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21. These features are not present in some phocids although they are almost certainly secondary modifications; A. R. Wyss, *Am. Mus. Novit.*, no. 2924 (1988).
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23. This interpretation requires acceptance of a reversal of this feature among walruses.
24. The extinct Desmatophocidae include *Allodesmus* and *Desmatophoca*. Skeletal elements for *Desmatophoca* are known but undescribed; however, on the basis of cranial characters this taxon is recognized as a member of this clade.
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Anomalous Scattering Study of the Bi Distribution in the 2212 Superconductor: Implications for Cu Valency

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The distribution of the bismuth atoms over the cation sites in the 2212 Bi-Sr-Ca-Cu-O superconductor has been determined by anomalous scattering synchrotron crystallography. The analysis of reflection pairs measured at wavelengths of 0.9243 and 0.9600 angstrom shows a delocalization of the bismuth atoms over the calcium and strontium sites. The "mixed" plane between the CuO_2 layers contains 6.0(1.4) percent bismuth (where the number in brackets represents the statistical standard deviation derived from the least-squares refinement of the data), and a much smaller amount of strontium than often assumed. The strontium deficiency is charge-compensated by the creation of electron holes in the CuO_2 layer. The result supports the view that neither extra oxygen nor overlap of the bismuth 6*p* and copper 3*d* bands is needed to account for the holes, which are an essential feature of the superconductivity mechanism.

THE BI-SR-CA-CU-O SUPERCONDUCTORS contain CuO_2 layers separated by a cation layer of mixed composition, as well as layers consisting of bismuth and oxygen and strontium and oxygen atoms. The mixed layer has been described as containing Sr and Ca in about equal amounts (*1–5*), though other authors have described the layer's composition as either Sr/Ca or Bi/Ca (*6*), and as containing 20% Bi (*7*). The highest Bi percentage is listed by Sastry *et al.* (*8*), who estimate that there is a substantial amount (>50%) of Bi/Sr at the Ca sites, in addition to 30% Bi at the Sr sites. The exact composition of a site in the complex crystals is hard to determine from single wavelength x-ray diffraction data because the occupancies correlate with the atomic temperature factors. But the chemical occupancy is of importance, as substitution of a bivalent atom (Ca or Sr) by a trivalent atom (Bi) changes the hole concentration in the CuO_2 planes, as does a deficiency in the occupancy of the cation layers (*9*). Cheetham *et al.* (*10*) propose that the oxidation of Cu is controlled by a depletion of the Sr content according to the general formula $Bi_2Sr_{2-x}CaCu_2O_8$.

We report here the application of x-ray anomalous scattering techniques to the study of the cation distribution in high transition temperature (T_c) superconductors. The method used is applicable to many elements and can provide crucial information not available with other techniques.

The strong variation of the Bi scattering factor in the immediate vicinity of the Bi L_{III} edge at 0.924 Å (13.42 keV) makes it possible to do Bi-specific diffraction experiments by means of tunable synchrotron radiation. The real part of the anomalous scattering factor f' varies from −21.15 at 0.924 Å (the edge) to −9.51 at 0.9600 Å (Fig. 1). The variation of the imaginary part f'' is of less importance in this almost centrosymmetric structure, which has commonly been described in the space group *Amaa*. The variation of f'' can be minimized by a judicious choice of wavelengths at the lower part of the edge and well below the edge.

With a (220) perfect Si double-crystal monochromator at the SUNY X3 beamline at the National Synchrotron Light Source an energy resolution of about 5.4 eV was obtained. Using new software (*11*) and a single crystal described previously (*2*), we have collected 154 pairs of reflections with $\sin\theta/\lambda < 0.54$ Å^{-1} and $I(\lambda_2) - I(\lambda_1) > 3\,\sigma(\Delta I)$, at wavelengths of 0.9243 and 0.9600 Å, where λ, θ, and I are the wavelength, the Bragg angle, and the intensity of the diffracted beam, respectively. The two reflections of a wavelength pair were measured sequentially to reduce the effect of instabilities in the synchrotron source. Intensities were scaled with an incident beam monitor count and the variation of two standard reflections measured at regular intervals every 30 reflections.

Data were corrected for absorption by means of an analytical integration procedure (*12*), and values of the absorption coefficient of 377.7 cm^{-1} and 369.4 cm^{-1} at the two wavelengths, respectively. These values were obtained by calculation (*13*) and subsequent interpolation for the on-edge-wavelength, using our experimental EXAFS curve (Fig. 1). X-ray scale factors at each wavelength were obtained by refining the scale factor for each of the data sets, keeping the other parameters fixed. Scattering factors for Bi at each of the wavelengths were averaged over the experimental band width. Values of f' of −18.56 and −9.51 for λ = 0.9243 and 0.9600 Å, respectively, were obtained, while f'' equals 3.96 and 4.21 at the two wavelengths.

After scaling $\Delta F = F(\lambda_2) - F(\lambda_1)$ values were calculated. As the scattering factors of the other atoms show very little variation (<0.15 electrons), the ΔF values are only dependent on the scattering of the Bi atoms.

