

Supermodulation in the atomic structure of the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ from *ab initio* calculations

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We present results of density functional theory (DFT) calculation of the structural supermodulation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ structure, and show that the supermodulation is indeed a spontaneous symmetry breaking of the nominal crystal symmetry, rather than a phenomenon driven by interstitial O dopants. The structure obtained is in excellent quantitative agreement with recent x-ray studies, and reproduces several qualitative aspects of scanning tunneling microscopy (STM) experiments as well. The primary structural modulation affecting the CuO_2 plane is found to be a buckling wave of tilted CuO_5 half-octahedra, with maximum tilt angle near the phase of the supermodulation where recent STM experiments have discovered an enhancement of the superconducting gap. We argue that the tilting of the half-octahedra and concomitant planar buckling are directly modulating the superconducting pair interaction.

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The Bi-based family of high-temperature superconducting cuprate materials is alone among the several families of cuprates in possessing an incommensurate structural *supermodulation*. It is not known whether this wavelike distortion of the ideal periodic crystal structure represents a spontaneous symmetry breaking originating in a mismatch between the preferred bond lengths in the perovskite and rock salt layers of the crystal, or is driven by disordered interstitial oxygen atoms which dope the system. Interest in this phenomenon, until recently viewed as a curiosity, has been reawakened by scanning tunneling microscopy (STM) experiments¹ which show a strong positive correlation of the supermodulation phase with the superconducting energy gap, a local measure of the strength of electron pairing. Theoretical calculations^{2,3} suggest that the structural modulation may couple to local electronic structure, which in turn influences the effective local pairing interaction. Knowledge of how the lattice distorts in the presence of the supermodulation could be used to calculate local electronic structure and electron-phonon couplings, and guide a theory of local pairing in the high-temperature superconductors.

The structure of idealized $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, with two CuO_2 planes per unit cell and a critical temperature of $T_c \approx 90$ K, is shown in Fig. 1. The half-cell shown is connected to an identical half-cell on the top or bottom translated with respect to the one shown along the *a* or *b* axis by half a lattice constant. The supermodulation is now a density wave superposed on the structure of Fig. 1, characterized by a wave vector \mathbf{q}_{SM} which corresponds to a wavelength of approximately $\lambda_{SM} = 2\pi/q_{SM} \approx 26 \text{ \AA} \approx 4.8$ unit cells. The wave vector is perpendicular to the wave fronts along the *a* axis, i.e., at 45° with respect to the Cu-O bond direction. Thus superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (BSCCO) is an almost-periodic crystal, since, strictly speaking, no two unit cells are identical.⁴ Such structures were characterized mathematically by de Wolff,⁵ and are known to occur in other materials such as Na_2CO_3 as well. The supermodulation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ leads to displacements of the atomic positions of up to 0.6 \AA from their ideal crystalline locations, as determined by a series of early x-ray diffraction⁶⁻¹⁰ and scan-

ning tunneling microscopy (STM) experiments.¹¹

Historically, the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ supermodulation has been regarded as largely irrelevant to high-temperature superconductivity because the material has a critical temperature of about 90 K, similar to other cuprates with two CuO_2 layers per unit cell which do not display this effect. Thus this type of lattice distortion does not appear to have an essential role in either enhancing or suppressing superconductivity *globally*. A good deal of attention has been paid to the effect of macroscopic distortions of unit cell geometry on the critical temperature when external pressure is applied.¹²⁻¹⁴ In this case, however, exact changes in atomic displacements with pressure are impossible to determine because the materials are so complicated, even when structures are truly crystalline. On the other hand, a recent scanning tunneling spectroscopy (STS) measurement¹ has shown that the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ supermodulation is correlated *locally* with the energy gap, one of the most fundamental observables

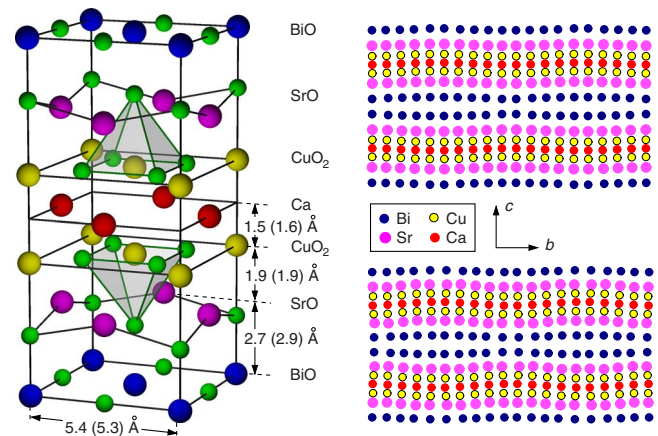


FIG. 1. (Color online) Left: Upper half of a nominal Bi-2212 unit cell. Lattice constants shown are between cations in each layer, values taken from Levin *et al.* (Ref. 16) (from this work). Right: Side view of cation distribution for a layer of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ one unit cell thick for (top) DFT bulk calculation, and (bottom) x-ray diffraction experiment (Ref. 16).

