functions being compared are identical. If $P_1 = P_2$,

$$F(R) = F(R^{-1}). \qquad (14)$$

This introduces a twofold increase in symmetry and a related set of Dirichlet points must be included,

$$[{}^iSQ({}^jS)]^{-1} = ({}^iV^j)^{-1} = ({}^iV^j)^T. \qquad (15)$$

These $({}^iV^j)^T$ and the original ${}^iV^j$ lead to $2n^2$ asymmetric domains.

Concluding remarks

A rotation function between two Patterson functions with arbitrarily high symmetry can be divided easily into unique or asymmetric regions by an approach based on Dirichlet domains. If the rotational-symmetry groups of the two Patterson functions are of order n and m then rotation space is partitioned into $n \times m$ equivalent domains; for a self-rotation function, the number of equivalent domains is $2n^2$. The generality of the method makes it applicable to cubic space groups, for which the problem of the rotation-function asymmetric unit was previously unsolved. Because the analysis is cast in terms of rotation matrices, it is independent of the particular choice of Eulerian-angle conventions. For example, two programs using different angle conventions can be made to refer to the same asymmetric region of rotation space. The method also applies to point-group symmetries that are not crystallographic (*e.g.* icosahedral) and generalizes to rotations in higher-dimensional space.

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Combined X-ray Single-Crystal and Neutron Powder Refinement of Modulated Structures and Application to the Incommensurately Modulated Structure of $Bi_2Sr_2CaCu_2O_{8+y}$

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Abstract

A method is described for the refinement of modulated structures from a combined set of single-crystal and powder diffraction data or from powder data only. The method is especially useful when information on light atoms is to be obtained and no single crystals of suitable size for neutron diffraction are available. The program in which the method is encoded allows for differences in composition between the single-crystal and powder samples. Application to the incommensurately modulated superconductor $Bi_2Sr_2CaCu_2O_{8+y}$ (2212) using powder neutron and single-crystal X-ray data confirms that the oxygen modulation in the Bi-O layer is sawtooth-like, as observed in the preceding study based solely on X-ray data [Petricek, Gao, Lee & Coppens (1990). *Phys. Rev. B*, **42**, 387-392], but with improved accuracy in the resulting parameters. The extra oxygen content is explicitly related to the modulation model and corresponds to 0.14 (4) per formula unit. With the refined site occupancies for the heavy atoms and the results of an anomalous-scattering study on the bismuth distribution [Coppens, Lee, Gao & Sheu (1991). *J. Phys. Chem. Solids*, **52**, 1267-1272], a copper valency of 2.31 is obtained for the single-crystal sample. The powder value of 2.40 is somewhat less reliable as no anomalous-scattering data are available for the powder sample.

Introduction

The widespread occurrence of incommensurate modulations in the high-T_c superconducting phases

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and related compounds illustrates the importance of modulated structures. Several of the high-T_c superconducting phases have been studied in detail. They include the structures of the two-Cu-O-layer $Bi_2Sr_2CaCu_2O_{8+y}$ (2212) phase (Petricek, Gao, Lee & Coppens, 1990) and its Fe-substituted analog, $Bi_2Sr_3Fe_2O_9$ (LePage, McKinnon, Tarascon & Barboux, 1989), the one-Cu-O-layer $Bi_2Sr_{2-x}Ca_xCuO_6$ (221) phase (Gao, Lee, Yeh, Bush, Petricek & Coppens, 1989) and the corresponding Pb-substituted (Gao, Lee, Graafsma, Yeh, Bush, Petricek & Coppens, 1990) and Mn-substituted (Tarascon, LePage, McKinnon, Ramesh, Eibschutz, Tselepis, Wang & Hull, 1990) phases.

For incommensurate modulations the periodicity of the modulation wave is an irrational multiple of at least one of the basic lattice repeats of the crystal. The modulation in $Bi_2Sr_2CaCu_2O_8$ (2212) is one-dimensional and incommensurate along the *a* axis. With the superspace-group approach introduced by de Wolff, Janssen & Janner (1981), one- and two-dimensionally incommensurately modulated crystals are described in four- and five-dimensional periodic space, respectively.

The modulation in the high-T_c superconductors involves both the metal and the O atoms. The modulation of the O atoms in the Bi-O plane is pertinent as it provides the mechanism for the incorporation of extra O atoms in the layer and thereby contributes to the hole concentration in the Cu-O plane, which is a central concept in the theories of the superconductivity mechanism. But since X-ray intensities are dominated by the scattering of the heavier atoms, oxygen modulations obtained by X-ray analysis are relatively inaccurate.

