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Structural properties of $Ba_2RCu_3O_7$ high-T_c superconductors

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The crystal chemistry of several $Ba_2RCu_3O_7$ high-T_c superconductors (R = Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm) has been studied by x-ray diffraction on twinned crystals. All samples except the Pr compound show superconductivity around 90 K. From the variation of the interatomic distances with different rare-earth ions, we infer the presence of a [CuO_2-BaO-CuO□-BaO-CuO_2] building unit.

Superconductivity at 94 K is exhibited by the compound $Ba_2YCu_3O_7$ which crystallizes in an oxygen-deficient perovskite-type structure.[1] Cation ordering leads to a tripled c axis, with a Ba-Ba-Y-Ba-Ba-Y-$\cdots$ stacking sequence. Surprisingly, substitution of trivalent rare-earth (R) atoms for Y has little effect on the superconductivity.[2,3] Also, relatively little change is observed in the cell constants for Pr, Sm, Eu, Gd, Dy, Ho, Er, and Tm substitutions.[2,3] Among these elements, only Pr suppresses superconductivity.[3] We report here a systematic investigation of the x-ray structures of R substituted compounds in order to find common structural features, and to determine whether the lack of superconductivity in the Pr compound has a structural origin. Previous x-ray studies on $Ba_2YCu_3O_7$ crystals were refined in space group *Pmmm* or *P4/mmm*.[4-7] Subsequent neutron-diffraction experiments[8-10] revealed the symmetry to be *Pmmm* with the oxygen vacancies in $z=0$ ordered in the $(\frac{1}{2},0,0)$ position (setting of origin as in Ref. 5). In addition, these studies also showed that the z coordinates of the oxygen-atoms forming the base of the pyramidal Cu site are almost equal. All the samples used in the present study are multiple domain crystals with both the orientations of the axes in the pseudotetragonal cell, i.e., microtwins describable with [001] 90° rotation or {110} twin laws. Assuming that the structural features are preserved through the whole series, it is possible to obtain the single-crystal structure from domain crystals. The domain size observed by electron microscopy[11] depends on the preparation procedure and can vary from a few 100 to a few 1000 Å. Because of the twinning, these structures would best be determined from powder neutron data. However, because of the large amount of material necessary and because several R compounds are hampered by strong neutron absorption, x rays were deemed appropriate for a comparative study of $Ba_2RCu_3O_{7-x}$ with R = Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm and $x \simeq 0.0-0.5$. With the exception of the nonsuperconducting praseodymium compound, T_c is above 90 K. Accurate atomic positions can be obtained for the metal atoms. For the oxygen positions, somewhat larger standard deviations occur. Nevertheless, we can establish trends of the effect of differently sized rare-earth atoms on the crystal lattice of $Ba_2RCu_3O_{7-x}$. In this paper, we report the x-ray crystal structure determinations of $Ba_2RCu_3O_{7-x}$ with R = Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm.

Small crystallites suitable for x-ray studies were obtained by standard ceramic techniques. The crystallites chosen were always thin platelets with the c axis perpendicular to the platelet plane. The platelets were mounted either on a Nonius CAD4 κ-axis diffractometer or a Picker four-circle diffractometer, driven by programs developed at the National Research Council of Canada.[12] All measurements were done in ω-scan mode, sampling over all the individual grains, using Mo $K\alpha$ radiation. A Gaussian-integration absorption correction was applied. All calculations were carried out using the NRCVAX structure package.[13] The refinement was carried out in space group *P4/mmm*, using unit weights for all reflections. This choice of space group over *Pmmm* is appropriate since the twinning renders the crystals pseudotetragonal. As mentioned earlier, the neutron-diffraction studies[8-10] showed the z coordinates of the atoms in $(0,\frac{1}{2},z)$ and $(\frac{1}{2},0,z)$ positions to be equal. This is crucial to the refinement, since these are the atoms that become symmetry related in space group *P4/mmm*. For the oxygen atom in $(0,\frac{1}{2},0)$, another in $(\frac{1}{2},0,0)$ is generated by the fourfold symmetry; therefore the value for the occupation parameter for O(3) is averaged over both orientations and is a good measurement for the overall oxygen stoichiometry. Refinement in *Pmmm* usually yielded different occupation parameters for the oxygen atoms in $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,0)$, giving an estimate of the relative occurrence of the two twin orientations. The largest difference was observed in $Ba_2GdCu_3O_{7-x}$ with a pronounced difference in the a and b axis and approximately a 2:1 ratio of the two possible orientations. Despite the twinning, orthorhombic lattice parameters can be obtained by centering on the maximum peak height of each reflection, given that the separation of the two peaks stemming from the different twin orientation is sufficient. The crystallographic data obtained are given in Tables I–IV. Table I gives the lattice parameters obtained from twinned crystals by centering a minimum of 40 reflections above $2\theta = 40°$. In Table II, the number