characterizing the superconducting state. By carefully imaging the positions of Bi atoms imaged on the surface layer of a cleaved $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ crystal, the authors were able to associate to each pixel in the topographic scan a “supermodulation phase” ϕ_{SM} , defining the relative position of each Bi relative to the maximum in the incommensurate density wave. They observed a $\sim 10\%$ sinusoidal variation of the energy gap, determined by the half of the local energy separation of the “coherence peaks” at positive and negative tip bias, with maxima generally coinciding with supermodulation phase $\phi_{SM}=0$.

This measurement raises the intriguing possibility of an unusual approach to understanding the origins of high-temperature superconductivity: by identifying in detail the atomic displacements which enhance superconductivity, one may be able to determine the changes in local electronic structure or electron-phonon coupling which modulate the pairing interaction itself. While atomic-scale information is conventionally thought to be irrelevant to superconductivity, these materials have coherence lengths approaching the nominal unit cell size, and there is evidence from STM studies to suggest that the pairing interaction can indeed vary on a scale of a few Å (Ref. 15) in the presence of interstitial oxygen atoms.

The key missing step in this program is the precise identification of the actual positions of the atoms present in the supermodulation of the complex BSCCO material. In principle, this information can be obtained by x-ray analysis, and considerable effort has been expended^{16–20} in this endeavor. The analysis is hampered by the difficulty of analyzing superpositions of incommensurate harmonics,¹⁹ as well as the presence of considerable disorder in the sample, thought to consist primarily of Bi/Sr substitutions on the lattice sites, as well as interstitial O disorder.²¹ The recent STM measurements do provide high-resolution imaging of atomic positions, but they are limited to the Bi atoms on the cleaved surface.

In this work we report the results of density functional theory (DFT) calculations for the atomic positions in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ system, including the possibility of a supermodulation. While application of DFT to cuprates has been somewhat neglected because of its early failure to predict the insulating state of the parent compounds, it should produce accurate results for electronic states far from the Fermi level, and its success in making structural predictions in a variety of complex materials is well known.

Details of the application of the DFT method to local structure problems in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ have been given earlier in Refs. 22 and 23. The supermodulation to be studied in this work represents a wave of small deviations from the positions represented in Fig. 1. In DFT treatment of solids, a small set of atoms is periodically repeated. Such an approach is clearly impossible in the case of an incommensurate supermodulation, so we exploit the fact that the wavelength λ_{SM} of 4.8 nominal Bi-Bi unit cell constants of 5.4 Å is very close to five cells. We therefore perform DFT calculations with a periodically repeated set of 5×1 or 5×2 nominal unit cells, each of which involves 150 atoms (1420 electrons) or 300 atoms (2840 electrons), respectively. By alternating the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ unit cell with an insulating blocking

layer in the c direction, we can also study the BiO surface for comparison to, e.g., STM experiments. However, these calculations were performed for nominal *half*-unit cells only, due to computer time constraints.

In addition, we study similar systems where a single dopant O atom has been added. The lowest energy position for the dopant in the nominal unit cell was determined in Ref. 23, and shown to improve qualitatively the fit to the angle-resolved photoelectron spectroscopy (ARPES) Fermi surface.^{23,24} In the case of a supermodulation, the dopant may find new low energy minima in each of the five inequivalent unit cells, and this calculation is therefore performed independently for starting positions of the dopant in each of them, allowing the system to relax in each case.

We begin by noting that it is far from obvious that such a calculation will find that the system, in the absence of disorder, spontaneously deforms from its nominal structure shown in Fig. 1 to create a supermodulation. Although the much simpler one-dimensional (1D) Peierls-type distortion has already been reproduced within the DFT, calculation of a structural deformation extending over several unit cells in a complex layered material is a challenging task. Since the discovery of the supermodulation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, it has been controversial whether the phenomenon is in fact an unusual spontaneous deformation of a 3D periodic structure which lowers the total energy of the system, or whether the interstitials necessary to dope the superconducting material stabilize the supermodulation. Our first result is therefore that, within DFT, the supermodulation indeed occurs spontaneously, as shown in Fig. 1. The waves of displacement from the nominal crystalline positions have significant amplitudes in all layers of the bulk system, and the largest displacements are in the xy plane, as also found in x-ray analyses.