A neutron diffraction study of the 2212 phase excluding the modulation has been reported by Bordet, Capponi, Chaillout, Chenavas, Hewat, Hewat, Hodeau, Marezio, Tholence & Tranqui (1988). Yamamoto and his co-workers have applied a combined refinement method based on X-ray and time-of-flight neutron powder data to the 2212 (Yamamoto, Onoda, Takayama-Muromachi, Izumi, Ishigaki & Asano, 1990) and 221 phases (Yamamoto, 1991). Although the method led to a successful refinement of the 2212 structure, the conclusion that the value of y in the formula $Bi_2Sr_2CaCu_2O_{8+y}$ equals 1.0 is not supported by the extensive evidence available from other sources.

As the large single crystals needed for neutron diffraction are often not available but single-crystal methods have obvious advantages, we have developed a combined refinement approach in which single-crystal X-ray data are combined with powder neutron data. The latter are treated with the Rietveld (1969) method, while the former are analyzed as described previously (Petricek, Coppens & Becker, 1985; Petricek & Coppens, 1988). The method may be compared with combined Rietveld refinements of two or more sets of powder diffraction data reported previously for conventional (Williams, Kwei, Von Dreele, Larson, Raistrick & Bish, 1988; Maichle, Ihringer & Prandl, 1988) and modulated structures (Yamamoto *et al.*, 1990). Since neutron data are more sensitive to oxygen scattering, the combined X-ray and neutron refinement is capable of providing a reliable description for both heavy-atom and O-atom modulations.

Formalism

The analytical formalism for calculating structure factors in a modulated crystal has been described in detail by Petricek, Coppens & Becker (1985) and Petricek & Coppens (1988). A scattering vector **Q** of a reflection in a one-dimensionally modulated crystal is defined by four indices *h*, *k*, *l* and *m*:

$$\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} = \mathbf{H} + m\mathbf{q} \qquad (m = 0, \pm1, \pm2, \ldots), \quad (1)$$

where m is the index of satellite reflections and $\mathbf{q}$ the wave vector of the modulation. When $m = 0$, $\mathbf{Q} = \mathbf{H}$ and the scattering vector corresponds to a main reflection. In a one-dimensionally displacively modulated crystal, the structure factor for reflection $\mathbf{Q}$ (h, k, l, m) is given by

$$\begin{aligned}\mathbf{F}(\mathbf{Q}) = \sum_{\nu} f_{\nu}(\mathbf{Q}) \sum_{s} \exp\,[2\pi i(\mathbf{Q}^s - m\mathbf{q}^s)\cdot\mathbf{r}_{\nu}^{0} + \mathbf{S} + m\boldsymbol{\tau}]\\ \times \sum_{m_1,\ldots,m_l=-4}^{4} \prod_{j=1}^{l} J_{-m_j}\{2\pi\mathbf{U}_{\nu}^{s}(j)\\ \times \exp\,[-im_j\chi^s(j)]\}, \qquad (2)\end{aligned}$$

where $f_{\nu}(\mathbf{Q})$ is the X-ray scattering factor or neutron scattering length for atom ν, m_j ($j = 1, 2, \ldots, l$) is the order of Bessel function J_{-m_j}. The possible m_j values obey the condition $m_1 + 2m_2 + \ldots + lm_l = m$. Values of m_j from -4 to 4 were included in the calculation. $\mathbf{U}_{\nu}^{s}(j)$ and $\chi^s(j)$ are, respectively, the jth harmonic modulation-wave amplitude and phase for atom ν as transformed by the sth symmetry operation. The summation is over all s symmetry operations. $\mathbf{Q}^s$ and $\mathbf{q}^s$ are the scattering vector and the modulation wave vector after transformation by the rotational part of the symmetry operation. $\mathbf{r}_{\nu}^{0}$ is the position of atom ν in the reference unit cell. S and $\boldsymbol{\tau}$ are the translational components of the symmetry operator in the three-dimensional real space and in the fourth dimension, respectively. The modulation wave is expressed as a sum of l harmonic components,

$$\begin{aligned}\mathbf{U}_{\nu} = \sum_{j=1}^{l} \{\mathbf{u}_{\nu}^{x}(j) \sin\,[2\pi\mathbf{q}\cdot(\mathbf{r}_{\nu}^{0} + \mathbf{n})]\\ + \mathbf{u}_{\nu}^{y}(j) \cos\,[2\pi\mathbf{q}\cdot(\mathbf{r}_{\nu}^{0} + \mathbf{n})]\}, \qquad (3)\end{aligned}$$

where $\mathbf{n}$ is the lattice translation vector. For each harmonic displacement function associated with atom ν, there are six refinable variables (components of $\mathbf{u}_\nu^x$ and $\mathbf{u}_\nu^y$). When the atom ν is located at a special position, the number of refinable variables will be reduced due to local symmetry restrictions (Petricek & Coppens, 1988).

