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## The next 25 years of surface physics

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### Abstract

The 20th International Seminar on Surface Physics commemorates the last quarter of a century in surface physics and serves as the commencement of the next millennium. This article attempts to identify the guiding directions for the next 25 years of surface physics relevant to the field of condensed matter physics. The message is that Surface Science and specifically surface physics must undergo a Cultural Revolution from a technique-driven to science-driven discipline. There are tremendously exciting opportunities for surface physics but to take advantage of them will require a change in our culture and most importantly in the education of the next generation of surface scientist. Some of the opportunities that exist in complex highly correlated systems in reduced dimensionality will be presented to illustrate the pivotal role that surface physicists can play in contemporary Condensed Matter Physics. © 2001 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

The objective of this paper is to attempt to identify the opportunities and challenges for the field of surface physics in the arena of modern condensed matter physics (CMP) as we enter the new millennium. Very exciting opportunities exist outside of the field of physics, in biology, chemistry, environmental sciences, etc. Even within the discipline of physics, there are exciting prospects that have little to do with CMP, such as biophysics, atomic and molecular physics, even astrophysics.

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The previous papers by Professors Naumovets and Davison has outlined the history of this Seminar Series on Surface Physics and presented their *outlook* for the future, which is aimed in most cases at more practical applications of surface science. Here, we address only one question about the future. How can a surface physicist be in the main stream of CMP, or why is not surface physics in the main stream of CMP?

To understand where we are going, we need to understand the history of surface science. The successes of the field have been documented in a special issue of Surface Science: The First Thirty Years [1], and Naumovets and Davison in the previous article have succinctly summarized the present environment. Surface physics has been very successful and it is now a mature field. But being a mature field is a disaster, since by definition the field is not at the frontier of physics. It means there is nothing exciting left to do. Mature means dying. Nuclear Physics is a mature field. A clear indicator of what is happening to surface physics is given by the sessions of the March American Physical Society meeting devoted to surfaces. In 1985, 14% of the sessions were devoted to surface physics, even in 1990 when high  $T_c$  was in full swing 15% of the sessions were on surfaces. But in the recent March meetings the percentage has fallen to  $\sim 4\%$ . The APS is considering revamping the sorting categories, eliminating most of the categories under surfaces and interfaces and placing them under the other major categories, i.e., surfaces of semiconductor sessions are organized in the semiconductor category. This is a not so subtle statement that surface physics, as a discipline, does not need to exist.

How can surface physics be a mature-dying field, when surfaces and interfaces are so important? In this age of Nanotechnology, where the promise is to shape the world atom by atom, leading to the next industrial revolution [2], surface physics should be at the very forefront. What is wrong? Is there anything wrong? These questions can be answered by rephrasing the questions. Will surfaces and interfaces be important in the Nanotechnology world? The answer is undoubtedly yes! Will our community participate in the great discoveries awaiting us in the next 25 years? The answer is not so clear. Maybe the kind of surface scientist that we have been training will not be engaged in the discovery of new emergent phenomena.

The problem that has arisen is related to our past culture. We have worked so hard to develop both experimental and theoretical techniques capable of probing surfaces that this has become an end in itself. We are a technique-driven discipline. It is acceptable to publish papers that report one more precise measurement. It is acceptable to publish a paper that reports an agreement between theory and experiment, without any attempt to explain what is going on. It is acceptable to do spectroscopy for spectroscopy. It is acceptable and encouraging to do surfaces for surfaces. A quotation from Phil Anderson's 1978 Nobel lecture challenges our culture.

Very often a simplified model throws more light on the real workings of nature than any number of ab initio calculations of individual situations, which, even where correct, often contain so much detail as to conceal rather than reveal reality. It can be a disadvantage rather than an advantage to be able to compute or measure too accurately, since often what

one measures or computes is irrelevant in terms of mechanism. After all, the perfect computation simply reproduces Nature, it does not explain her.

Understanding surfaces has been so hard that we have fallen into the trap of believing that the end is a better measurement or a better calculation. In this mode it really does not matter what you measure or what you calculate, so why not keep on doing the same thing. A good example is CO on Ni.

For the surface community to contribute in a significant way to CMP in the next 25 years we must change our culture. If we do not learn to evolve, then Surface Physics as a discipline will go the way of the dinosaurs and the APS surface sorting categories.

- We must move from a technique-driven discipline to a science-driven discipline.
- We must put a premium on understanding, not the act of measuring or calculating.
- We must stop studying surfaces for the sake of surface science, but ask about the impact on CMP. No more CO on Ni!
- We must move from the simple systems to complex systems.
- We must engage in contemporary CMP.

In Section 2, we will address some of the major themes in modern CMP, one being that synthesis of new complex materials is driving the science and technology. Therefore, we will introduce the concept of science-driven synthesis. In the past 25 years, it was fair to ask any and every new Ph.D., “What piece of equipment did you build”. Now we must ask “What new material did you synthesize or fabricate, and what new science did you learn?”

Our challenge to every reader is to write your own version of the next sections. Section 2 is about the contemporary focus of your field. What are the big questions that scientists are asking? and Section 3, how can surface scientists *engage* and have an impact?

## 2. Contemporary CMP: some philosophy!

Since the discovery of high-temperature superconductivity (HTS) less than 15 years ago, the materials community has learned to appreciate the beauty and importance of *complexity*. For example, the properties of HTS, ferromagnetism, ferroelectricity, colossal magnetoresistance (CMR) and good metallic electrical conductivity all can be obtained from just the  $ABO_3$  ‘perovskite’-structure compounds, which are themselves only a subset of the much larger family of complex metal oxides (CMOs). Such richness of properties within only a subset of materials is an example of a significant new theme in materials science: the *fundamental* importance of learning how to synthesize and manipulate increasingly *complex* materials, because of the startling properties and the new and unexpected insights that they reveal [3–10]. Coupled with this is a new recognition, *cross-cutting many disciplines*, that *complex systems constitute most of the tangible universe* [11]

and are the basis for future technology [2]. Consequently, the development of methods and models to *synthesize* and *simulate* complex systems is *extremely useful* to society.

It is now clear that discoveries of new phenomena result from exploring the *frontiers* of complexity in all its forms, and that the materials community must develop special tools to synthesize and to simulate complex systems in order to make rapid progress. Though there are many aspects of complexity, we have learned that one key characteristic is the possibility of *creating* spectacularly new phenomena simply by adding new components to a given material. This is illustrated by the discoveries of CMR and HTS. A second successful approach to create new phenomena is to artificially grow complex, multilayered structures out-of-equilibrium, in order to place dissimilar materials in close proximity, thereby producing unusual and potentially useful *couplings* of cooperative phenomena, for example, magnetic ordering and a structural transition, or magnetism and electrical conductivity or superconductivity. What we have learned from both approaches is that complex or composite systems do not behave simply as a linear combination of the properties of the parent materials. In a much earlier time, Sir Arthur Eddington aptly and eloquently described this situation in saying

We used to think if we knew one, we knew two, because one and one are two. We are finding that we must learn a great deal more about ‘and’.

But the most important thing we have learned is that complexity is a Fountain of Youth. Pushing the *frontiers* of chemically and structurally complex materials will always cause new phenomena to emerge. Consequently, the subjects of complexity and cooperative phenomena are *fundamental, long-term* interests of science and society. Some time ago Phil Anderson presciently observed that [12]

... at each new level of complexity, entirely new properties appear, and the understanding of these behaviors requires research which I think is as fundamental in its nature as any other.

A survey of recent Nobel Prizes clearly illustrates this point – two prizes associated with the quantum and fractional quantum hall effect in artificially constructed layered semiconducting materials; a prize for high  $T_c$  in complex transition-metal oxides; chemistry prizes for synthesis of  $C_{60}$  and conducting polymers.

The opportunity, for those who seize it (and the risk, for those who ignore it) is that *whoever controls complex materials controls science and technology*, i.e., progress is *materials-driven*. We are entering a “New World of Designer Materials,” designed for scientific and technological impact. As surface physicists, let us become *engaged!*

Intimately associated with the world of complex and artificially structured materials are two important concepts, reduced dimensionality and broken symmetry. Many of these materials are layered, highly correlated and inhomogeneous, leading to absolutely new physics. Birgeneau and Kastner in their editorial in the special issue of *Science*, devoted to Correlated Electron Systems wrote, “In the mid-1970s, many solid-state physicists, including ourselves, felt that our field was reaching maturity – our self-satisfaction was completely misplaced. A remarkable variety of

new materials have been discovered that cannot be understood at all with traditional ideas – highly correlated electron systems present us with profound new problems that almost certainly will represent deep and formidable challenges well into this new century”.

These contemporary CMP questions seemed to be designed for a surface physicist. We have the tools and the experience to make a real impact, if we *engage*. In the following, we try to illustrate ways to *engage*; first to take our surface systems and use them to illustrate the physics relevant to questions being asked by the CMP community, second to use our techniques, both experimental and theoretical, on new materials in the CMP community, and third to make new materials.

### 3. Surface physics and CMP

#### 3.1. A surface science system; defect-mediated phase transitions, from charge density waves to defect density waves

In this section, we draw from our experience to address the question of how to use our systems to impact the CMP community. The general subject addressed here is the role of defects in a 2D phase transition, a subject that has created a lot of speculation in the CMP community [13–17]. Mutka, in his article on the influence of defects and impurities on charge density waves (CDWs) comments [14]

Defects in CDW compounds are inevitable and their influence on the CDW phenomena is more a rule than an exception. The strong connection to defects influences the whole physics of CDWs with consequences that are manifest in a wide space and time scale from microscopic to macroscopic. This is the reason why microstructural characterization of the CDW is of primary importance...

