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Structure and physical properties of single crystals of the 84-K superconductor $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$

S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover,
R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak,
J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974-2070

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Single crystals of the 84-K superconductor $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$ were characterized by x-ray diffraction, dc magnetic susceptibility, electrical resistivity, and microwave absorption. The structure has $[CuO_2]_\infty$ planes separated by calcium atoms, edge-shared bismuth oxide double layers, and an incommensurate superlattice along b with a period of 4.76. The in-plane resistivity above T_c is linear in T, with $\rho_{RT} = 130$ $\mu\Omega$ cm. Initial results on Pb substitution yielding T_c's of 107 K are reported.

Indications of superconductivity in copper oxide systems containing bismuth[1-3] have been reported with onsets above 100 K.[2,3] To date, these latter studies have been on multiphase samples in the Bi-Sr-Ca-Cu-O system with what appear to be three superconducting phases with T_c's near 120, 105, and 80 K. In this study, we report resistivity and dc magnetization measurements on flux-grown single crystals of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$ that show bulk superconductivity at 84 K. Addition of lead to this system is also shown to raise T_c above 100 K. The crystals of $Bi_2CaSr_2Cu_2O_8$ exhibit an incommensurate superlattice ($\approx 4.76 \times b$) based on an orthorhombic subcell with dimensions $5.414 \times 5.418 \times 30.89$ Å. The structure of the subcell has been determined and is considerably different from those for the previously known 40- and 90-K T_c materials, with infinite $[CuO_2]$ planes widely separated (≈ 12 Å) by Bi-O double layers.

To unambiguously associate a particular crystal structure with a particular T_c, single crystals with a layered morphology were grown by a flux technique.[4] These crystals have the approximate composition $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_x$. Near zero field, microwave absorption was used to screen the small single-crystal samples for superconducting transitions. This technique is extremely sensitive and good signals can be obtained on very small crystallites. At a superconducting transition, strong field-dependent absorption changes are observed.[5] This test indicated superconductivity above 80 K in all the crystals measured.

Figure 1 presents the temperature-dependent resistivity and magnetization for single crystals of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_8$. Resistivity was measured in the a-b plane on a single crystal of dimensions $1000 \times 500 \times 1$ μm in the van der Pauw-Price configuration which geometrically averages anisotropy in the plane. The room-temperature resistivity is 130 $\mu\Omega$ cm, and decreases linearly with temperature as in the other two classes of copper oxide-based superconducting materials. We note that the resistivity is substantially lower than for $Ba_2YCu_3O_7$. The current density used for the measurement was approximately 200 A cm^{-2}. The transition from the superconducting to normal state begins at 84 K and is roughly 90% complete at 90 K. The gradual curvature above 90 K is tentatively ascribed to fluctuation conductivity. There is no sign of a T_c above 100 K in this crystal. The dc magnetization, measured on a single crystal in a superconducting quantum interference device (SQUID) magnetometer (SHE 905), is shown in the inset to the figure. The samples were slowly cooled in a field of 18 Oe applied parallel to the planes with the data taken during warm-up. The signal from a 42-μg crystal corresponds to 70% of the value expected for a full Meissner effect, thus confirming bulk superconductivity with a T_c of 84 K. Several other crystals were also measured and each showed $T_c > 80$ K.

The single crystal used in the structural refinement measured $100 \times 120 \times 2$ μm and was examined on two x-ray diffractometers, a sealed-tube machine with Mo $K\alpha$

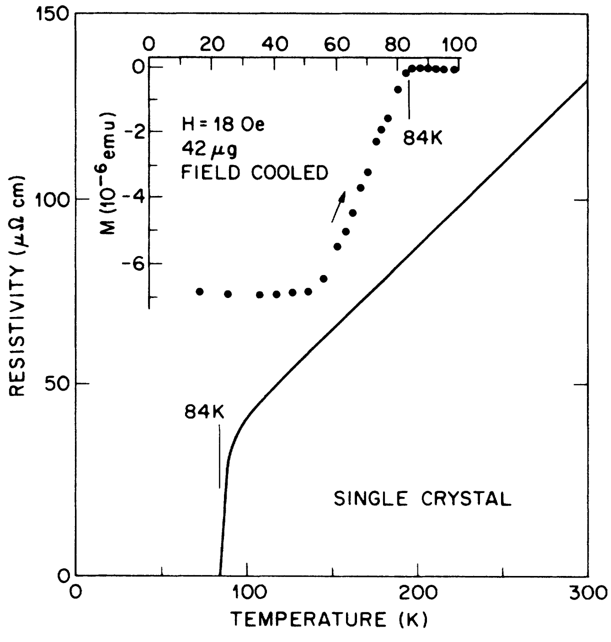

FIG. 1. Resistivity of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$ as a function of temperature. The inset shows dc susceptibility indicating 60–70% of the ideal diamagnetic value for complete flux exclusion.