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The relative scale of the two sets was checked by calculating the ΔF Fourier map, which showed peaks in the Bi, Sr, and Ca planes, but no significant features in the Cu-O plane. The Bi occupancies of the metal atom sites in the Bi, Sr, and Ca planes were refined, keeping positional and temperature parameters constant at the values from the conventional refinement of the data on the same crystal specimen. The structural modulation of the cations was treated as in our previous work (*2*). Results, listed in Table 1, indicate significant Bi occupancies of about 5 and 6%, respectively at the Sr sites in the "pure" Sr layer at $z = 0.14$, and the "mixed" layer at $z = 0.25$. The agreement factors obtained in this refinement, listed in Table 1, are compatible with the ratio of about 10 between the ΔF values and their standard deviations derived from the counting statistics of each of the measurements.

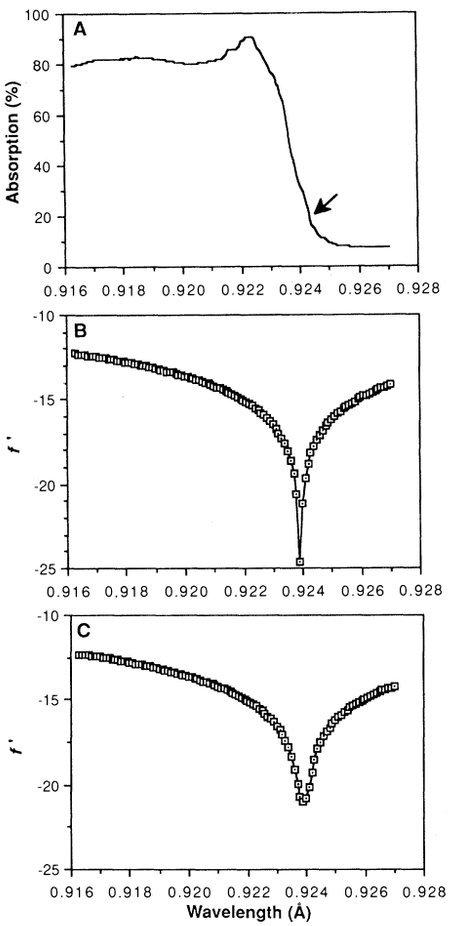

Fig. 1. (**A**) Extended x-ray absorption fine structure curve of the 2212 Bi-Sr-Ca-Cu-O sample, indicating the wavelength used to collect the "on edge" diffraction data. (**B**) Variation of f'(Bi) with λ in the same interval. (**C**) As (B), but averaged over the 5.4-eV bandwidth of the Si (220) monochromator.

After completion of the analysis of the synchrotron data, the conventional data set (*2*) was reanalyzed, keeping the Bi occupancies at the values from the anomalous scattering experiment. The fact that the agreement factors are identical to those of the original refinement demonstrates the insensitivity of conventional x-ray data to the detailed chemical occupancy of the metal sites. The mixed plane contains 15(8)%, Sr, in addition to Bi and Ca (here and elsewhere the number of brackets represents the statistical standard deviations from the least-squares refinement; a 3 standard deviation difference between two results is usually considered significant). While this amount is not significant, a partial occupancy of this site by strontium atoms cannot be ruled out.

Taking into account the different multiplicities of the sites, the occupancies listed in the table correspond to the formula $Bi_{1.91}Sr_{1.72}Ca_{0.80}Cu_2O_8$. This leads to an average valency of 2.62(6) for the Cu atoms, thus confirming the existence of holes in the CuO_2 layers. The stoichiometry may be compared with the composition $Bi_2Sr_{1.67}Ca_{0.99}Cu_2O_8$ given by Chippindale *et al.* (*14*). Except for a perhaps significant difference in Ca content, which is common between different preparations (*14, 15*), the two results are in good agreement, particularly regarding the (Sr + Ca)/Bi ratio of 1.32, rather than 1.5 in the idealized composition.

The value of 2.62(6) for the average Cu valency may be compared with values obtained by other techniques, such as chemical titration: ≤ 2.30 (*16*), Hall effect measurements: 2.42 (*17*), and the disappearance of superconductivity on Y^{3+} substitution: 2.3 (*18*). The fact that our value is higher suggests a possible overestimate of the deficiency of Bi in the Bi-O layers. Nevertheless, the Bi occupancy of the Sr and Ca sites, which is a novel result of this study, and the resulting Sr deficiency, strongly support earlier conclusions that Cu valency is controlled by the Sr,Ca deficiency (*10*).

The deficiency (that is, a value of less than three for Ca+Sr as in the idealized formula $Bi_2Sr_2Ca_1Cu_2O_8$) accounts for the increase in Cu valency and the corresponding creation of electron holes in the CuO_2 layers. Neither extra oxygen nor overlap of the Bi 6*p* and Cu 3*d* bands (*19*) is needed to create the holes, which are the charge carriers leading to superconductivity in these compounds.

Table 1. Site occupancies and agreement factors from the least-squares refinement. Numbers in parentheses represent statistical standard deviations.

Quantity	Synchrotron ΔF	Conventional	
		Gao *et al.* (*2*)	This work
Occupancies*			
Bi/Bi	0.874 (12)	0.90 (2)	0.874
Bi/Sr	0.052 (14)	—	0.052
Sr/Sr		0.94 (4)	0.790 (30)
Bi/Ca	0.060 (14)	—	0.060
Sr/Ca		0.356 (72)	0.144 (76)
Ca/Ca		0.644	0.796
R factors			
R	15.52	11.92	11.92
R_w	17.83	13.94	13.93
Number of reflections	154	597†	597†

*The layer positions are Bi: $z = 0.0522$; Sr: $z = 0.1409$; Ca: $z = 0.25$. †Including 108 first-order satellite reflections.

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