He speculates on the proposition of metastable defect configurations, and to the concept of defect-density waves (DDW) [14]. Baldae has hypothesized that a modulation of the occupation probability of defects along the one-dimensional (1D) lattice occurs in potassium cyano-platinide (Krogmann salt) [15,16].

Before discussing the scanning tunneling microscope (STM) experiments on the dynamic role of defects in a CDW condensation it is appropriate to describe the surface system being studied and its history. Fig. 1 shows on the left the marble model for the  $1/3$  of a monolayer adsorbate (aqua colored) in a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure on top of the (1 1 1) face of Ge or Si. This is a commonly observed structure for adsorbates on these surfaces, but the adsorbates of interest here are other elements (Sn and Pb) in the IVa column of the periodic table, shown on the right of Fig. 1. This room temperature (RT) structure is referred to as the  $\alpha$ -phase, whose family of adsorbate-substrates has been studied by the surface community for  $\sim 20$  years [18], but it was not until 1996 that someone cooled the sample and discovered that there was a phase transition to a  $(3 \times 3)$  structure [19,20]. Carpinelli discovered that for both Sn or Pb on Ge(1 1 1) the low temperature phase was a

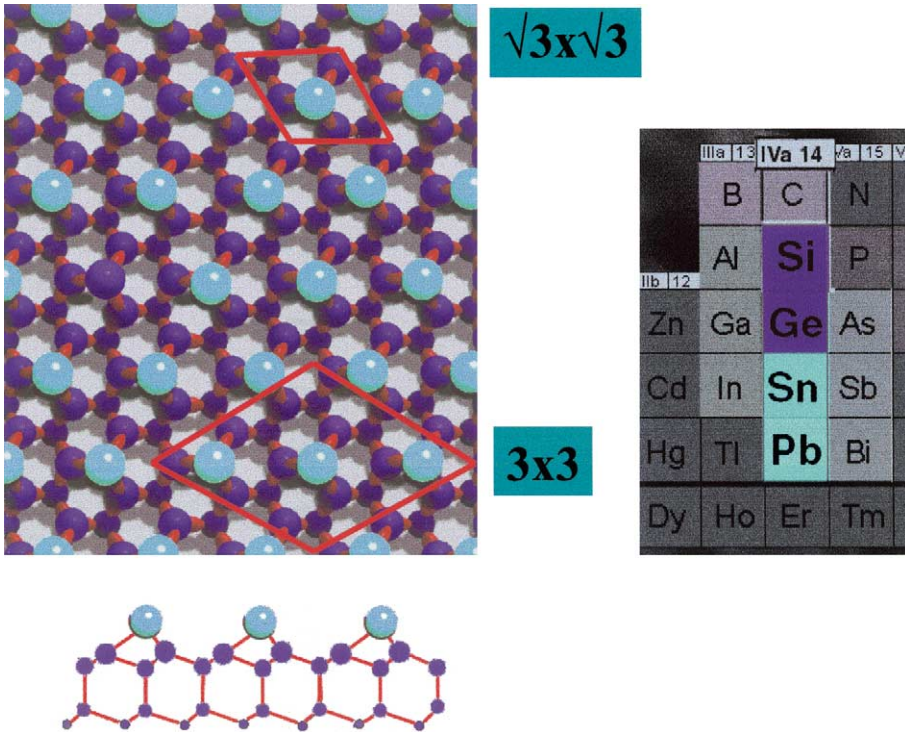
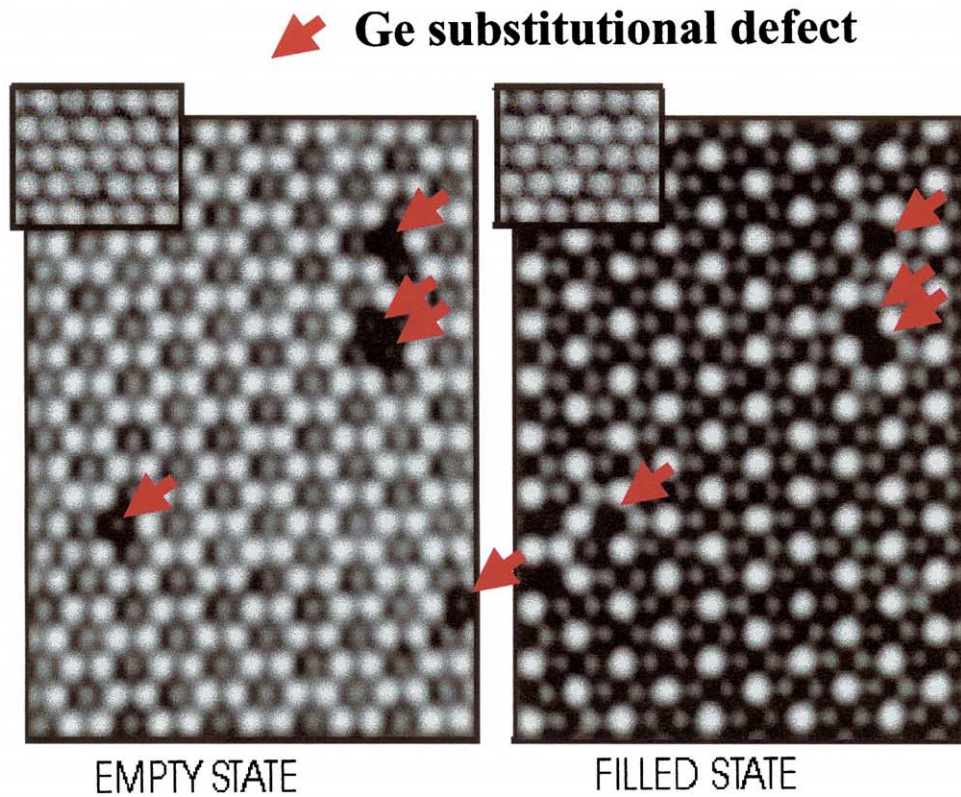


Fig. 1. Marble models for  $1/3$ -monolayer  $\alpha$ -phase of adsorbates (aqua) on (1 1 1) surface of Ge or Si. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  unit cell is shown at top and  $(3 \times 3)$  unit cell of CDW phase is shown at bottom. On right is a cut out of IVa column of periodic chart.

CDW [19,20]. On the left of Fig. 2 the STM images from Carpinelli are displayed. At RT (small insets) both the filled state and empty state images display the same structure consistent with the known structure of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase [21]. In contrast, the low temperature images with the  $3 \times 3$  symmetry are completely complementary, the definition of a CDW. The empty-state images display a honeycomb structure and the filled-state image a hexagonal one. In the new  $3 \times 3$  unit cell, two atoms are bright and one dark in the empty state image and vice versa for the filled state image. Two adsorbate atoms have a deficiency in charge and one an excess.

This discovery of a CDW transition has created a lot of activity in the surface community. The Sn or Pb on Ge(1 1 1) systems have been studied with STM, UPS, XPS, AREPS, HREELS, LEED, and XRD and over 10 first principles calculations have been published. Yet, all this work has had very little impact on the CMP community. Why? First, the CMP community believes that they have already seen this type of behavior in the metal chalcogenides [22], and second no new understanding of these CDW systems has come from experiments or calculations. It is cute, and the pictures made the cover of Nature, but that is all there is. This is surface



**Joe Carpinelli**

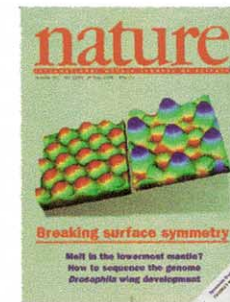


Fig. 2. Empty and filled state STM images of CDW transition observed by Carpinelli (pictured on the right) and published in Nature, for Sn and Pb  $\alpha$ -phase on Ge(111) [19,20]. Small insets are RT image and big panels display images at  $\sim 60$  K. Images at low temperature are complimentary.

science for surface science. It is a good example of what Anderson was talking about in his 1978 Nobel Lecture.

Melechko's realization that the defects were controlling and intimately involved in this CDW transition has attracted the attention of the CMP community, because now the surface scientist can address fundamental questions, at the atomic scale, associated with defect mediated 2D phase transitions [23–25]. The arrows in Fig. 2 point to the defects in the Sn/Ge film. The vast majority of the defects are Ge substitutional atoms in the Sn overlayer. About 10% of the defects are vacancies. Fig. 3 shows an expanded view of a single Ge substitutional defect on the left and a single vacancy on the right for the Sn/Ge system. The white lines on this figure show that, even at RT, the presence of a Ge defect wants to create a honeycomb structure and the vacancy a hexagonal distortion. Melechko observed that as he dropped the temperature the spatial extent of the damped CDW increased, growing until the damped CDW waves from different defects overlapped, giving very intricate interference patterns in the STM images [23,24]. The experimental observations lead to the construction of the following ansatz to fit the experimental images:

$$I(\vec{r}) = f_{\sqrt{3} \times \sqrt{3}}(\vec{r}) + \sum_n A_n e^{-\frac{|\vec{r}-\vec{r}_n|}{l(T)}} \sum_i^3 \cos(\vec{k}_i(\vec{r} - \vec{r}_n) + \phi_n). \quad (1)$$

The first term is the intensity in the RT  $\sqrt{3} \times \sqrt{3}$  filled-state image and the second term describes the damped CDW waves. The first sum is over the three  $\mathbf{k}$  vectors that describe the  $3 \times 3$  phase, and the second sum is over all defects  $n$ . The only parameters are the phase of the wave at the defect  $\phi_n$  and the decay length  $l(T)$ . The