TABLE I. Lattice parameters (twinned crystals) for $Ba_2RCu_3O_7$. The estimated standard deviations (in parentheses) refer to the last digit printed. The radii for R^{3+} are taken from Ref. 19.

	a (Å)	b (Å)	c (Å)	Radius (Å)
Pr	3.905(2)	3.905(2)	11.660(10)	1.013
Sm	3.891(1)	3.894(1)	11.660(1)	0.964
Eu	3.869(2)	3.879(3)	11.693(6)	0.950
Gd	3.854(2)	3.896(2)	11.701(7)	0.938
Dy	3.830(3)	3.885(3)	11.709(3)	0.908
Y	3.827(1)	3.877(1)	11.708(6)	0.905
Ho	3.846(1)	3.881(1)	11.640(2)	0.894
Er	3.812(3)	3.851(4)	11.626(2)	0.881
Tm	3.829(3)	3.860(3)	11.715(2)	0.869

TABLE III. Crystallographic data of $Ba_2RCu_3O_7$ for an orthorhombic lattice, space group *Pmmm*, $a=3.891(1)$ Å, $b=3.894(1)$ Å, $c=11.660(1)$ Å, $Z=1$. The estimated standard deviations (in parentheses) refer to the last digit printed.

Atom	x	y	z	B_{iso} (Å^2)	Occupancy
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.185 30(18)	0.92(5)	
Sm	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.30(5)	
Cu(1)	0	0	0	1.48(14)	
Cu(2)	0	0	0.3554(4)	0.41(8)	
O(1)	0	0	0.158(3)	2.8(6)	
O(2a)	$\frac{1}{2}$	0	0.3734(21)	0.7(4)	
O(2b)	0	$\frac{1}{2}$	0.3748(20)	0.5(4)	
O(3)	0	$\frac{1}{2}$	0	0.6(4)	0.6(2)

of measured, unique and observed reflections are given, together with the $\mathcal{R}$ values defined $\mathcal{R}=\sum(F_{\text{obs}}-F_{\text{calc}})/\sum F_{\text{obs}}$ (F being the observed and calculated structure factors). An observed reflection has an intensity greater than $2.5\sigma(I)$. The complete atomic positions for $Ba_2SmCu_3O_{7-x}$ are shown in Table III, and Table IV gives the refined position and occupancy parameters for all the compounds studied.

The normal perovskites of type ABO_3 usually have a large atom on the A site and a small one on the B site. Rare-earth atoms typically occupy the A site, since they are quite large. However, tetravalent R atoms such as Ce, Pr, and Tb are small enough to fit in the B site if they are accompanied by a large A atom such as Ba. This is the case of $BaCeO_3$, $BaPrO_3$, and $BaTbO_3$.[14] In an oxidizing atmosphere, these R atoms are likely to become tetravalent and therefore readily form these normal perovskites. Praseodymium can also be stabilized in its trivalent state and can occur in the $Ba_2YCu_3O_7$-type structure.[2,3]

The coordination polyhedra in the normal perovskite ABO_3 are quite simple. For the A site, one finds the familiar truncated cube with coordination number 12, and for the B site the octahedron with coordination number 6. In the case of the $Ba_2RCu_3O_{7-x}\square_{2+x}$ we encounter an oxygen-deficient perovskite with general formula $A_2A'B_3O_{7-x}\square_{2+x}$. The unit cell is three times the normal perovskite cell, with $a\approx b\approx c/3$. The ordering of the vacancies results in very different coordination polyhedra for all the atoms involved, resulting in a truly two-dimensional layer structure, with the layers perpendicular to the c axis. Figure 1 depicts a view of the $Ba_2RCu_3O_7$-type structure, and Fig. 2 shows several unit cells where the Cu-O planes and chains are emphasized. In the following we briefly discuss the different coordination polyhedra present in the structure.