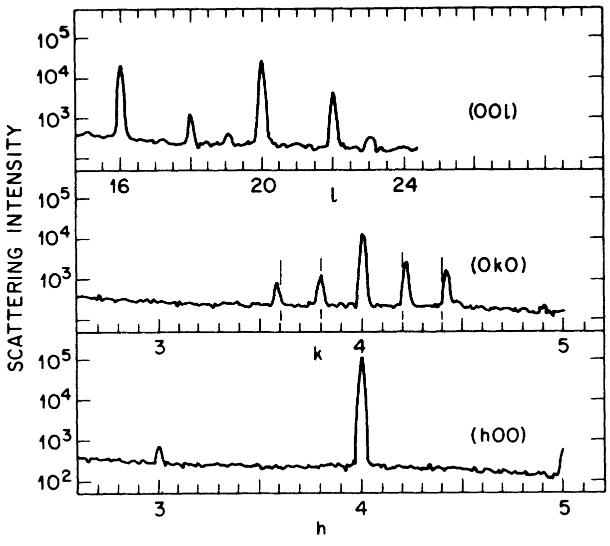

FIG. 2. Scans along each of the principal directions of the crystal used in the structural refinement. The horizontal axes of all scans represent equivalent momentum transfers. An incommensurate superlattice with an average periodicity of 4.76 unit cells is prominent along [0*k*0]. Weak peaks that violate *Fmmm* symmetry can be seen in the [*h*00] and [00l] scans.

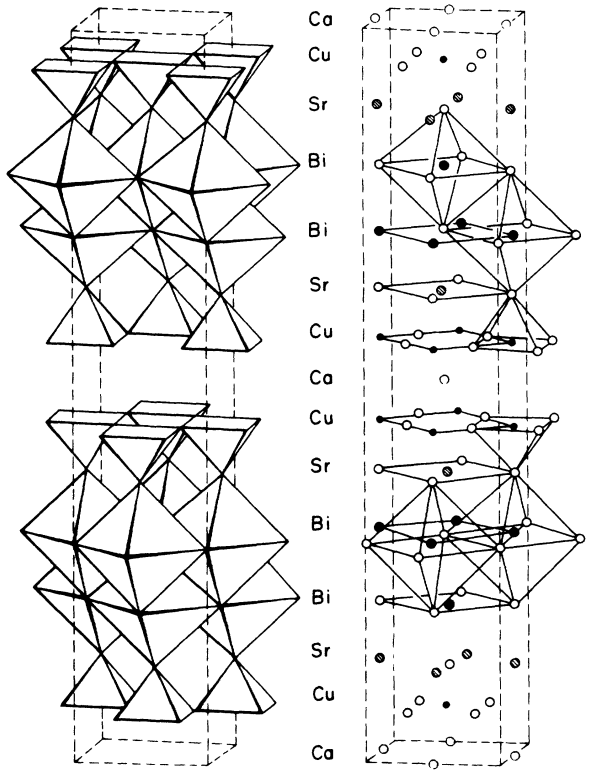

FIG. 3. Two views of the $Ba_2Sr_2CaCu_2O_8$ subcell.