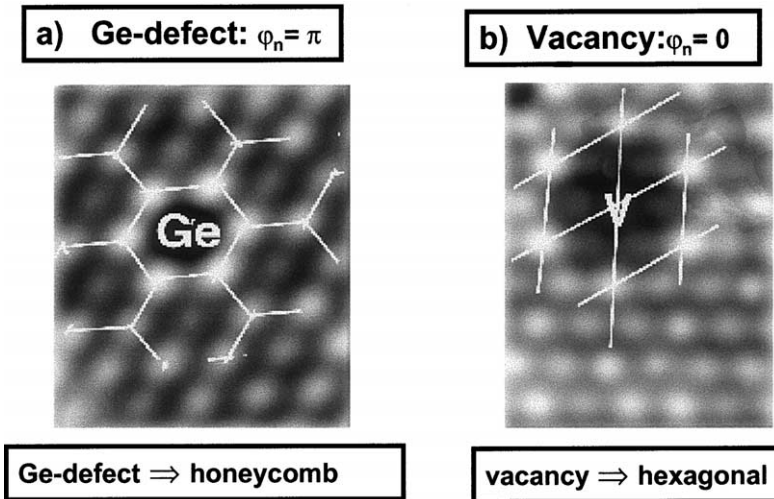


Fig. 3. STM images at RT of effect of single defect for  $\alpha$ -phase of Sn on Ge(1 1 1) [23,24]. (a) Ge substitutional defect and (b) a vacancy.



phase is determined by the nature of the defect and is shown in Fig. 3. A Ge substitutional atom does not want to be at a charge maximum, so the phase is  $\pi$ . Experience showed that all of the STM images could be uniquely fitted with a single parameter  $l(T)$ .

Fig. 4 displays the measured inverse decay length  $1/l(T)$  as a function of temperature for Sn/Ge(1 1 1) [24]. The two STM images on the right show a simulation (top) and an actual filled-state image at the bottom ( $T = 165$  K). The best fit for  $l$  is 24 Å, which reproduces the details of the experimental image.  $l(T)$  diverges at  $T_1 \sim 70$  K indicating that a single defect would induce a phase transition at this temperature. That a real phase transition occurs is indicated by the image at the lower left taken at 55 K. Images at this low temperature show CDW domains and very sharp domain walls, neither of which can be simulated by (1). There are two potential problems with this interpretation. First, a single Ge substitutional defect would generate a honeycomb filled-state image, as seen in Fig. 3 and expressed by (1). The low temperature filled-state images have a hexagonal array of bright atoms. The second problem is associated with the defect density. At a 4–5% defect density, there is an average spacing  $l_{av}$ , shown by the dashed horizontal line in Fig. 4. When  $l(T) \sim l_{av}$ , the defects begin to feel each other. Remember that each defect is propagating a damped CDW and Ge substitutional defects do not like being at a charge maximum. All of these complications indicate that the defects play a dynamic role in the CDW condensation.

The speculation that the defects are dynamic participants in the CDW condensation has been proven using the variable temperature STM. The  $(3 \times 3)$  unit cell in Fig. 1 shows that there are three Sn atoms in each cell. If we arbitrarily color the three blue, red and yellow, as in the bottom left of Fig. 5, it is clear that each defines a different  $3 \times 3$  lattice shown at the top of Fig. 5. The consequence of this is that there can be three different CDW domains depending upon where you start constructing your lattice. The hexagonal array of bright (negatively charged) atoms in the filled-state image of the CDW phase (see Fig. 2) indicates that in each domain all the atoms on a given lattice will be bright, while the atoms on the other two lattices will be dark. For illustration, let us assume we have a CDW with the negatively charged atoms on the red lattice. All Sn atoms on the red lattice are negatively charged and all Sn atoms on the blue or yellow lattices are positively charged. Now consider a random distribution of Ge substitutional defects in this “red” CDW domain. 1/3 of these defects would find themselves on the red lattice where they do not want to be, because of the excess charge. There is an electrostatic force pushing the defects off of the red lattice. Do they move? The STM image on the right of Fig. 5 shows that they do move. The “B” domain in this figure is CDW on the red lattice and when you count the number of defects on each lattice you find 16 on yellow, 18 on blue and only 4 on the red lattice. At RT, such a count would have showed a random distribution on all three lattices.

Melechko and Braun performed a careful statistical counting of the defects to prove that the defects moved. A sampling grid ( $80 \text{ \AA} \times 80 \text{ \AA}$ ) slightly smaller than the average CDW domain size ( $100 \text{ \AA} \times 100 \text{ \AA}$ ) was used to quantify the defect alignment on a large number of STM images at RT [23,24]. If all of the defects were on two of

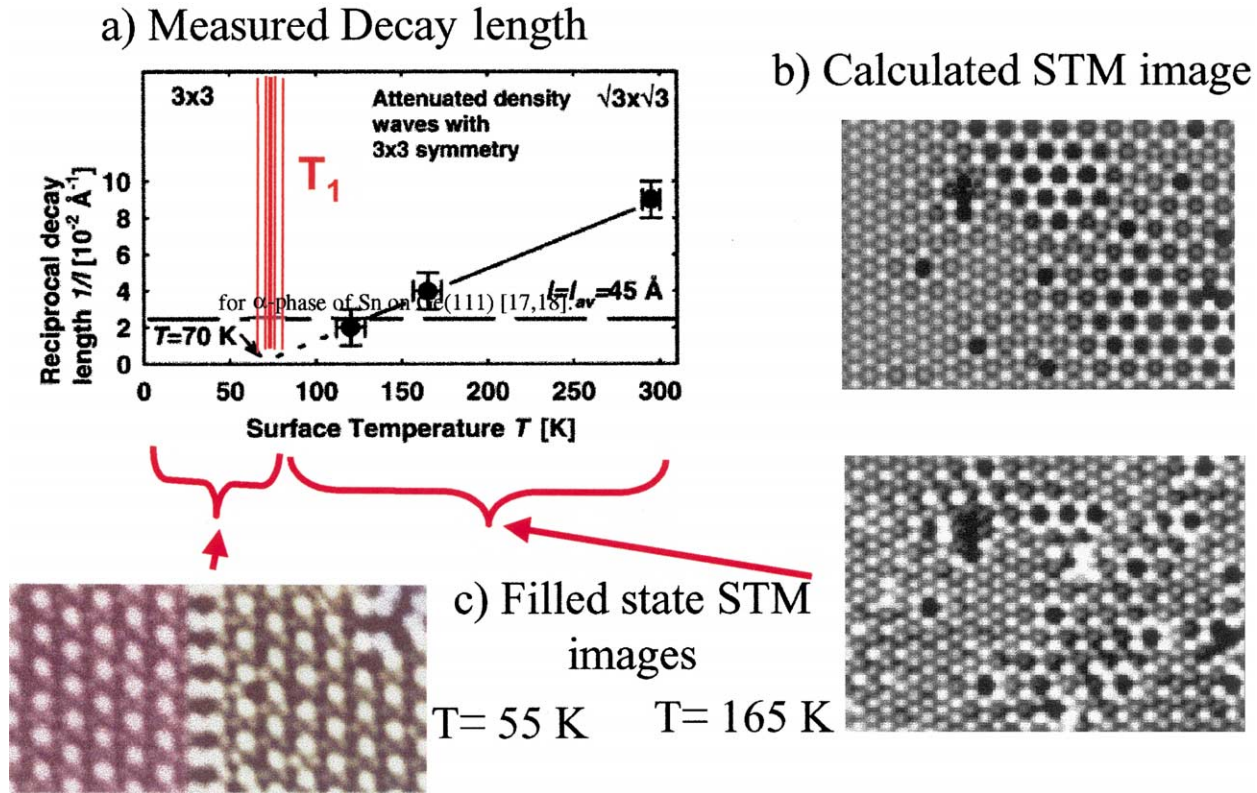
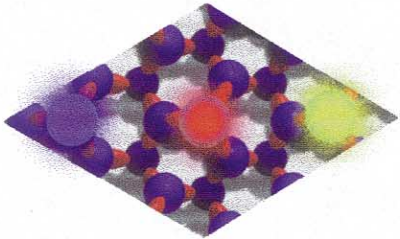
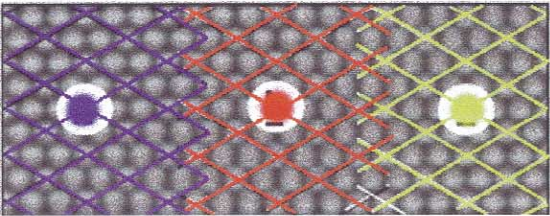


Fig. 4. (a) Measured decay length  $k(T)$  of damped CDW emanating from defects in  $\alpha$ -phase of Sn on Ge(111) [24]. STM images on right show simulated (b) and real image (c) at  $T = 165 \text{ K}$  for  $l = 24 \text{ \AA}$ . Image at bottom left shows CDW domain walls at  $T = 55 \text{ K}$ .

