyBa₂Cu₄O₈ with 90% probability thermal ellipsoids. The illustration is oriented with the *c* crystallographic axis vertical, *a* horizontal, and *b* into the page. Only half of the *A*-centered unit cell is shown. Planar-coordinated copper and oxygen atoms display prolate vibration ellipsoids with major to minor axial ratios exceeding 2:1. Note the dimpled Cu2-O planes parallel to (001) and the deviations from ideal square coordination of Cu1-O groups in the edge-sharing strips in the (100) plane.

by a fifth oxygen (Cu2-O1 distance is 2.287 Å). These capping O1 oxygens border Cu1-O(1,4) strips parallel to (100). Unlike the corner-sharing single chains of four-coordinated copper in 1-2-3, however, these unique strips consist of edge-sharing square planes with twice as many copper atoms (Fig. 1). The configuration of this doubled chain causes an offset of (001) copper planes, thus giving an *A*-centered cell and doubled *c* axis. The average Cu-O distance of four-coordinated Cu1 is 1.894 Å. The Cu1, O1, and O4 atoms are constrained to lie in the *x* = 0 plane, so the strip feature is flat. Short O4-O4 shared edges (2.584 Å) compared to O1-O4 unshared edges (2.768 Å), however, result in significant deviations from ideal square coordination of copper. The O4-Cu1-O4 angle is thus 171.2° instead of the ideal 180°.

Anisotropic thermal vibrations reflect bonding anisot-

TABLE II. Interatomic distances (Å) and angles (°) for DyBa₂Cu₄O₈. Figures in square brackets indicate bond multiplicities. Symmetry codes (a) *x*, 1/2 - *y*, 1/2 - *z*; (b) *x*, -*y*, -*z*; (c) 1 + *x*, *y*, *z*; (d) *x*, 1 + *y*, *z*.

Dy-O2	2.409(5)	[4]	Ba-O1	2.745(1)	[4]
Dy-O3	2.407(5)	[4]	Ba-O2	2.963(7)	[2]
Average	2.408		Ba-O3	2.943(6)	[2]
			Ba-O4	2.981(7)	[2]
			Average	2.876	
Cu1-O1	1.834(9)		Cu2-O1	2.287(10)	
Cu1-O4	1.942(1)	[2]	Cu2-O2	1.939(1)	[2]
Cu1-O4 ^a	1.860(9)		Cu2-O3	1.951(1)	[2]
Average	1.894		Average	2.013	
Cu1-Cu1 ^a	2.790(2)	[2]	Cu1-O4-Cu1 ^c	171.2(5)	
O1-Cu1-O4 ^b	94.4(3)		Cu2-O2-Cu2 ^c	165.2(5)	
O1-Cu2-O2	97.4(3)		Cu2-O3-Cu2 ^d	166.2(5)	
O1-Cu2-O3	96.9(3)				
O2-Cu2-O3	89.1(1)				

ropy in 1-2-4. Eight-coordinated Dy and ten-coordinated Ba possess near isotropic vibrations, with amplitude parallel to the *b* crystallographic axis slightly smaller than those parallel to *a* or *c*. Similarly, the O2 and O3 atoms, each of which is coordinated to two Cu2, two Dy, and two Ba, are close to isotropic with equivalent isotropic temperature factors (B_{eq}) 0.7 and 0.8 Å², respectively. Four-planar coordinated Cu1 and Cu2 and three-planar coordinated O1 and O4, on the other hand, display extremely anisotropic prolate thermal vibration ellipsoids, with maximum amplitudes perpendicular to the planes of bonding. B_{eq} for three-coordinated O1 and O4 are both 1.2 Å², which are 50% greater than those for O2 and O3. Note, however, that the thermal vibrations of these three-coordinated oxygens are significantly less than the 2.0 Å² values for the two-coordinated oxygens in the 1-2-3 structure.²² This difference in oxygen coordination is responsible for the significant difference in thermal vibration behavior, which may result in significantly reduced oxygen diffusion of 1-2-4 compared to 1-2-3.

The 1-2-4 compounds may provide an ideal system to investigate the effects of subtle structural variations on T_c . At least nine different rare-earth element end members have been synthesized, as well as samples with partial substitution of Sr and Ca for Ba. Bulk samples produced by Morris *et al.*¹⁶ do not display the variable oxygen content characteristic of 1-2-3, but do show a range of T_c from 80 K for YBa₂Cu₄O₈ to 57 K for NdBa₂Cu₄O₈. Single-crystal x-ray diffraction studies on several 1-2-4 endmembers are in progress to correlate structure with superconducting properties.

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