radiation configured for crystallographic structure determinations and high-intensity rotating-anode generator with Cu *Kα* radiation configured for high-resolution scans along arbitrary directions in reciprocal space. The unit cell of the single crystal was determined to be orthorhombic with lattice parameters of 5.414×5.418×30.89 Å and pseudosymmetry *Fmmm* in substantial agreement with Hazen *et al.*[3] Scans with resolution of 0.04 $Å^{-1}$ full width at half maximum along each of the principal directions of the crystal shown in Fig. 2 indicate a prominent incommensurate superlattice along [0*k*0] giving a 4.76× increase of the unit cell in that direction. The absence of extra peaks along [*h*00] shows that there is little (*a*,*b*) twinning associated with the superlattice. The superlattice peaks are instrumentally narrow along [0*k*0] with an intensity that is generally less than 10% of the subcell peak intensity. In the structural analysis presented in this work, we consider only the subcell peak intensity, although we speculate about possible origins of the superstructure. For the structure refinement 1200 reflections to $2-\theta=60°$ were measured, giving 404 unique reflections. Atomic positions are presented in Table I. The structure (without the superlattice) is illustrated in Fig. 3. The structure as shown has an ideal formula of $Bi_2Sr_2CaCu_2O_8$ and is closely related to the Aurivillius phases.[6] This formula is similar to that proposed on the basis of electron diffraction.[3] Each of the cations in the idealized cell is on a distinct crystallographic site. However, it is clear that there is greater electron density on the Ca site which we address later. Although location of the oxygen atoms in difference Fourier maps is difficult, the oxygen atoms in the $[CuO_2]_\infty$ planes are prominent. The most striking feature of the structure is the presence of infinite $[CuO_2]_\infty$ planes separated by Ca in the same way that the planes of $Ba_2YCu_3O_7$ are separated by Y. A

TABLE I. Crystallographic data of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_8$. Orthorhombic cell (pseudotetragonal substructure): $a=5.414(2)$ Å, $b=5.418(2)$ Å, $c=30.89(1)$ Å. Space group *Fmmm* (No. 69), $Z=4$, $\mu=553\ \mathrm{cm}^{-1}$, $d_{\mathrm{calc}}=6.58\ \mathrm{g/cm}^3$. 404 unique reflections, 154 observed, $R_i=0.173$, $R_w=0.094$.

Atom	Position	x	y	z	Occupancy	B_{iso} ($Å^2$)
Bi(1)	8*i*	0	0	0.1989(2)	1.0	5.8(4)
Sr	8*i*	0	$\frac{1}{2}$	0.1091(4)	1.0	2.3(4)
Ca	4*b*	0	$\frac{1}{2}$	0	0.8(1)	3.2(4)
Bi(2)	4*b*	0	$\frac{1}{2}$	0	0.2(1)	3.2(4)
Cu	8*i*	0	0	0.0543(7)	1.0	3.5(8)
O(1)	16*j*	$\frac{1}{4}$	$\frac{1}{4}$	0.051(3)	1.0	5.7(19)
O(2)	8*i*	0	$\frac{1}{2}$	0.198(4)	1.0	9(4)
O(3)	8*i*	0	0	0.120(5)	1.0	18(8)

unique feature distinguishes the observed Bi layers from those in the Aurivillius phases; in this phase they form a double layer of edge-shared octahedra rather than infinite $[Bi_2O_2]^{2+}$ layers. The edge-shared bismuth layers may be thought of as arising by occupation by Bi of some of the Ti sites in the Aurivillius-type $Bi_4Ti_3O_{12}$ structure. The Bi bonding and total geometry is highly unusual. The Bi coordination is basically octahedral, with six bonds to oxygen (one each at 2.44 and 3.19 Å and four at 2.71 Å). Additionally, an oxygen layer is vacant allowing collapse of the $[Bi_2O_2]$ layers.