In a single-crystal diffraction pattern the reflections are well resolved and their intensity is given by

$$I_c^{\rm cal}(\mathbf{Q}_i) = k_1 c_1 |F_{\rm cal}(\mathbf{Q}_i)|^2, \tag{4}$$

where k_1 is a scale factor and c_1 includes X-ray polarization and Lorentz corrections as well as the necessary absorption and extinction corrections. But in a powder pattern, considerable overlap may occur between reflections with similar $(\sin\theta)/\lambda$ values. The intensity at a certain value of 2θ can therefore have contributions from several (n) overlapping reflections,

$$I_p^{\rm cal}(2\theta_j) = k_2 \sum_{i=1}^{n} \alpha_i(2\theta_j)|F_{\rm cal}(\mathbf{Q}_i)|^2 - I_b(2\theta_j) \qquad (j = 1, \ldots, n_p), \tag{5a}$$

$$\alpha_i(2\theta_j) = M_i L_i(\Delta_{2\theta}/\Delta_{2\theta_i}) P[\theta_i, (2\theta_j - 2\theta_i)/\Gamma_i], \tag{5b}$$

where k_2 is a scale factor, n_p is the number of data points, M_i is the reflection multiplicity factor, L_i contains the Lorentz and polarization corrections (the latter for X-ray scattering only), and the intensity is corrected for preferred orientation of the crystallites in the sample. $\Delta_{2\theta}$ is the step size in the 2θ scan. $P[(2\theta - 2\theta_i)/\Gamma_i]$ is the normalized shape function of a peak with full width at half-maximum Γ_i, $I_p^{\rm cal}$ is corrected for peak asymmetry following the formalism of Hastings, Thomlinson & Cox (1984). $2\theta_i$ is the calculated peak position for reflection $\mathbf{Q}_i$.

The peak-shape functions allowed in the program include Gaussian and Lorentzian functions, the Voigt function, which is a convolution of Gaussian and Lorentzian functions, and the pseudo-Voigt function, which is a linear combination of Gaussian and Lorentzian functions.*

The intensity at each data point j can be assigned to neighboring reflections in proportion to the calculated contributions of each of the reflections to the data point. The 'observed' value of F, which can be used in a Fourier summation, is then

$$|F_{\rm obs}(\mathbf{Q}_i)| = \left\{\left[\sum_{j=j_1}^{j_2} \alpha_i(2\theta_j)|F_{\rm cal}(\mathbf{Q}_i)|^2(I_p^{\rm obs}/I_p^{\rm cal})\right] \times \left[\sum_{j=j_1}^{j_2} \alpha_i(2\theta_j)\right]^{-1}\right\}^{1/2}, \tag{6}$$

where j_1 and j_2 are the lower and upper limits for reflection i. $F_{\rm obs}$ is assigned the phase of $F_{\rm calc}$.

An element of the least-squares normal matrix, c_{ij}, is the summation over all observations of the weighted products of the partial derivatives of the observations E with respect to the variables p_i and p_j,

$$c_{ij} = \sum_{k=1}^{n_t} W_k(\partial E_k/\partial p_i)(\partial E_k/\partial p_j) \qquad (i, j = 1, \ldots, N). \tag{7}$$

In a combined refinement of two sets of data, the summation is over both types of observations. The variables p_i $(i = 1, \ldots, N)$ include those common to both sets of data, such as parameters for average atomic positions, atomic thermal vibrations and modulation amplitudes,† and also parameters solely determined by one set of data. For the powder set, the latter include up to six unit-cell parameters, the components of the modulation-wave vectors, peak-width parameter U, V, W, X and Y (see footnote *), the 2θ-zero correction factor, and preferred-orientation (Dollase, 1986) and profile-asymmetry parameters (Hastings, Thomlinson & Cox, 1984). Only the X-ray scale factor is solely dependent on the X-ray measurements. As the compositions of the single-crystal and powder samples may differ because of details of the syntheses employed, two sample-specific site-occupancy variables are allowed for each atom.

The partial contribution of the powder data set to the variable p_i is derived from

$$\varphi_p^i = \sum_{k=1}^{n_p} w_k(\partial E_k/\partial p_i)^2 \Big/ \sum_{k=1}^{n_t} w_k(\partial E_k/\partial p_i)^2 \tag{8}$$

(Coppens, Boehme, Price & Stevens, 1981). The partial contribution to p_i from the single-crystal data is then $\varphi_c^i = 1 - \varphi_p^i$.

The algorithms presented above have been implemented in a program *GJANA*, which is a combination of the program *JANA* (Petricek, Coppens & Becker,

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* The pseudo-Voigt function is an approximation to the Voigt function. The program *GJANA* adopts the numerical expression described by Thompson, Cox & Hastings (1987), Cox, Toby & Eddy (1988) and Cox (1992) in which

$$\Gamma = (\Gamma_G^5 + 2.69269\Gamma_G^4\Gamma_L + 2.42843\Gamma_G^3\Gamma_L^2 + 4.47163\Gamma_G^2\Gamma_L^3 + 0.07842\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{1/5},$$

where Γ_G and Γ_L are Gaussian and Lorentzian half-widths defined as:

$$\Gamma_G = [U(2t_r^2 - t_r) + V(1 - 4t_r^2) + W(2t_r^2 + t_r)]^{1/2};$$

$$\Gamma_L = Y/\cos\theta_i + X\tan\theta_i;$$

$$t_r = [\tan\theta_i - 0.5(\tan\theta_a + \tan\theta_b)]/(\tan\theta_b - \tan\theta_a).$$

θ_i is the theta angle for reflection $\mathbf{Q}_i$ and θ_a and θ_b are the starting and finishing angles for the whole powder pattern. U, V, W, X and Y are refinable variables. The modification of the usual quadratic expression for Γ_G permits observed values of Γ_G to be input without an explicit knowledge of U, V and W.