In the right panel of Fig. 1, we illustrate the remarkable success of these calculations by comparing a side view of the cation positions in the DFT calculation to those reported in the x-ray measurements of Levin *et al.*¹⁶ The structures are nearly indistinguishable to the eye. Such a representation obscures the fact that the displacements in the x - y plane from nominal crystalline positions are quite large and more complex, however. These are displayed in Fig. 2, where they are indicated by arrows relative to the nominal sites. In the BiO layer, bulk DFT calculations and x-ray data are again in nearly perfect agreement. On the other hand, while certain regions of the SrO layer show quite good agreement between experiment and theory, significant discrepancies appear elsewhere.

This is because the atomic positions given by the bulk DFT calculations shown neglect the O dopant atoms, which were in fact located by Levin *et al.* at the sites shown in the lower panel of Fig. 2. The effect of these dopant interstitials on the crystal structure was examined from the point of view of DFT both without²³ and with the supermodulation present. The local displacements including the supermodulation are roughly as described in Ref. 23, but the supermodulation is found to break the symmetry of the effective potential for the dopant among the five nominal unit cells, leading to two effective potential minima 0.2 eV below other minima in the same layer, degenerate to within 0.01 eV, indicated by crosses in the figure. Thus we expect interstitial O dopants to

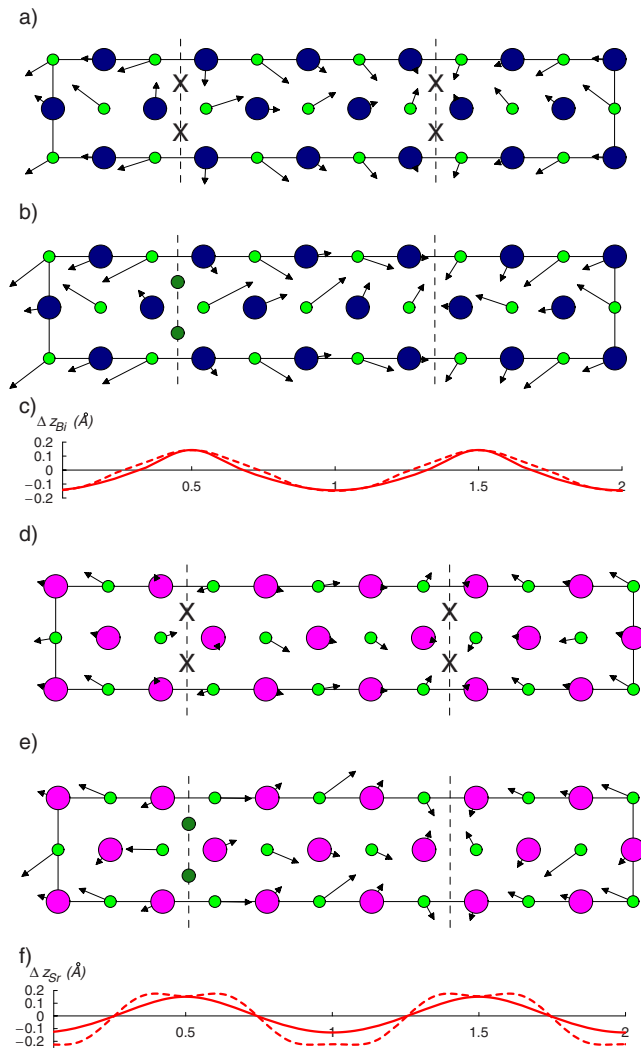


FIG. 2. (Color online) Displacements in the BiO layer projected into the x - y plane for (a) DFT bulk calculation and (b) x-ray (Ref. 16). Dashed lines are mirror planes, and X's mark points of stability found for O dopants by DFT. Small circles without arrows (dark green) mark positions deduced by x-ray experiment (c) Average z displacements of Bi for DFT (solid line) and x ray (dashed line). (d)–(f) Same as (a)–(c), but for the SrO layer. All arrow lengths were multiplied by 2 for clarity.

populate these two different symmetry sites (shown in Fig. 2) randomly with close to equal probability. The existence of these two stable dopant positions is in agreement with STM,¹ but the x-ray work¹⁶ identified only one.

Once the existence of these dopants in the crystal is accounted for, it is seen in Fig. 2 that the largest discrepancies in the position of the O(Sr) (apical oxygen) between theory and experiment arise simply because the dopants push the apical O's to the side. The x-ray data display the displacements of this type averaged over the random positions of all O dopants. The dopants do not influence the BiO layer as much because the spontaneous supermodulation displacements move the stoichiometric O's near the dopant sites away from those sites.