**b) STM image of CDW domains**

**a) Model of 3-sublattices**



**T = 50 K**      ● = 16, ● = 4, ● = 18

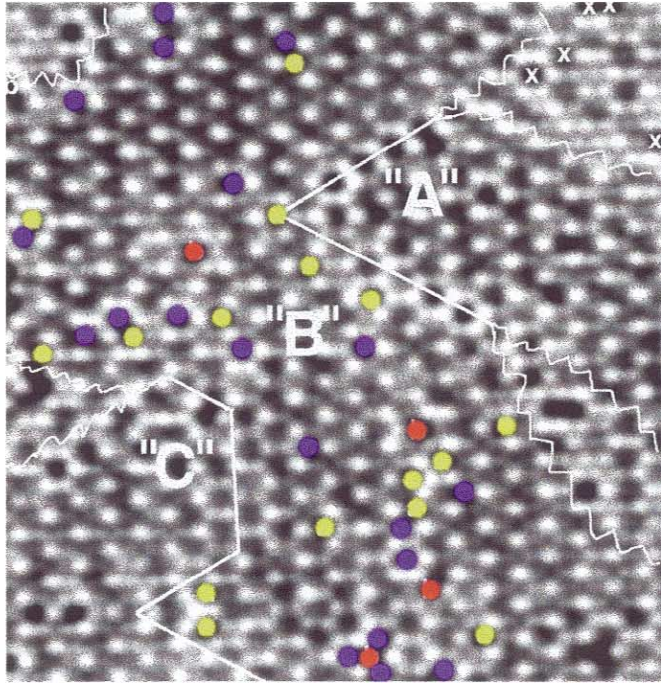


Fig. 5. Observation of defect alignment within individual CDW domains (b). (a) is a representation of three lattices available for formation of a CDW domain. On bottom right is a model of unit cell for (3 × 3) structure [24].

the three lattices, the probability  $P_C$  was defined to be 1, and if they were equally distributed on three lattices, then  $P_C = 0$ . The right panel of Fig. 6 shows the measurements. For this domain and sampling grid size, simulations showed that a value of 0.5 indicated perfect alignment in each domain. Therefore, the data show that below a temperature  $T_2 \sim 120$  K the defects move to align themselves within each CDW domain. The nature of the phase transition will depend upon the defect density.

The defect–defect interaction can be modeled with a simple electrostatic interaction created by the damped CDW waves, which grow with decreasing temperature. Fig. 7 displays a simple Monte Carlo simulation using an adjustable activation barrier for Ge–Sn place exchange. As the temperature decreases, there is a slight increase in  $P_C$ , but at 100 K (determined by the activation barrier) there is a sudden alignment of the defects, i.e., no defects on the red lattice [26].

Surely, everyone would expect that Sn and Pb would behave the same on Si and on Ge since they are isoelectronic and form the same  $(\sqrt{3} \times \sqrt{3})R30^\circ \alpha$ -phase at RT. But they do not [27–29]! For the Sn/Si system, the STM reveals a new periodicity at low temperature not seen in electron diffraction, i.e., an electronic transition [29]. The defects, primarily Si substitutional atoms, are aligned commensurate with the 1D electronic wave, which appears to be incommensurate with the substrate. There is no sign of the CDW  $(3 \times 3)$  phase transition seen for Sn/Ge or Pb/Ge. Fig. 8(a) displays an empty-state image of the  $\alpha$ -phase of Sn on Si(1 1 1) at 60 K. Every other horizontal row of atoms appears bright, indicating a new structure which, at first glance, would be a  $2\sqrt{3} \times \sqrt{3}$  reconstruction. But the Fourier transform (FT) in Fig. 8(b) shows that the long-range order is incommensurate and 1D. The six outside

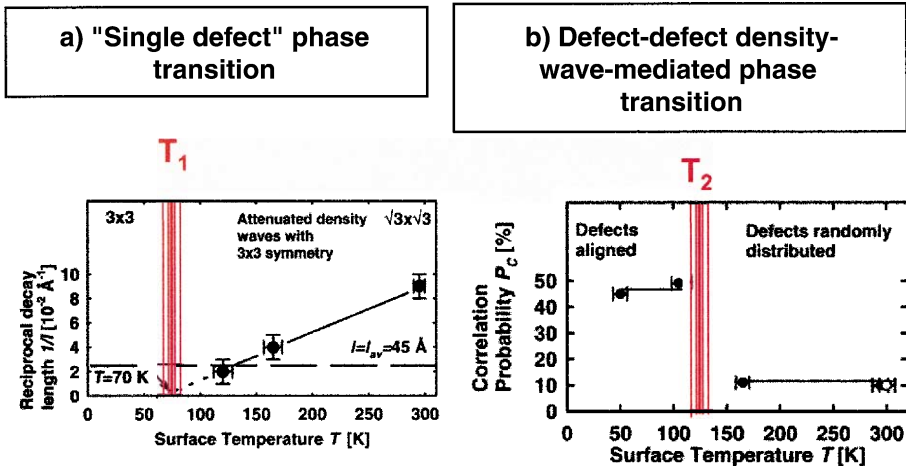


Fig. 6. (b) Temperature dependence of measured defect–defect correlation probability  $P_C$  on right showing an alignment at  $T_2 \sim 120$  K. This is compared to inverse decay length  $l(T)$  (a) already shown in Fig. 5. The transition temperature  $T_2$  will be a function of defect density.



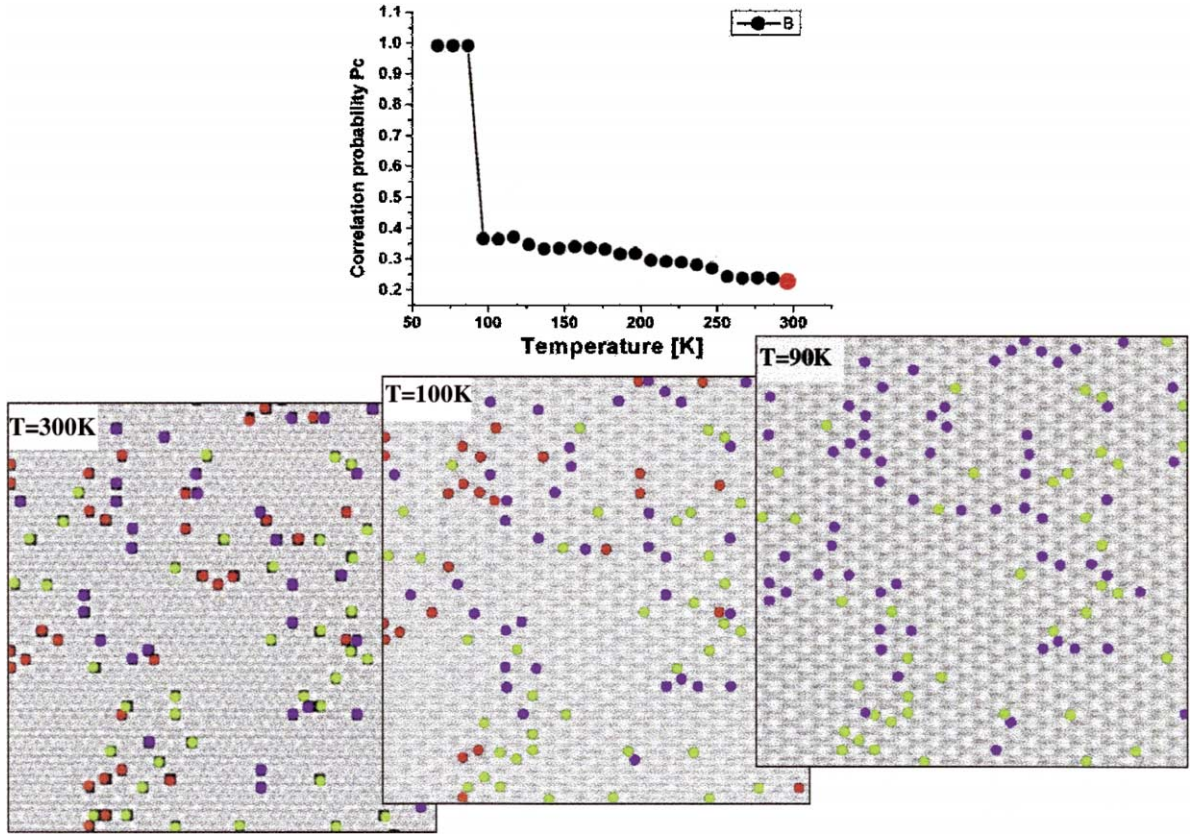


Fig. 7. Simulation of defect–defect interaction as function of temperature. At 300 K there are an equal number of defects on three different lattices (red, blue and yellow) indicated in the left panel. At 90 K they have totally aligned on blue and yellow lattices.

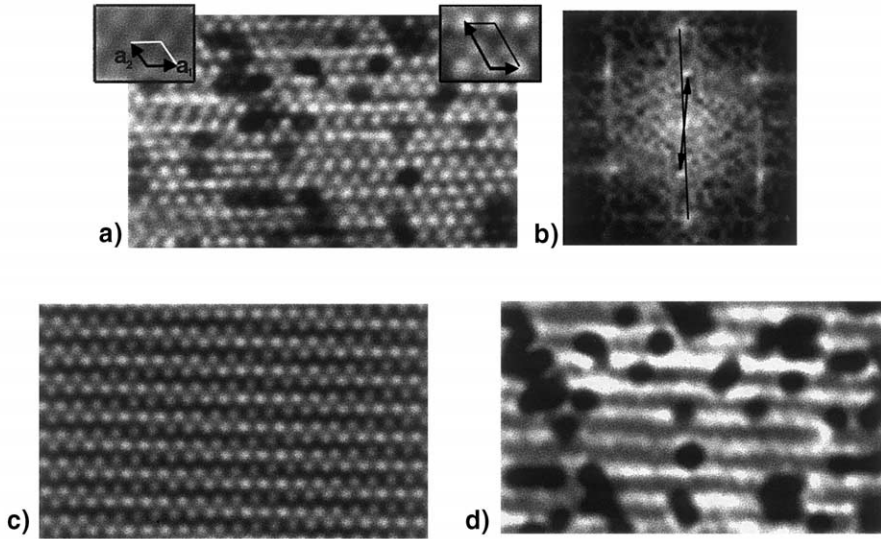


Fig. 8. (a) Empty state STM images of  $\alpha$ -phase of Sn on Si(111). (b) FT of image in (a). (c) STM image constructed from diffraction spots in FT in (b). (d) STM image created by back FT of FT in (b) without  $\sqrt{3} \times \sqrt{3}$  diffraction spots [29].

spots are from the  $\sqrt{3} \times \sqrt{3}$  structure and there is a new “spot” marked by the arrows. This spot is not where a  $2\sqrt{3}$  spot should be, but rotated  $7\text{--}8^\circ$  from the vertical. Most important is the observation that there is no new LEED pattern at low temperatures. You are seeing a pure electronic reconstruction with no accompanying lattice distortion.