† Small differences between X-ray and neutron parameters that occur for atoms with pronounced asphericity of the charge density (Coppens, Boehme, Price & Stevens, 1981) are ignored in this analysis.

1985) written for the analysis of single-crystal data and the program *PROFV*, which is a locally modified version of the Rietveld–Hewat program (Rietveld, 1969; Hewat, 1973). *GJANA* allows refinements of modulated structures in a four-or five-dimensional superspace with diffraction data from both single-crystal and powder samples.

Experimental

In a previously described study (Gao, Lee, Coppens, Subramanian & Sleight, 1988), main and satellite reflections up to second order were collected on a single-crystal sample of 0.175×0.05×0.01 mm. The modulation-wave vector was found to be 0.210(3) $\mathbf{a}^*$.

The powder sample was prepared from a mixture of $SrCO_3$, $CaCO_3$, Bi_2O_3 and CuO powders with a nominal starting composition of $Bi_2Sr_{1.75}Ca_{1.25}Cu_2O_8$. The ground mixture was heated for 16 h in air at 1093 K in an alumina boat and reground and heated again for 16 h at 1133 K. The sample was then pelletized and arc melted and the as-cast material annealed at 1153 K in air for 24 h and finally quenched. Compositional analysis was performed on a JEOL JXA-35 microscope equipped with a wavelength-dispersive spectrometer. Six determinations on different regions of the specimen yielded the composition $Bi_{2.12\pm0.10}Sr_{1.79\pm0.10}Ca_{0.92\pm0.05}Cu_2$ with Cu normalized at 2. AC susceptibility measurement showed the superconductivity transition to be sharp with a midpoint of 90 K (the 10% onset is 92 K and the 90% completion is near 82 K). Neutron powder data were collected at the High-Flux Beam Reactor at Brookhaven National Laboratory using a fixed wavelength equal to 2.373 Å.

Refinement and results

In the refinement, the single-crystal occupancies of Bi at Sr and Ca sites were fixed at the values based on the X-ray anomalous-scattering analysis (Lee, Gao, Sheu, Petricek, Restori, Coppens, Darovskikh, Phillips, Sleight & Subramanian, 1989; Coppens, Lee, Gao & Sheu, 1991). The powder occupancy of Sr at the Sr site was fixed according to the nominal starting Sr composition, while the occupancies of Bi at Sr and Ca sites were treated as variables.

The initial model for the modulation was taken from the earlier analysis. While the modulation of most of the atoms is properly described by a superposition of harmonic functions (3), Fourier maps in the x–x_4 section (where x_4 is the coordinate in the fourth dimension) based on the single-crystal data indicate that the displacement of the O atoms in the Bi layer should be described by a sawtooth-shaped function (Petricek, Gao, Lee & Coppens, 1990),

$$\mathbf{u} = 2\mathbf{u}_0[(x_4 - x_4^0)/\Delta] \qquad (x_4^0 - \Delta/2 < x_4 < x_4^0 + \Delta/2), \tag{9}$$

where u_0 and Δ are, respectively, the amplitude and the periodicity of the sawtooth function, x_4 is the fractional coordinate of a modulated atom in the fourth dimension. $\mathbf{u}_0$, Δ and x_4^0, a phase reference point in the fourth dimension, are adjustable parameters (Fig. 1). If Δ is greater than 1, adjacent sawteeth overlap by $(\Delta - 1)/2$. This means that additional $\Delta - 1$ O atoms exist in the region as illustrated in Fig. 1. To investigate whether this model is confirmed by the neutron data, which are more sensitive to oxygen scattering, neutron structure factors were calculated from the powder diffraction pattern with (6) and used to calculate a difference Fourier map in the x–x_4 plane through O(4). Though the results shown in Fig. 2 suffer from series-termination effects because only first-order satellites were available from the powder data, they confirm the previous X-ray analysis.

In the combined refinement, single-crystal data with $(\sin\theta)/\lambda < 0.8\ \text{Å}^{-1}$ and powder diffraction

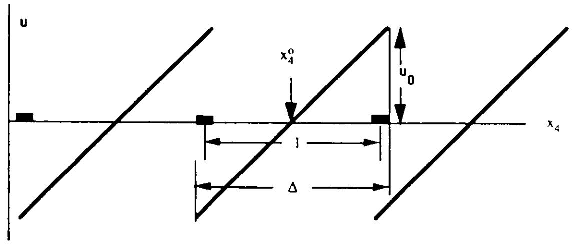

Fig. 1. The sawtooth-shaped function describing the O(4) modulation.