(i) R coordination: The R atom at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ sits in the center of a distorted square prism with coordination number 8. The square prism is compressed, and is close to a cube. This particular geometry results from the complete absence of oxygen in the $z=\frac{1}{2}$ plane. A similar reduction of coordinating oxygen atoms is observed in $Ba_3La_3Cu_6O_{14+x}$ (Ref. 15) and in the T'-K_2NiF_4 structure of Nd_2CuO_4.[16]

(ii) Ba coordination: Ba at $(\frac{1}{2},\frac{1}{2},z)$ with $z=0.1847$ to 0.1892 is coordinated by ten oxygen atoms for $x=0$. The usual truncated cube found in the normal perovskites becomes a distorted, elongated bicapped square prism oriented along the a axis. The two capping oxygen atoms are shared with adjacent square prisms, forming the base of the pyramidal coordination of the Cu(2) atoms. Two such prisms related by the $z=0$ mirror plane share one edge and form a building unit. This particular unit shares faces along the a axis and edges along the b axis, with the capping oxygen atoms reinforcing the connections along b. The Ba-O distances do not vary greatly with different sizes of R-atoms. Only small variations are expected,

TABLE II. Data collection—number of measured, unique, and observed reflections and $\mathcal{R}$ values. Observed reflections have intensities greater than 2.5σ. $\mathcal{R}_{F_{\text{all}}}$ includes nonobserved reflections, whereas $\mathcal{R}_{F_{\text{obs}}}$ only the ones with $I>3\sigma(I)$.

	Measured	Unique	obs	$\mathcal{R}_{F_{\text{obs}}}$	$\mathcal{R}_{F_{\text{all}}}$
Pr	944	292	243	0.060	0.060
Sm	666	222	177	0.041	0.051
Eu	222	222	169	0.048	0.062
Gd	1108	503	318	0.049	0.098
Dy	1590	221	207	0.039	0.040
Y	426	220	159	0.058	0.072
Ho	246	226	187	0.041	0.053
Er	286	218	168	0.038	0.061
Tm	1724	220	206	0.029	0.031

TABLE IV. Refined z coordinates and site occupancy. The estimated standard deviations (in parentheses) refer to the last digit printed.

	z(Ba)	z(Cu(2))	z(O(1))	z(O(2))	occ(O(3))
Pr	0.1840(3)	0.3507(8)	0.157(5)	0.371(4)	1.0(2)
Sm	0.1853(2)	0.3554(4)	0.158(3)	0.374(2)	0.6(2)
Eu	0.1847(3)	0.3530(8)	0.159(5)	0.374(4)	0.4(2)
Gd	0.1855(2)	0.3546(4)	0.151(2)	0.377(2)	0.7(2)
Dy	0.1864(2)	0.3564(3)	0.157(2)	0.378(2)	0.7(2)
Y	0.1874(3)	0.3565(4)	0.157(3)	0.379(3)	0.8(2)
Ho	0.1858(2)	0.3577(4)	0.159(3)	0.378(2)	0.6(2)
Er	0.1866(2)	0.3579(4)	0.159(3)	0.381(2)	0.8(2)
Tm	0.1892(1)	0.3593(2)	0.155(2)	0.380(1)	0.5(1)

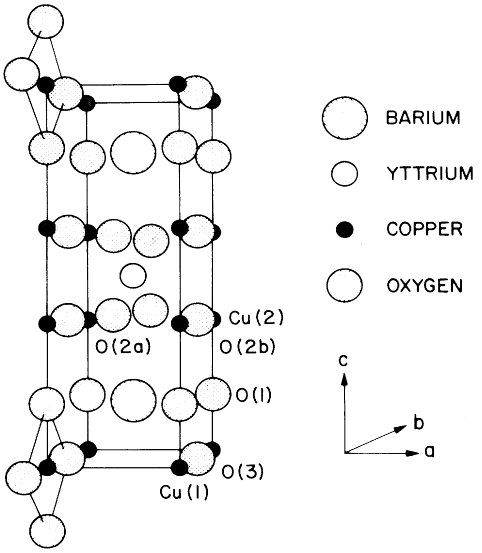

FIG. 1. Unit cell of the $Ba_2RCu_3O_7$-type structure. The labeled atoms refer to Tables III and IV.

since these building units are rigid.