It is quite easy to isolate the different phenomena in this image by filtering the FT and then back FT to reproduce a real-space image. Fig. 8(c) is constructed by using only the spots in FT of Fig. 8(b), i.e., the  $\sqrt{3}$  spots and the incommensurate new spot. This real-space image has no defects and clearly shows the 1D electronic distortion on the  $RT$   $\sqrt{3} \times \sqrt{3}$  phase. In Fig. 8(d) we have removed the  $\sqrt{3} \times \sqrt{3}$  lattice by removing the diffraction spots in the FT of Fig. 8(b) and then back transforming. Now we can see the 1D wave, but it is also obvious that the defects have aligned themselves commensurate with this one-dimension incommensurate electronic wave.  $\sim 75\%$  of the defects are in the dark regions of the electronic wave. This is the first direct observation of a DDW [29].

Together, the thin-film systems presented here serve as a magnificent arena for the study of the dynamics of defects in a two-dimensional (2D) phase transition. But this type of behavior is not restricted to the systems shown in Fig. 1. If you scan the literature, you can find many tempting STM figures. For example, a little filtering of the  $RT$  image of hydrogen terminated SiC(0001) indicates the presence of waves [30]. Will there be a transition as the temperature is lowered? The images of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface show beautiful domain walls like we have reported for the CDW structure of Sn on Ge(111) [31].

### 3.2. Ferromagnetism at surface of *p*-wave superconductor $\text{Sr}_2\text{RuO}_4$

In this section, we illustrate the impact that can be achieved by using the arsenal of experimental and theoretical surface tools to study complex systems currently of interest to the CMP community. It is our contention (the reader can be the judge) that we have proven Phil Anderson wrong. You can do very sophisticated measurements and first principles calculations to learn new physics, if you treat them as tools and keep focused on the physics. This example concerns the observation of a surface reconstruction at the surface of the unconventional superconductor  $\text{Sr}_2\text{RuO}_4$  [32], driven by surface stress and aided by a soft bulk soft phonon. Theory confirms the origin of the reconstruction and predicts that the surface ground state is ferromagnetic (FM), i.e., a ferromagnetic surface on a superconductor [33].

The strong mutual coupling between charge and spin of the electrons and the lattice degrees of freedom in transition-metal oxides (TMOs) results in effects such as charge-, orbital-, and spin-ordering; colossal magnetoresistance; and unconventional superconductivity [5–10,34]. Fig. 9 shows schematically this close coupling in these highly correlated systems. For example, the application of a magnetic field (magnetism) drives a metal-to-insulator transition (electronic structure) and, in many cases, a lattice distortion [34]. Conceptually, creating a surface by cleaving a single crystal is a controlled way to disturb the coupled system by breaking the symmetry without changing the stoichiometry. This unique environment at the surface could produce new phenomena, while providing a fresh approach to the study of the spin-charge-lattice coupling in these complex materials. Here we show, using the unconventional superconductor  $\text{Sr}_2\text{RuO}_4$ , that all of these expectations can be realized. Even for this layered material, where the bonding between layers is weak and the electrons are strongly localized to the layers, the surface has a surprising new phase, which clearly elucidates the close coupling in the bulk between lattice distortions and

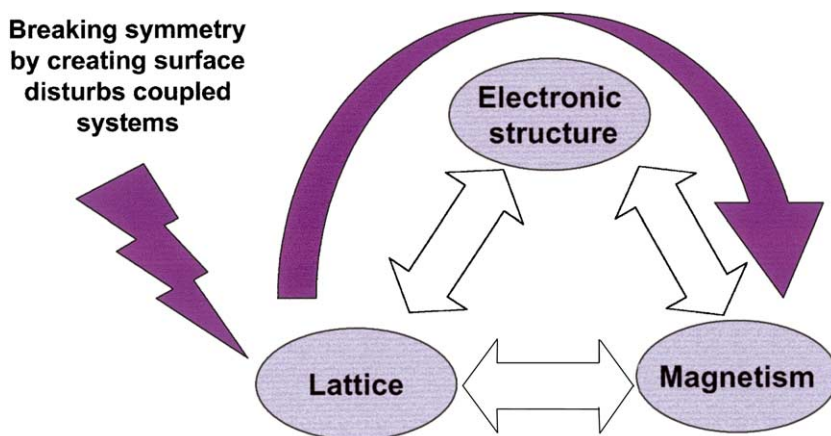


Fig. 9. Schematic illustration of close coupling between spin-charge-lattice degrees of freedom in TMOs. Breaking symmetry by creating surface can be used to modify and probe this close coupling.

magnetism. Furthermore, the influence of surfaces and interfaces on thin-film properties is of technological interest for the design of TMO devices [35].

In Section 1 we briefly mentioned the perovskite compounds, and that they were a member of a broader class of materials called the Ruddlesden–Popper (RP) series (see Fig. 10), with the general formula  $(R_{1-x}A_x)_{n+1}M_nO_{3n+1}$ . In these compounds,  $R$  is usually a trivalent rare-earth,  $A$  is a divalent alkaline-earth, and  $M$  is a transition-metal ion. The structure of the RP phases is made up of  $n$  consecutive perovskite layers ( $AMO_3$ ) alternating with rock salt layers, so that their formula can be represented by  $(AO)(AMO_3)_n$ , where  $n$  represents the number of connected layers of vertex sharing  $MO_6$  octahedra.  $n = 1$  is a 2D layered material with only one layer of octahedra.  $n = 2$  has two connected layers of octahedra. As  $n$  increases, the materials become more 3D in character and the electronic band width increases. The properties of these materials are controlled by tuning the band filling by adjusting the relative concentration of divalent ( $A$ ) and trivalent ( $R$ ) atoms. In most of the interesting cases, the transition metal can have multiple valency, leading to charge, spin and orbital ordering [8,34]. Here we will discuss the  $n = 1$  member of this series, known as 214 materials, because they are layered and cleave easily. In the last section, measurement on the  $n = \infty$  systems have been made using thin-films grown via laser molecular beam epitaxy [36].

$Sr_2RuO_4$ , the only known layered perovskite without copper that exhibits superconductivity, has attracted much attention, because it shows spin-triplet pairing with a p-wave order parameter [37]. The bulk has a non-distorted tetragonal  $K_2NiF_4$  structure with a nonmagnetic ground state. However, this ground state is close to structural and magnetic instabilities, characterizing a common feature in this class of

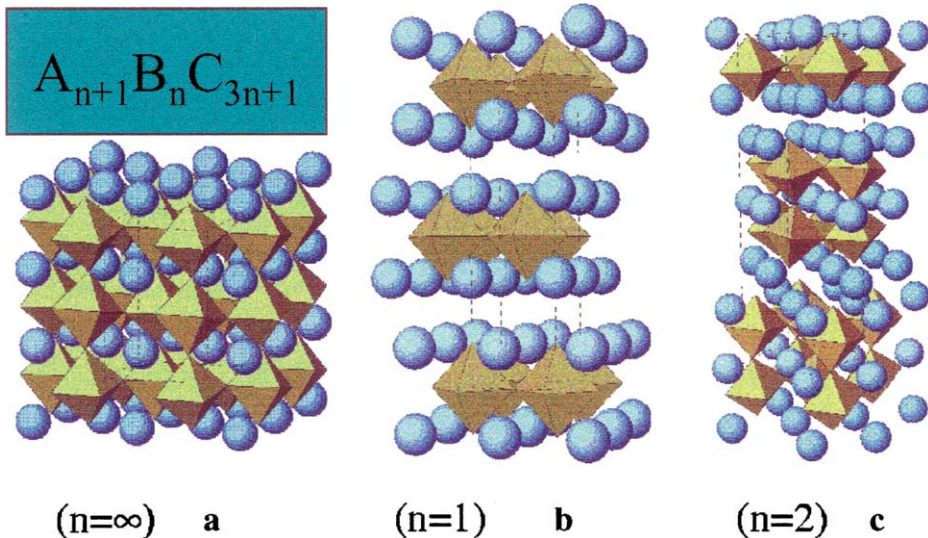
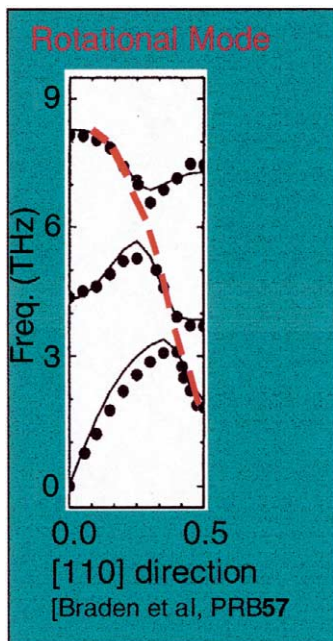
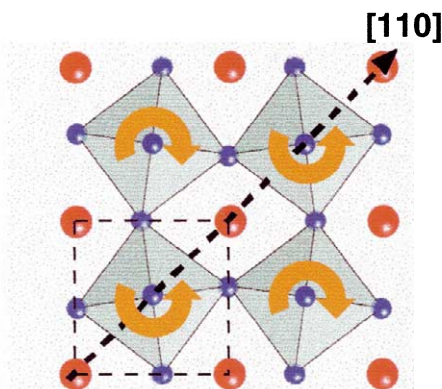


Fig. 10. Three members of RP series  $n = 1, n = 2$ , and  $n = \infty$ . Aqua colored balls are di or trivalent atoms, where transition metal–oxygen octahedra are shown in light green.