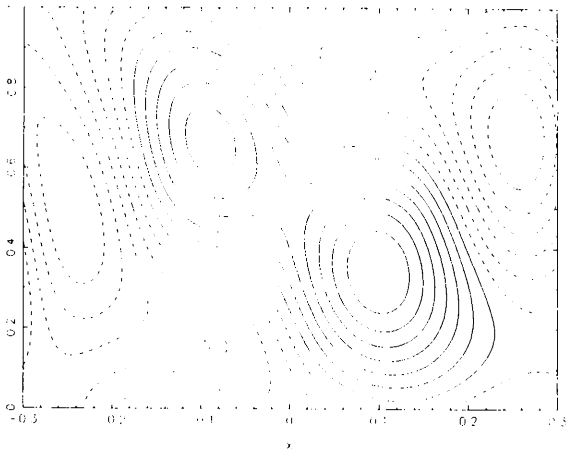

Fig. 2. Difference Fourier map based on neutron powder diffraction in the x–x_4 section containing O(4) ($y = 0.150$ and $z = 0.057$). The contribution of O(4) has been omitted from the calculated structure factors. The maximum peak height is 1.93 fm and the contour interval is 0.25 fm. Dashed lines represent negative contours. 257 unique reflections (146 main reflections and 111 first-order satellites) with $(\sin\theta)/\lambda < 0.4\ \text{Å}^{-1}$ were used in the Fourier synthesis.

Table 1. *Agreement factors of the X-ray and neutron combined refinement*

The X-ray refinement data are from Petricek, Gao, Lee & Coppens (1990).

	X-ray and neutron refinement		X-ray refinement
	R values	Number of observations	R values
Overall R_w factors	0.092	2001	
R for X-ray single-crystal data			
All reflections	0.076	662	0.072
Main reflections	0.073	412	0.070
First-order satellites	0.072	189	0.065
Second-order satellites	0.154	61	0.161
R_I for neutron powder data			
All reflections	0.084	256	
Main reflections	0.060	145	
First-order satellites	0.216	111	
GOF for all data	4.796	2001	
GOF for single-crystal data	6.733	662	
GOF for powder data	3.943	1339	

The overall R_w factor is defined as

$$R_w = [\sum w_i(|F_i^{\rm obs}| - |F_i^{\rm cal}|)^2 / \sum w_i |F_i^{\rm obs}|^2]^{1/2}$$
$$+ [\sum w_j(|y_j^{\rm obs}| - |y_j^{\rm cal}|)^2 / \sum w_j |y_j^{\rm obs}|^2]^{1/2}.$$

The summation is over all reflections from single-crystal data ($i = 1, \ldots, n_c$) and all data points in the powder diffraction pattern ($j = 1, \ldots, n_p$).

$$R = \sum \| F_i^{\rm obs}| - |F_i^{\rm cal}\| / \sum |F_i^{\rm obs}|$$

and

$$R_I = \sum \| F_i^{\rm obs}|^2 - |F_i^{\rm cal}|^2| / \sum |F_i^{\rm obs}|^2,$$

where the observed structure factors for calculating R_I are defined in (6). The goodness of fit (GOF) is defined as

$$\mathrm{GOF}_{\rm all\ data} = [\sum w_i(|F_i^{\rm obs}| - |F_i^{\rm cal}|)^2 + \sum w_j(|y_j^{\rm obs}| - |y_j^{\rm cal}|)^2]/(n_t - N)$$

$$\mathrm{GOF}_{(\text{X-ray})} = [\sum w_i(|F_i^{\rm obs}| - |F_i^{\rm cal}|)^2]/(n_c - N_c)$$

and

$$\mathrm{GOF}_{\rm neutron} = [\sum w_i(|y_i^{\rm obs}| - |y_i^{\rm cal}|)^2]/(n_p - N_p),$$

where $n_t = n_c + n_p$, the summation of all observations from both X-ray and neutron data sets, and $N = N_c + N_p = \sum \varphi_c^i + \sum \varphi_p^i$, the summation being over all refined variables. The quantities $\varphi_{c,p}^i$ are defined by expression (8).

intensities in the range $5 \leq 2\theta \leq 137°$ were used. R values are given in Table 1. R values of the single-crystal data are comparable with those obtained in the earlier X-ray analysis.

In a joint refinement, the goodness of fit of each data set is affected by the respective weighting schemes. The weight for each X-ray reflection is based on Poisson counting statistics and instrumental instability as obtained from standard reflections repeatedly measured during the data collection. For the neutron powder data, the weight for each data point is based on Poisson counting statistics only. The goodness-of-fit parameters for the single-crystal and powder data are reasonably close, indicating a nearly equal contribution to the refinement process from the two data sets.