Within the framework of the DFT calculation, all qualitative information about the all-important CuO_2 plane is al-

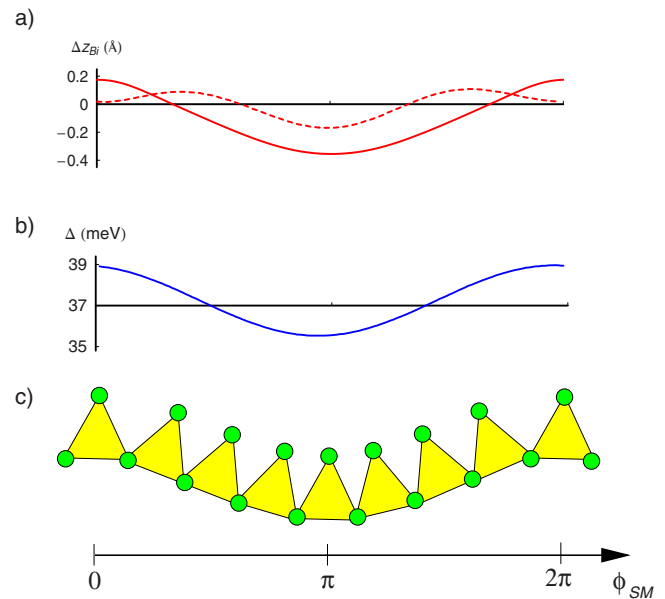


FIG. 3. (Color online) (a) z displacements of Bi atoms in DFT surface calculation (solid line) and STM measurement (Ref. 1) (dashed line); (b) modulation of measured spectral gap for overdoped BSCCO sample vs supermodulation phase angle ϕ_{SM} from Ref. 1; (c) schematic tilting of CuO_5 half-octahedra and its dependence on ϕ_{SM} . Tilt angles have been exaggerated for clarity.

ready given in Fig. 2. This is because in all our calculations the CuO_5 half-octahedra are always found to be extremely rigid,²³ and tilt as a unit when an apical oxygen is pushed to the side as found here. Thus significant buckling [$\mathcal{O}(0.4 \text{ \AA})$] of the CuO_2 plane when the half-octahedra tilt is also a characteristic of the supermodulation. Note that the x-ray measurements do not find the same rigidity of the half-octahedra; we believe this is because the measurement averages over both filled and unfilled dopant sites.

In the lowest energy convergent DFT result for the free surface (“cleaved” at the BiO layer) we have obtained thus far, the supermodulation structure is qualitatively similar to that obtained in the bulk case, with some minor surface reconstruction. For example, the amplitude of the z displacement of the Bi atoms is enhanced somewhat, to about 0.57 \AA between minimum and maximum, as shown in Fig. 3. This pattern should now be compared to the Bi positions obtained from STM. The smoothed Bi z displacements from Slezak *et al.*¹ are displayed for comparison in the same figure: while the agreement is not bad, it is clear from examination of the topographic images in this reference and other STM works that there are also some fundamental differences between the x - y displacements observed by the two probes, suggesting a more significant surface reconstruction than we have been able to reproduce by DFT. The STM pattern is found to correspond to a compression and rarefaction of the Bi positions, or alternatively to a wave in the Bi-O bond angles, with no evidence for the Bi-O-Bi chain formation discussed by Levin *et al.*^{16,25} We have found DFT solutions of this general type, but they are higher in energy, possibly because the half-cell calculations we have performed do not constrain the supermodulation sufficiently. Thus we believe a DFT de-

scription of the surface structure is possible, but requires further work. The goal is to complete the logical connection between the structural supermodulation, the gap modulation observed by STM [Fig. 3(b)], and the wave of tilted half-octahedra shown schematically in Fig. 3(c).

We have shown that DFT calculations with unit cell five nominal unit cells long describe quantitatively the displacements of atoms in the bulk of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ material with its well-known supermodulation. This is an *ab initio* calculation able to accurately predict a 3D spontaneous structural deformation of this type, and it provides strong evidence that the supermodulation is a spontaneous breaking of crystal symmetry rather than being driven by interstitial defects. Calculations for a free BiO surface agree qualitatively in some respects with STM measurements, but differ in significant ways which we do not understand at this time. All calculations indicate, however, that the crucial structural element modulated in the 2212 case is the CuO_5 half-octahedra; these objects deform rigidly and in such a way that the maximum tilt angle corresponds to the maximum gap observed by STM. This conclusion is identical to one we

reached earlier in the case of O dopant atoms. The fact that two independent perturbations of the crystal lead to (a) similar distortions of the half-octahedra, and (b) similar local enhancements of the superconducting gap, strongly suggests that the electronic structure changes caused by these tilts are directly related to the local pair interaction. The obvious next step is to downfold this information to obtain local variations in hopping matrix elements, superexchange constants, and electron-phonon couplings. This work is in progress.