## a) Bulk phonon mode

b) RuO<sub>6</sub> octahedron rotation at zone boundary

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Fig. 11. Diagram showing soft-bulk phonon mode [38] (a) and the zone boundary rotation of octahedron (b).

materials that the energy difference between different structural/magnetic phases is very small. Inelastic neutron scattering experiments show that the phonon mode corresponding to the in-plane octahedron rotation with  $\Sigma_3$  symmetry exhibits a significant drop in energy near the zone boundary (see Fig. 11) [38]. The existence of spin fluctuations has been documented by nuclear magnetic resonance experiments. This is important, because theory suggests that the spin-triplet pairing for the unconventional superconductivity in Sr<sub>2</sub>RuO<sub>4</sub> is mediated by exchange of FM spin fluctuations [39].

Fig. 12 shows a large-scale STM image of a surface cleaved inside the vacuum system and transferred to the STM stage. It shows very large flat terraces with an extension up to 10  $\mu\text{m}$ . All step heights are integral multiples of half the unit cell (6.4  $\text{\AA}$ ) shown on the left. Both LEED  $I$ - $V$  measurements and calculations prove that the surface is the SrO plane, as expected. High resolution STM images and LEED diffraction show that the surface is not bulk truncated but reconstructed into a  $(\sqrt{2} \times \sqrt{2})R45^\circ$  structure, as can be seen in the STM image and LEED pattern displayed in Fig. 13. There are missing fractional-order spots in the LEED pattern indicating the presence of glide planes and a  $p4gm$  plane group symmetry. Given the restrictions of  $p4gm$  symmetry, and the fact that there is a soft-bulk zone boundary

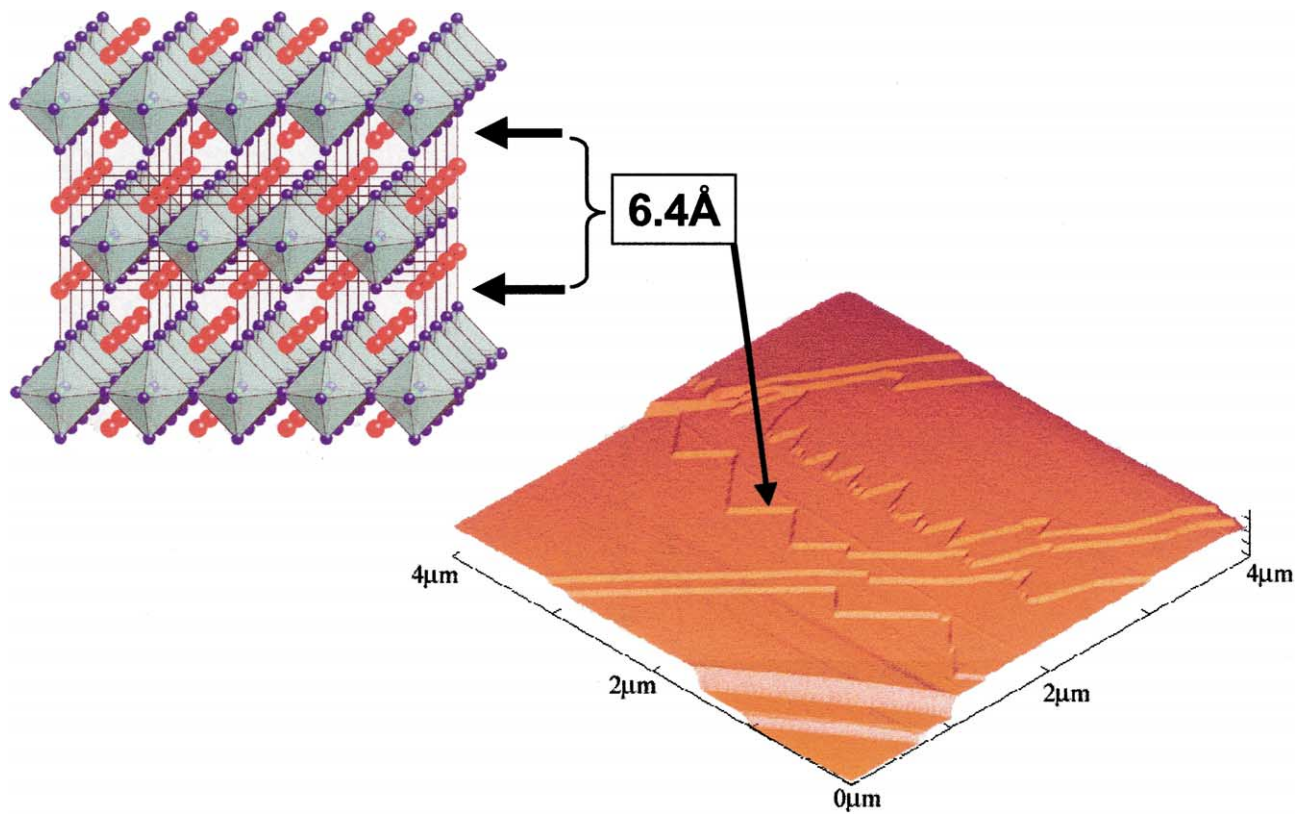


Fig. 12. Large-scale STM image of  $\text{Sr}_2\text{RuO}_4$  cleaved in vacuum on the right. The figure on the left shows cleavage planes and step height. The crystal cleaves without breaking the  $\text{RuO}_6$  Octahedra.

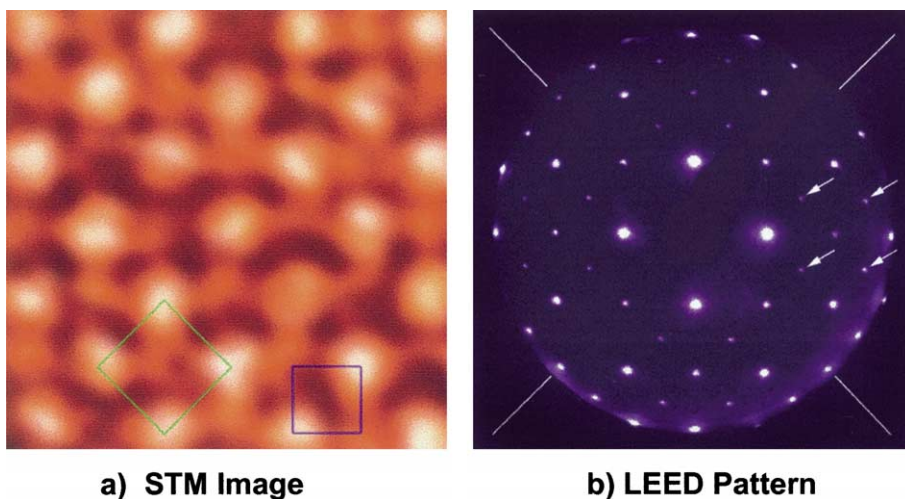


Fig. 13. High resolution STM image (a) and LEED pattern (b) of freshly cleaved surface. Surface reconstructs to  $(2 \times 2)$  configuration with new unit cell shown by green box on left. The STM image is taken at room temperature with sample bias voltage +0.5V.

phonon corresponding to rotation of the octahedron (Fig. 11(b)), the surface structure could have been deduced. This approach would have been Anderson's way, but we are surface physicists (and not nearly as smart), so we did it the hard way.

Fig. 11 displayed on the left the bulk phonon modes with the mode of interest highlighted in red [38]. On the right is the zone boundary rotation pattern of this bulk phonon in the plane of the surface. Our results show that at the surface this dynamic bulk mode freezes into a static lattice distortion. The structure was determined using LEED  $I-V$  analysis. The intensity vs. energy of five nonequivalent integer beams and three nonequivalent fractional beams has been measured and compared with calculated intensities for surface model structures compatible with the  $p4gm$  symmetry. The best fit to experimental spectra was obtained for a surface structure with the octahedra rotated by  $9 \pm 3^\circ$ . First-principles calculations of the ground-state surface structure have been conducted within the generalized gradient approximation (GGA). Our calculations confirm that octahedra rotation indeed happens on the surface but not in the bulk (Fig. 14). The optimized structure for a nonmagnetic surface is a surface layer with octahedra rotated by  $6.5^\circ$  (Fig. 14). This reconstruction, driven by compressive strain in the  $\text{RuO}_2$  layers, lowers the energy by 14 meV per formula unit (f.u.). The calculation of the surface structure for FM ordering in the surface illustrates what is so unique about these materials. The FM ordering stabilizes the distortion further and increases the rotation angle to  $9^\circ$  (Fig. 14) to gain additional energy of 51 meV/f.u.