The inclusion of the satellite reflections in the model described above improves the R factor of powder profile fitting from 0.127 to 0.074. Fig. 3 illustrates the observed and calculated powder diffraction pattern. A pair of strong satellite reflections $201\bar{1}$ and 2011 that do not overlap with main reflections are marked in the figure.

Neutron data make a significant contribution to the determination of oxygen parameters. The value of φ_p^i averaged over the 41 refined oxygen parameters is 0.60, the highest value being 0.89 for the Δ value of O(4). On the other hand, the neutron data contribute much less to the heavy-atom variables, which are mainly determined by the X-ray data. For parameters associated with Bi atoms, the neutron scattering contributions are less than 0.02. For Sr and Cu atoms, the largest neutron contributions are to the z coordinates of Sr (0.18) and Cu (0.32) and to the temperature factors of Cu (0.14, 0.16 and 0.18 Å^2 for U_{11}, U_{22} and U_{33}). While the results of the combined refinement are basically in agreement with the previous X-ray analysis, the accuracy is evidently improved as demonstrated in Table 2. For the average atomic coordinate z, the e.s.d.'s are reduced by at least a factor of two. A similar reduction in the e.s.d.'s is achieved for the modulation parameters. In particular, the e.s.d. of the Δ value of the O(4) atom is reduced by a factor of four compared to the X-ray analysis. The final Δ value, 1.07 (2), corresponds to 8.14 (4) O atoms per formula, which is equal within experimental error to the X-ray result.

Initial refinements suggested the Ca sites of the powder sample to be occupied by Ca plus a small fraction of more strongly scattering atoms, which, on the basis of the neutron scattering lengths, could be Cu, Sr or Bi. In the single-crystal sample, the Ca site contains both Sr and Bi in addition to Ca, according to the earlier analysis. In the powder refinement, however, only Bi contamination is assumed as it is

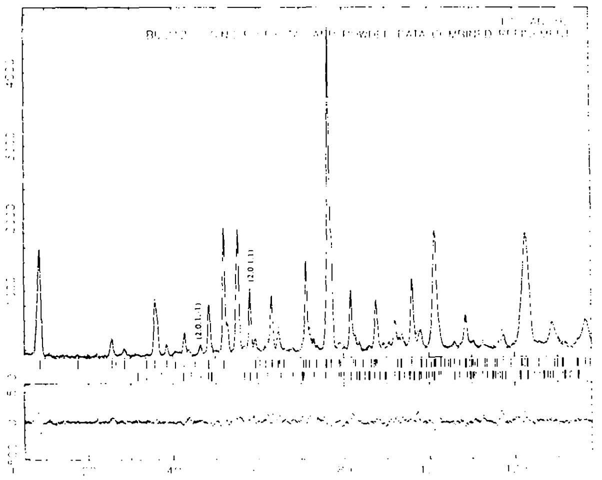

Fig. 3. Least-squares fit of the neutron powder diffraction pattern using the Rietveld refinement method including first-order satellite reflections.

Table 2. *Cell dimensions* (Å) *and modulation wave vector*

	Neutron data, refined values	X-ray single crystal
a	5.4150 (3)	5.408 (1)
b	5.4149 (3)	5.413 (1)
c	30.861 (5)	30.871 (5)
$\mathbf{q}$	0.2095 (5)$\mathbf{a}^*$	0.210 (3)$\mathbf{a}^*$

Table 3. *Site occupancies of heavy atoms*

Atom/site	Single crystal	Powder
Bi/Bi	0.96 (1)	0.93 (1)
Sr/Sr	0.84 (2)	0.875
Bi/Sr	0.05	0.04 (1)
Cu/Cu	1.00	1.00
Ca/Ca	0.80 (4)	0.96 (4)
Sr/Ca	0.14	0.00
Bi/Ca	0.06	0.04

Table 4. *Positional and thermal parameters* ($Å^2 \times 10^3$) *of the average structure*

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.504 (2)	0.2333 (4)	0.0523 (1)	72 (3)	21 (2)	12 (2)	−6 (3)	9 (3)	−4 (2)
Sr	0.00	0.2527 (5)	0.1408 (1)	25 (3)	6 (1)	23 (2)	0	0	5 (3)
Cu	0.50	0.2502 (6)	0.1966 (1)	13 (2)	−1 (3)	29 (3)	0	0	−3 (3)
Ca	0.00	0.25	0.25	7 (3)	4 (2)	19 (5)	0	0	−6 (6)
O(1)	0.75	0.00	0.1983 (5)	2 (5)					
O(2)	0.25	0.50	0.1980 (5)	4 (6)					
O(3)	0.51 (1)	0.277 (3)	0.1163 (6)	4 (7)					
O(4)	0.03 (1)	0.151 (2)	0.0571 (6)	18 (7)					

Table 5. *Modulation amplitudes of the positional* (Å) *and thermal* ($Å^2 \times 10^3$) *parameters*