The ideal formula from the crystallographic subcell of $Bi_2CaSr_2Cu_2O_8$ requires Cu^{2+} and Bi^{3+} for the formal valence of the variable oxidation state ions. This is not reasonable in light of the metallic conductivity and superconductivity. We must postulate either that Bi:Sr:Ca is variable or that the superlattice is responsible for the oxidation. The composition determined by microanalysis is slightly different from the ideal, and we have observed variations in composition from grain to grain in ceramic preparations. However, formal oxidation of the sample requires either an increased alkaline earth to Bi ratio or increased oxygen content. We have noted only very weak oxygen stoichiometry variations on heating polycrystalline material to 800 °C in oxygen gas by thermogravimetry, with little effect on T_c. The oxygen stoichiometry measured by H_2 reduction on a single-phase ceramic sample gave $Bi_{2.2}Sr_{1.7}Ca_{1.1}Cu_2O_{8.2}$, formally giving $Cu^{2.1+}$. The atomic arrangement of the superlattice is not known, but there is clear indication from the structural refinement that additional electron density is present on the Ca site and possibly at the vacant oxygen sites in that layer. Thus, the superlattice could be due to the presence and ordering of Sr or Bi on the Ca site with oxygen incorporation to complete its coordination sphere. The electron density at the Ca site is approximately 34 electrons which corresponds to a $\approx 4:1$ ratio of Ca to Bi and correlates with the superlattice along b. The superlattice observed here is close to the reported 5× superlattice,[3] but is clearly different. Extensive edge sharing as found in the bismuth layer causes considerable strain and is generally relieved by buckling. The super cell may be caused by such strain. The anisotropic temperature parameter of Bi shows an anomously large component along b indicating possible distortions. The copper-oxygen coordination polyhedron is a square pyramid of similar geometry to that found in $Ba_2YCu_3O_7$ but with an important difference in the bond length of Cu to the apical oxygen. The inplane Cu–O distances in $Bi_2Sr_2CaCu_2O_8$ are 1.875 Å, and the apical oxygen is at 2.05 Å, considerably shorter than that for either $Ba_2YCu_3O_7$ (2.3 Å) or $(La)(Sr)_2CuO_4$ (2.4 Å). This will considerably influence the charge distribution in the Cu–O planes, the shorter bond distance no doubt being due to the weakly electropositive character of Bi when compared to the rare-earth or alkaline-earth atoms which share the apical oxygen with Cu in the 40- and 90-K structure types.

The Bi coordination geometry is highly unusual. Although small displacive distortions may well be present (awaiting determination of the full supercell structure), the Bi coordination is basically octahedral as described earlier. This coordination is distinctly different from that of the Aurivelius phases, where the influence of a lone-pair is apparent. The total geometry is that of a highly covalently bonded Bi-O layer, evidenced by the extensive edge sharing. The Bi–O double layer is related to, but different from, that of the Aurivelius phases.

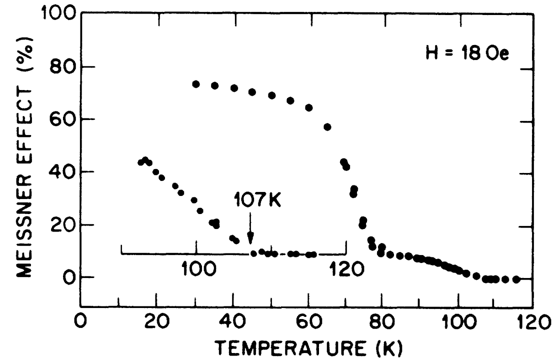

FIG. 4. dc magnetization data on a multiphase lead-substituted sample indicating a 10% Meissner effect with a T_c of 107 K and more than 70% for the 80-K phase.

Chemical substitution of lead is well known in many bismuth oxides. Initial substitutional studies with lead in the 84-K phase have yielded considerable improvement in T_c. Figure 4 shows magnetization data for a multiphase lead-substituted sample that shows an $\approx 10\%$ Meissner effect with a T_c of 107 K.

Another new phase in the Bi-Sr-Ca-Cu-O system has been identified and prepared in single-phase form. The phase $Bi_2(Sr,Ca,Bi)_2CuO_6$ has a considerable range of solid solution. This phase is semiconducting and is stable only below about 860 °C. The crystallographic subcell is $5.41 \times 5.43 \times 24.5$ Å and is closely related to that of the 80-K superconducting phase described above.[7] A detailed structure determination is in progress, but we propose that it is related to $Bi_2CaSr_2Cu_2O_8$ by the removal of the Ca plane and the collapse of the two CuO_5 planes into one plane containing CuO_6 octahedra.

In summary, we have characterized single crystals of $Bi_2CaSr_2Cu_2O_8$ by x-ray diffraction, dc magnetic susceptibility, and electrical resistivity. These measurements clearly demonstrate bulk superconductivity at 84 K. Two key structural features have been identified, namely, the atomic arrangement of the subcell and an incommensurate superstructure. The two new Bi-Sr-Ca-Cu-O structure types, $Bi_2Sr_2CaCu_2O_8$ and $Bi_2(Sr,Ca)_2CuO_6$, identified and characterized in this study, likely represent members of a larger class of compounds based on similar structural elements. Phases with these structural elements, perhaps stabilized via chemical substitutions, may yield bulk T_c's above 100 K.

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