We have been able to analyze the different d-orbital character of each band at the Fermi surface and address the coupling of these states to phonons and spin fluctu-

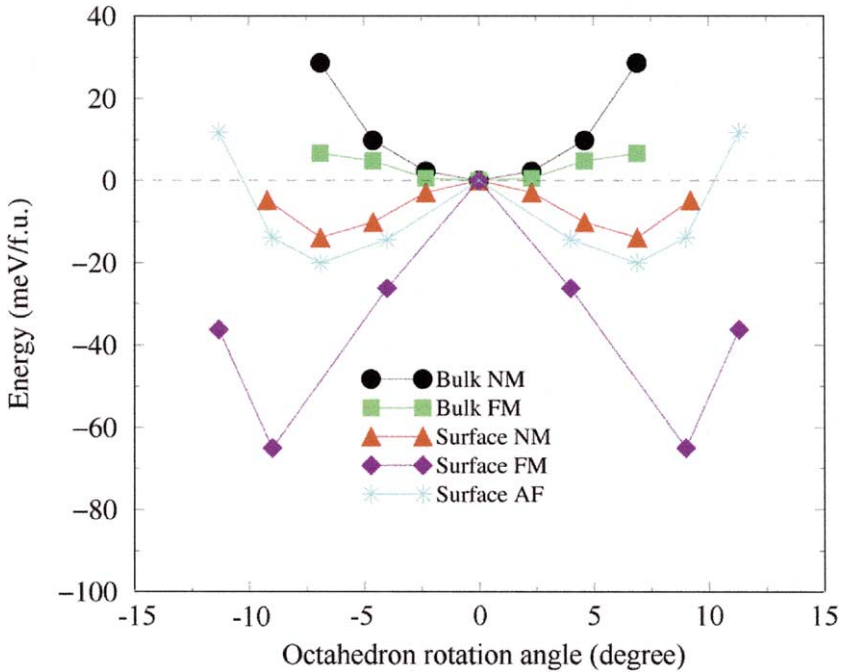


Fig. 14. First principles (GGA) calculation of total energy per f.u. versus octahedron rotations angle. Both FM and NM cases are displayed for bulk and surface. FM ordered state is commensurate with lattice, while AF state is calculated with planar  $\mathbf{Q} = (\pi/a, \pi/a)$ .

ations giving a clear picture of what occurs at the surface [33]. The key orbital is the  $d_{xy}$ , since the  $\Sigma_3$  bulk phonon mode couples strongly with this orbital which is primarily responsible for the van Hove singularity (VHS) slightly above  $E_F$  at the Brillouin zone boundary. Most importantly it is the  $d_{xy}$  orbital that is primarily responsible to FM spin-fluctuation. This observation at the surface of  $\text{Sr}_2\text{RuO}_4$  opens up many exciting prospects, relevant to the bulk and surface properties of these layered TMOs. One exciting and relevant example is the coexistence of FM order and superconductivity [40,41].

*What is wrong?* Not a single sample was synthesized by a surface physicists. We just characterized and calculated. *Who ever controls the materials controls the science and technology!*

Before leaving this subject, let us return to the question of the role of defects. Fig. 13 shows on the left a different region of the surface than displayed in Fig. 13, where the defect density is much higher. The defects, presumably vacancies, forming quasi-ordered rows, and stabilizing the bulk  $1 \times 1$  structure that can be seen in the STM image (top right). The STM image clearly shows that one out of the two atoms in each unit cell is being imaged, either Sr or O. A simple argument, based on the expected density of states near the Fermi energy, would conclude that the O atoms are being imaged. In fact, theoretical calculations of the surface local density of



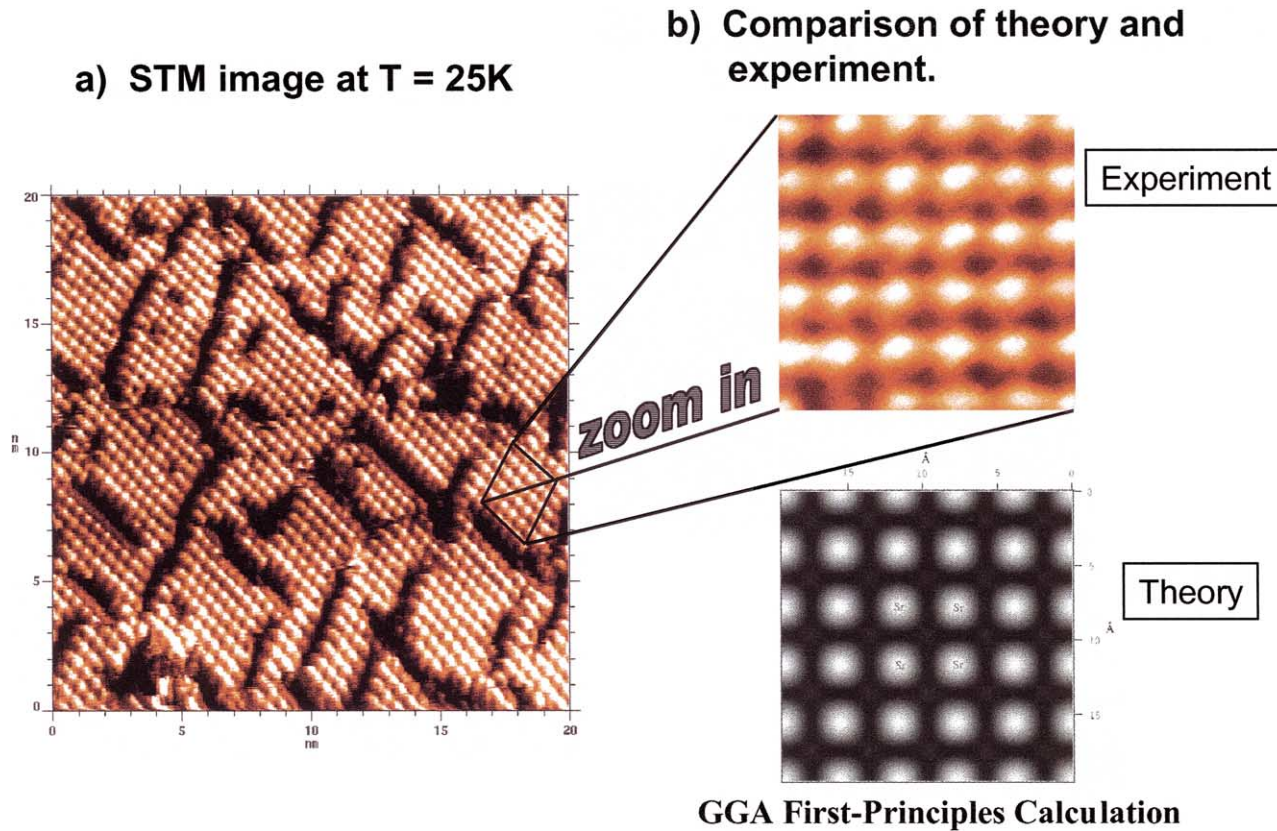


Fig. 15. (a) High resolution STM image of  $\text{Sr}_2\text{RuO}_4$  at 25K showing region of sample with high defect density. (b) Comparison of experimental imaged and theoretical calculation of image by Fang and Terakura. In (a) the sample bias voltage was +0.5 V.

states, shown at the bottom right of Fig. 15 prove that the STM image, “sees” the Sr atoms. The apparent contradiction is easily reconciled, when the orbital character of the wave functions being imaged is analyzed. What the STM is seeing are the in-plane O p-orbitals, all pointing in the direction of the Sr atoms. Preliminary observations indicate that this low temperature quasi-ordered array of defects (DDW) melts at elevated temperatures.

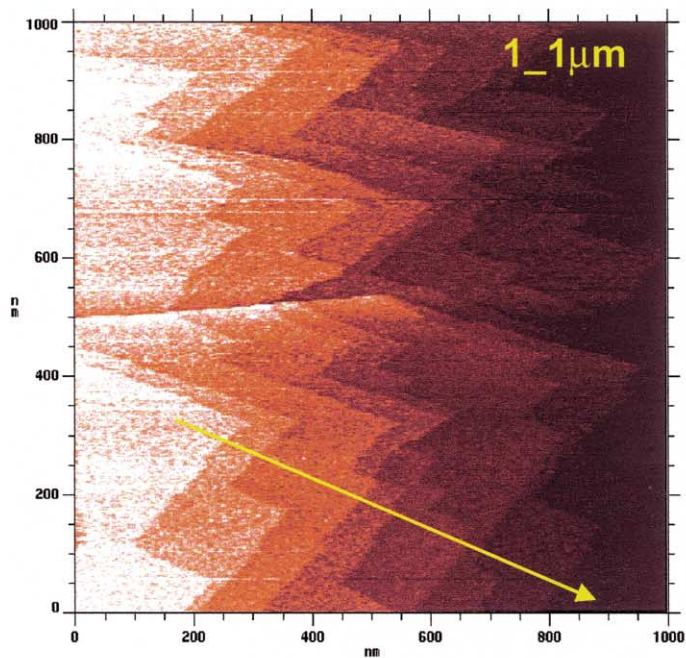
### 3.3. Electronic inhomogeneities in transition metal oxides

Electronic phase separation in highly correlated systems is one of the currently *hot* subjects in CMP [8,42–47]. Undoubtedly, the best known representative of this phenomena is “stripes” in the high temperature superconductors [8,44]. In this case, neutron scattering revealed the existence of correlated strips of spin and holes in the copper oxide superconductors [44]. This has led to what is referred to as “stripology”, generating exciting speculation about the nature of these spin and electron inhomogeneous phases in highly correlated systems [42,43]. Recent electron microscopy and STM studies of the CMR perovskites show electronic phase separation on the  $\sim \mu\text{m}$  scale. The temperature and magnetic field dependence of the phases indicates that conductivity in these materials is a percolation process [45,46]. The excitement here is that there is electronic phase separation without either a structural change or component phase separation.