Site	Waves	U_x	U_y	U_z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	$\sin(2\pi x_4)$	0.32 (1)	0.07 (1)	−0.02 (1)	−32 (4)	25 (4)	4 (4)	−7 (3)	−2 (2)	−4 (5)
	$\cos(2\pi x_4)$	0.07 (2)	−0.04 (1)	−0.16 (1)	53 (5)	−1 (4)	−6 (2)	24 (5)	3 (4)	−5 (2)
	$\sin(4\pi x_4)$	0.08 (1)	−0.00 (2)	−0.07 (1)	−13 (8)	4 (5)	−2 (5)	25 (5)	26 (3)	−28 (3)
	$\cos(4\pi x_4)$	−0.02 (1)	−0.11 (1)	−0.05 (1)	55 (4)	−13 (3)	−9 (4)	20 (6)	−8 (5)	1 (5)
Sr	$\sin(2\pi x_4)$	0.23 (1)	0	0						
	$\cos(2\pi x_4)$	0	0.03 (2)	−0.21 (1)						
	$\sin(4\pi x_4)$	0.11 (1)	0	0						
	$\cos(4\pi x_4)$	0	0.00 (3)	−0.06 (1)						
Cu	$\sin(2\pi x_4)$	0.06 (1)	0	0						
	$\cos(2\pi x_4)$	0	−0.03 (2)	−0.27 (1)						
	$\sin(4\pi x_4)$	−0.01 (1)	0	0						
	$\cos(4\pi x_4)$	0	0.10 (2)	−0.08 (1)						
Ca	$\sin(2\pi x_4)$	0	0	0						
	$\cos(2\pi x_4)$	0	−0.02 (3)	−0.27 (1)						
	$\sin(4\pi x_4)$	−0.03 (1)	0	0						
	$\cos(4\pi x_4)$	0	0	0						
O(1)	$\sin(2\pi x_4)$	0.07 (4)	−0.01 (6)	0						
	$\cos(2\pi x_4)$	0	0	−0.40 (4)						
	$\sin(4\pi x_4)$	−0.15 (4)	−0.01 (6)	0						
	$\cos(4\pi x_4)$	0	0	−0.07 (5)						
O(2)	$\sin(2\pi x_4)$	0.04 (3)	0.06 (6)	0						
	$\cos(2\pi x_4)$	0	0	−0.08 (5)						
	$\sin(4\pi x_4)$	0.15 (5)	0.03 (6)	0						
	$\cos(4\pi x_4)$	0	0	0.27 (5)						
O(3)	$\sin(2\pi x_4)$	0.52 (4)	0.07 (6)	−0.31 (6)						
	$\cos(2\pi x_4)$	0.21 (7)	0.23 (6)	−0.23 (4)						
	$\sin(4\pi x_4)$	0.21 (6)	0.24 (6)	−0.26 (6)						
	$\cos(4\pi x_4)$	0.18 (8)	0.10 (9)	0.06 (7)						
O(4)	$\mathbf{u}_0$	−1.46 (3)	0.12 (5)	0.42 (5)						
	x_4^0, Δ	0.42 (2)	1.07 (2)							

x_4^0 is the fractional coordinate of the phase reference point in the fourth dimension.

not possible to determine the presence of both Sr and Bi in the absence of wavelength-dependent X-ray scattering information. This assumption agrees with the nominal starting composition of Sr, which is accounted for by the Sr-site occupancy. The refined occupancies of heavy atoms of the single-crystal and the powder sample are listed in Table 3 while positional and thermal parameters are used in Table 4 and modulation amplitudes in Table 5. The composition of single-crystal and powder samples are $Bi_{2.14}Sr_{1.82}Ca_{0.80}Cu_2O_{8.14}$ and $Bi_{2.02}Sr_{1.75}Ca_{0.96}Cu_2O_{8.14}$, respectively. The latter is in excellent agreement with the electron microscopic determination quoted earlier. The corresponding Cu valences are 2.31 and 2.40.

The refined Ca compositions of both single-crystal and powder samples compare well with the c-axis length using the correlation of Niu, Fukushima, Takeno, Nakamura & Ando (1989). For this purpose, the powder-sample cell dimensions were redetermined by synchrotron X-ray diffraction at the X7A beamline at the NSLS. The resulting value of

30.863 (2) Å agrees with the refined value of 30.861 (5) Å (Table 2). According to Fig. 1 of Niu *et al.* (1989), the Ca composition corresponding to $c =$ 30.863 Å is close to the refined value of 0.96. The single-crystal unit-cell length c is 30.871 (5) Å (Table 2). This slightly larger value agrees with the lower Ca composition for the single-crystal sample determined in the refinement.