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- ¹J. A. Slezak, J. Lee, M. Wang, K. McElroy, K. Fujita, B. M. Andersen, P. J. Hirschfeld, H. Eisaki, S. Uchida, and J. C. Davis, Proc. Natl. Acad. Sci. U.S.A. **105**, 3203 (2008).
- ²B. M. Andersen, P. J. Hirschfeld, and J. A. Slezak, Phys. Rev. B **76**, 020507(R) (2007).
- ³K.-Y. Yang, T. M. Rice, and F.-C. Zhang, Phys. Rev. B **76**, 100501(R) (2007).
- ⁴We follow convention in referring to the nominal “unit cell” of the BSCCO crystal as being the approximate repeating unit containing 8 Bi atoms.
- ⁵P. M. deWolff, Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr. **30**, 777 (1974).
- ⁶V. Petricek, Y. Gao, P. Lee, and P. Coppens, Phys. Rev. B **42**, 387 (1990).
- ⁷A. F. Marshall, B. Oh, S. Spielman, M. Lee, C. B. Eom, R. W. Barton, R. H. Hammond, A. Kapitulnik, M. R. Beasley, and T. H. Geballe, Appl. Phys. Lett. **53**, 426 (1988).
- ⁸Y. Gao, P. Lee, P. Coppens, M. A. Subramania, and A. W. Sleight, Science **241**, 954 (1988).
- ⁹Y. Le Page, W. R. McKinnon, J.-M. Tarascon, and P. Barboux, Phys. Rev. B **40**, 6810 (1989).
- ¹⁰J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, Phys. Rev. B **37**, 9382 (1988).
- ¹¹M. D. Kirk, J. Nogami, A. A. Baski, D. B. Mitzi, A. Kapitulnik, T. H. Geballe, and C. F. Quate, Science **242**, 1673 (1988).
- ¹²J.-P. Locquet, J. Perret, J. Fompeyrine, E. Mächler, J. W. Seo, and G. Van Tendeloo, Nature (London) **394**, 453 (1998).
- ¹³G. G. N. Angilella, G. Balestrino, P. Cermelli, P. Podio-Guidugli, and A. A. Varlamov, Eur. Phys. J. B **26**, 67 (2002).
- ¹⁴X.-J. Chen, V. V. Struzhkin, R. J. Hemley, H. K. Mao, and C. Kendziora, Phys. Rev. B **70**, 214502 (2004).
- ¹⁵T. S. Nunner, B. M. Andersen, A. Melikyan, and P. J. Hirschfeld, Phys. Rev. Lett. **95**, 177003 (2005).
- ¹⁶A. A. Levin, Yu. I. Smolin, and Yu. F. Shepelev, J. Phys.: Condens. Matter **6**, 3539 (1994).
- ¹⁷X. B. Kan and S. C. Moss, Acta Crystallogr., Sect. B: Struct. Sci. **48**, 122 (1991).
- ¹⁸D. Grebille, H. Leligny, A. Ruyter, Ph. Labbé, and B. Raveau, Acta Crystallogr., Sect. B: Struct. Sci. **52**, 628 (1996).
- ¹⁹H. F. Fan, Microsc. Res. Tech. **46**, 104 (1999).
- ²⁰M. Izquierdo, S. Megtert, J. P. Albouy, J. Avila, M. A. Valbuena, G. Gu, J. S. Abell, G. Yang, M. C. Asensio, and R. Comes, Phys. Rev. B **74**, 054512 (2006).
- ²¹H. Eisaki, N. Kaneko, D. L. Feng, A. Damascelli, P. K. Mang, K. M. Shen, Z.-X. Shen, and M. Greven, Phys. Rev. B **69**, 064512 (2004).
- ²²L.-L. Wang, P. J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B **72**, 224516 (2005).
- ²³Y. He, T. S. Nunner, P. J. Hirschfeld, and H.-P. Cheng, Phys. Rev. Lett. **96**, 197002 (2006).
- ²⁴H. Lin, S. Sahrakorpi, R. S. Markiewicz, and A. Bansil, Phys. Rev. Lett. **96**, 097001 (2006).
- ²⁵J. A. Alldredge (private communication).