(iii) Cu coordination: Cu(1) has a distorted square planar coordination with the plane oriented parallel to the (b,c) plane. These units share corners, forming linear chains along the b axis. For an oxygen stoichiometry less than 7, the connecting oxygen atoms are randomly missing; the chains are therefore of finite length and some Cu(1) atoms have a reduced coordination number of 3 or even 2. In the latter case, Cu(1) is linearly coordinated, probably as Cu^+, similar to that found in $CuYO_2$ (Ref. 17) and $Ba_2YCu_3O_6$.[18] For Cu(2), a pyramidal coordination is found with the copper-atom shifted approximately 0.25 Å out of the distorted square base towards the apical oxygen atom. Due to the mirror plane at $z=\frac{1}{2}$, two such pyramidally coordinated copper atoms are present, forming a double layer holding the R atoms.

The formation of oxygen vacancies in the $z=\frac{1}{2}$ plane is due to the small size of the R atom. The location of the vacancy in the $z=0$ plane, on the other hand, has a different origin. The usual coordination of copper by oxygen is either a distorted octahedron with four short and two long bonds, a pyramidal coordination with four short and one long bond, or a square planar arrangement. Occasionally, a linear coordination of just two oxygen atoms can be found as well. In the case of the $Ba_2RCu_3O_7$ compounds we find the pyramidal coordination for Cu(2) with four short and one long bond. The apical oxygens at the same time form two short bonds to Cu(1). It is therefore only possible to have a square planar coordination for Cu(1), since octahedral or pyramidal coordination would necessitate a drastic elongation of the a or b axis in order to form the long bonds. The ordering of the vacancies produces a distorted square planar coordination and does not greatly affect the a and b axes. Therefore, the strain energy needed to distort the lattice is minimized.

As expected, interatomic distances involving a R atom scale with the R radius. For the R radii, we take the values given by Iandelli and Palenzona.[19] In contrast, interatomic distances not involving R atoms show only weak or no dependence on the R radii. The strongest variation is seen for the R-oxygen distance, as expected. In Fig. 3, we show the Cu(2)-Cu(2) distances, which measure the separation of the two planes holding the R atoms. The Cu(2)-Cu(2) distance across Ba varies in the opposite sense, since the sum of the two distances is equal to the c axis which is almost constant. In Fig. 4, we show the average Ba-Cu distance, which is constant as expected. The average R-Cu(2) distance, on the other hand, varies with a slope of 0.7, a value close to $1/\sqrt{2}$. This value is expected, since the distance can be expressed as the sum of two distances, R-O and Cu(2)-O, which are at right an-

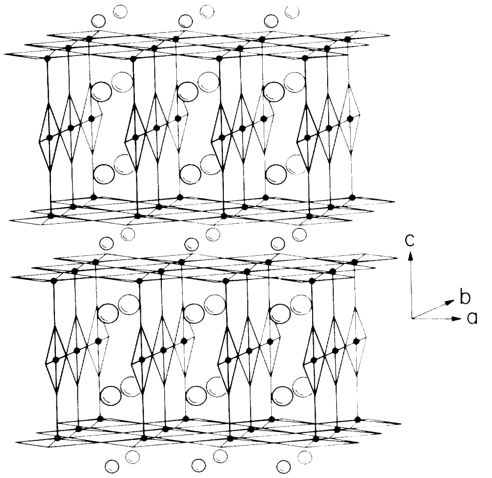

FIG. 2. Cu-O chains and planes in the $Ba_2RCu_3O_7$-type structure. Small spheres indicate Cu atoms, large spheres Ba, and intermediate spheres R atoms. To emphasize the Cu-O network, oxygen-oxygen bonds have been added. Two [CuO_2-BaO-CuO□-BaO-CuO_2] layers sandwiching the R atoms are shown.

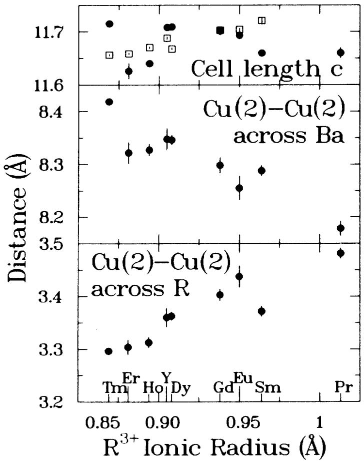

FIG. 3. Cu(2)-Cu(2) distances vs R ionic radius (Ref. 19). The Cu(2)-Cu(2) distance across the R atom increases with R radius, whereas the Cu(2)-Cu(2) distance across the Ba atom decreases. The cell length c is the sum of the two distances and is nearly independent of the R radius.