Despite the agreement between the unit length c and the refined powder Ca content, the refined composition of 0.96 is notably lower than the Ca content of 1.25 of the reaction mixture. Though this suggests Ca-containing impurities such as Ca_2CuO_3, $CaCu_2O_3$ and CaO in the powder sample, none of these can be identified unambiguously from the neutron diffraction spectrum. An observed but poorly fitted peak at $2\theta = 57.0°$ (Fig. 3) deviates by about 0.5° from the position of the strongest X-ray measured reflection, 011, from Ca_2CuO_3 as given in the JCPDS (1990) database.

Discussion

The most important results of this study are the confirmation of the sawtooth model for the modulation of the O atoms in the BiO planes and the oxygen occupancies that have been determined with significantly better accuracy by including the neutron data in the refinement. The O-atom positions near the Cu and Sr atoms are fully occupied. The 'interstitial' O atoms in the BiO layer amount to 0.14 (4) atoms per formula unit, or 0.67 (4) O atoms per period of the modulation wave. This value is much lower than that obtained in the previous study of the same phase by Yamamoto *et al.* (1990) using combined refinement of X-ray and neutron powder data. In the latter study, 4.76 extra O atoms were found per period of the modulation wave, which corresponds to one extra O atom per formula unit. However, our value is in good agreement with results from other studies (Tarascon, LePage, Barboux, Bagley, Greene, McKinnon, Hull, Giroud & Hwang, 1988; Sunshine, Siegrist, Schneemeyer, Murphy, Cava, Batlogg, van Dover, Fleming, Glarum, Nakahara, Farrow, Krajewski, Zahurak, Waszczak, Marshall, Marsh, Rupp & Peck, 1988; LePage, McKinnon, Tarascon & Barboux, 1989; Idemoto & Fueki, 1990; Irvine & Namgung, 1990) and corresponds to Cu valencies of 2.31 for the single-crystal and 2.40 for the powder sample. These values are in the generally accepted range also obtained by other techniques [see Petricek *et al.* (1990) for other values].

We conclude that the combination of single-crystal X-ray and neutron powder data is a powerful approach for analyzing crystal structures in which both heavy and light atoms are present. As large single-crystal samples suitable for neutron diffraction are often not available, the combined single-crystal/powder refinement offers an alternative that is preferable to the exclusive use of powder data. This is especially true for modulated structures, for which satellite reflections frequently overlap with main reflections in the powder pattern. In addition, the Rietveld refinement requires a starting list of main and satellite reflections which may not be obtainable without prior information from single-crystal studies.

The program *GJANA* can also be used to refine modulated structures using a single powder diffraction data set, either from X-rays or neutrons, providing that the initial model of modulation is available. We have successfully analyzed the modulated structures of a series of Li-intercalated $Bi_2Sr_2CaCu_2O_y$ compounds using only synchrotron X-ray powder diffraction data (Fleischer, Manassen, Coppens, Lee, Gao & Greenbaum, 1992).

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Correlating the Optical Rotation of α-Quartz with a Skew Matrix of a Dielectric Tensor

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Abstract

A beam of polarized light propagating along the helical axis of α-quartz interacts with $SiO_{4/2}$ groups consecutively. When a skew matrix of a resultant dielectric tensor is compared to a skew matrix of a rotation matrix, the polarizability components of an $SiO_{4/2}$ group, with two sets of results, may be derived since the specific rotation along the helical axis is known for 5892.9 Å light at 293 K. Both sets have the same mean value for the components. The mean is close to an empirical result based on the bond refractivity of Si-O. In comparison with the optical rotation sign (+ or −) along the optic axis, an opposite rotation sign is derived along the directions perpendicular to both the optic axis and any diad axis. In α-quartz, the inactive directions 33.83° from its optic axis are interpreted. The diad-axis directions are predicted to be inactive directions. Bunn's empirical formula is interpreted.

Introduction

Barron (1975) suggested that optical-rotation components can be isolated in the study of crystals. α-quartz was chosen for a theoretical study of the relationship between its helical structure and its rotatory properties. Because of the birefringence, it is difficult to determine experimentally the rotatory power of α-quartz in sections parallel to its optic axis (Wahlstrom, 1979). Since the specific rotation along the optical axis of α-quartz was known, the polarizability components of an $SiO_{4/2}$ group in a left-handed quartz with + optical rotation can be derived with the assumption that there is a relationship between the skew matrix of a resultant dielectric tensor and the skew matrix of a rotation matrix. Some inactive directions in α-quartz can be interpreted or predicted based on its structure and this assumption. Wahlstrom (1979) predicted that 'light traveling at right angles to the optic axis is rotated but in an opposite sense to that propagated along the optic axis'. The same proposal for helix optical activity was also mentioned by Barron (1982, p. 285). Based on the structure of α-quartz, the rotation sign changes as predicted.

The specific rotations along the two directions perpendicular to the optic axis were calculated. Note that the proportionality between the rotation angle and the thickness along the helical axis can also be interpreted through the multiplication of rotation matrices. Bunn's empirical formula (Bunn, 1961), used to calculate the directional polarizabilities of a molecule in order to optimize the molecular orienta-

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