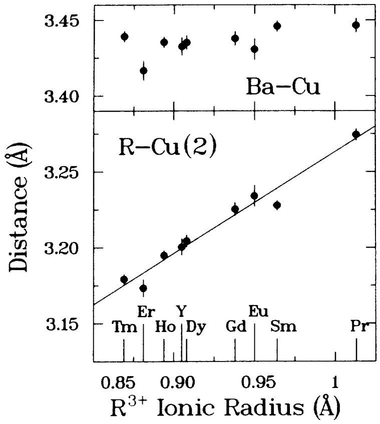

FIG. 4. Averaged Ba-Cu distance and *R*-Cu distance vs *R* radius. The averaged Ba-Cu distance is independent of the *R* radius. The *R*-Cu(2) distance is composed of a *R*-O and a Cu(2)-O distance (the latter is independent of the *R* radius) at right angles and therefore varies approximately with a slope of $1/\sqrt{2}$.

gles. In first order, the Cu(2)-O distance is constant, whereas the *R*-O distance varies with the *R* radii, giving the overall slope of 0.7. It is possible to describe the $Ba_2RCu_3O_7$-type structure as being comprised of alternate stacking of CuO_2, BaO, and *R* layers perpendicular to the *c* axis in a $[CuO\square\text{-}BaO\text{-}CuO_2\text{-}R\square\text{-}CuO_2\text{-}BaO]_\infty$ sequence. The *R* atoms sit between building blocks of $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ and do not substantially affect the internal geometry of these blocks. Changing the *R* atoms sandwiched between these building units only changes the distance between these units.

The variations of the lattice constants *a*, *b*, and *c* deduced from domain crystals do not accurately reflect the size of the *R* atom. It has to be kept in mind, however, that the mosaic structure hampers the accurate determination of the lattice constants from these twinned crystals. We attribute the nearly equal values of *a* and *b* for Pr, Sm, and Eu to mosaic effects. Lattice parameters from powder data[2,3] are more accurate than those from domain crystals because a larger number of grains are sampled. Therefore, they reflect the size of the *R* atoms more distinctly.

Among the $Ba_2RCu_3O_7$-type compounds investigated here, $Ba_2PrCu_3O_7$ is the only one not superconducting. The Pr atom seems to affect superconductivity quite strongly; in $Ba_2(Y_{0.9}Pr_{0.1})Cu_3O_7$, for instance, T_c is lowered by 10 K.[20] An extended x-ray study on a small crystallite with well-developed faces of approximate dimensions $100\times100\times20\ \mu m^3$ showed no evidence of a superstructure. The crystal had a large mosaic spread and therefore almost equal *a* and *b* axes of 3.905 Å and $c=11.660$ Å. As for all the other compounds studied, the symmetry of the Pr compound is pseudotetragonal and is isostructural with $Ba_2YCu_3O_7$, without any obvious differences. Anisotropic temperature factors, on the other hand, showed a large mean-square displacement of the O(1) atom perpendicular to the *c* axis. The amplitude of the displacement is approximately 9% of the lattice constant *a*. As praseodymium is a large atom, it may possibly occupy a Ba position as Pr^{3+}, leading to a strongly deformed coordination polyhedron. This might affect T_c if the part of the structure responsible for superconductivity is the chains containing Cu(1), since they would be adjacent to the magnetic atom. Pr^{4+} could in principle also substitute on a Cu position but the large difference in the radii of the two atoms makes this unlikely. Further investigations of this compound are underway.

Trivalent *R* atoms have little effect on the superconducting transition in $Ba_2RCu_3O_7$ phases, even though they carry a magnetic moment. Apparently the superconductivity is confined to the $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ building units (containing chains and planes of distorted square planar copper-oxygen units), which show remarkably little change through the whole series. In this respect, it is possible to regard the $Ba_2RCu_3O_7$ compounds as being composed of $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ units forming two-dimensional layers holding the *R* atoms. This new class of cuprate perovskites then resembles the well-known Chevrel phases containing *R* elements. In both cases, superconductivity, together with magnetism, occurs. Any change in the $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ unit, however, drastically affects T_c. Reducing the oxygen stoichiometry from 7 to 6, for instance, suppresses superconductivity entirely.[18] We therefore believe that the superconductivity is confined to the layers formed by the $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ units.

In summary, we have shown that the new class of high-T_c superconductors in the $Ba_2RCu_3O_7$ system contain discrete building units with the *R* atom only affecting the relative distance between the superconducting layers consisting of $[CuO_2\text{-}BaO\text{-}CuO\square\text{-}BaO\text{-}CuO_2]$ units.

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