Surface experiments using STM for topography and scanning tunneling spectroscopy (STS) for the electronic density of states promise to have a profound impact on this subject. Here is an area where surface physicists, with their knowledge of preparation and care of surfaces and of various spectroscopies, can impact CMP.

Let us begin by describing our experiments on another  $n = 1$  member of the RP series (Fig. 10),  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  [47,48]. The average manganese valence is  $\text{Mn}^{3.5+}$ , however, below  $T_c \sim 217$  K, the system forms an alternative  $\text{Mn}^{3+}/\text{Mn}^{4+}$  charge-ordered state [47,48] and  $e_g$ -electron orbital ordering on  $\text{Mn}^{3+}$  site [49]. Below  $T_N \sim 110$  K, this paramagnetic system becomes antiferromagnetically ordered [50]. The system becomes insulating in both the charge- and orbital-ordered phases from semiconducting at RT [50]. Fig. 16 shows a large-scale STM image after cleaving this material at RT in a vacuum. The surfaces are very flat with large terraces just like was observed for Sr ruthenate (Fig. 12). LEED patterns show only a  $1 \times 1$  structure and preliminary LEED I–V analysis indicates a bulk-like termination with the surface plane being the (La,Sr)O layer. This is not what should have been seen, since the charge-ordered state should have produced 1/2-ordered spots and the orbital-ordered state should have had 1/4-order spots. What is surprising is the electronic roughness of the surface. A line scan across the steps (yellow line) is shown in the upper right. The electronic roughness is almost as large as the step height. Fig. 17 shows a higher resolution STM image of one of the flat terraces. The size of the different domains is  $\sim 10$  nm and the corrugation with a one volt bias is  $\sim 6$  Å. The origin of the roughness is primarily electronic, because STS measurement show that the band gap is spatially varying, as shown for two positions in the bottom right panel of Fig. 17.

a) STM image of cleaved  
 $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$



Room temperature

b) Line scans for  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$   
and  $\text{Sr}_2\text{RuO}_4$

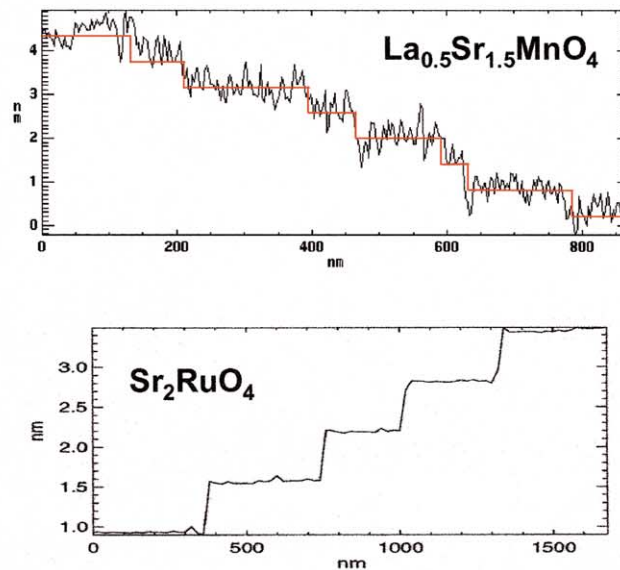


Fig. 16. (a) Large-scale STM image of freshly vacuum cleaved  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ . The yellow arrow show the position of the line scan shown in (b). (b) A comparison of the line scan across the steps for  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  and  $\text{Sr}_2\text{RuO}_4$ .

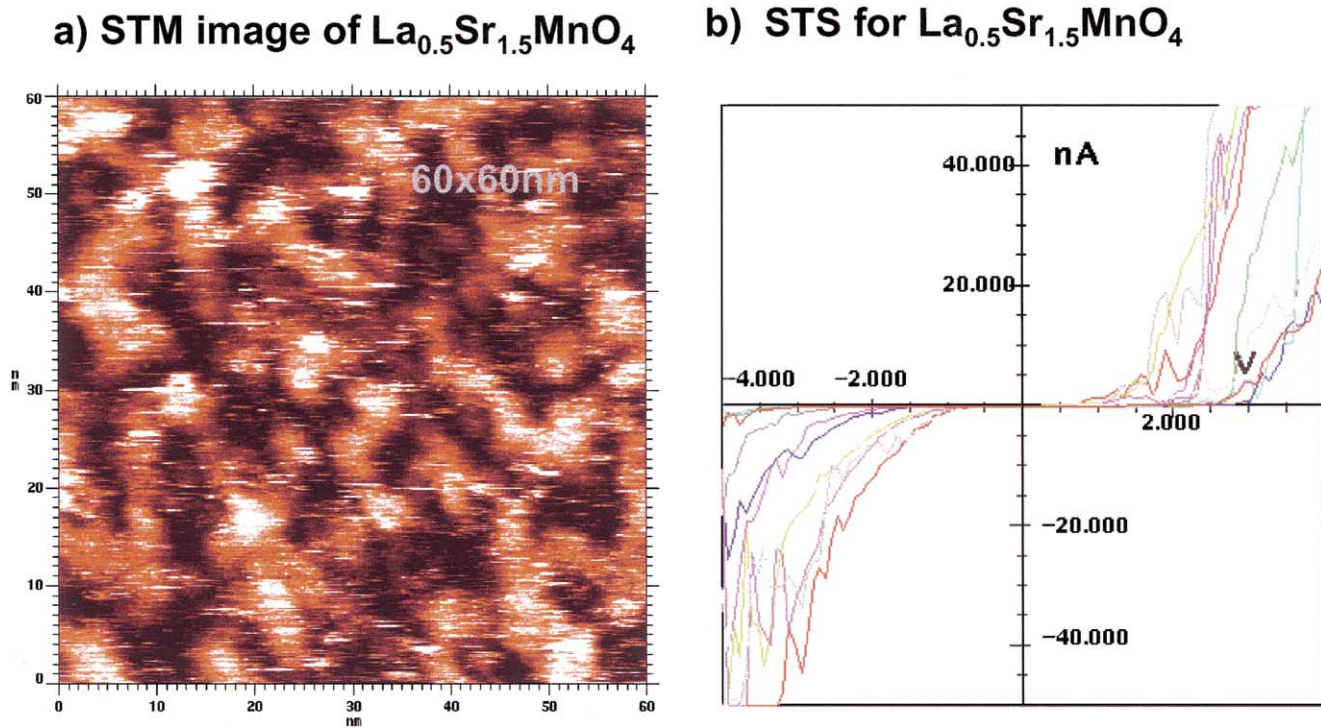
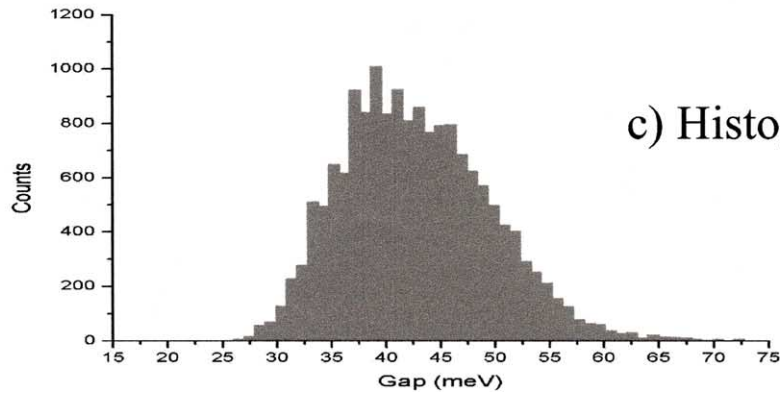
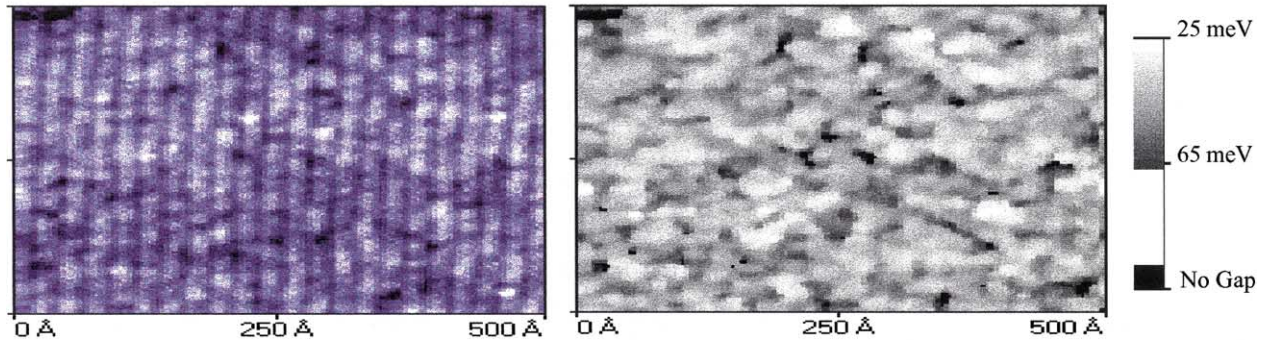


Fig. 17. Expanded image of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  taken with +1 V bias. (b) STS data for several regions of the sample showing a variation in the band gap.



a) Topography  
(Integrated DOS)

b) Energy-Gap ( $\Delta$ ) Map



c) Histogram of ( $\Delta$ )

Fig. 18. (a) Topographical STM image of  $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_{8+\delta}$  and (b) map of superconducting energy gap width ( $\Delta$ ). (c) is a plot of the distribution of superconducting gap size.

This type of image has been seen for several different TMO surfaces, including laser MBE grown films of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [36,51], cleaved samples of  $\text{La}_{1.0}\text{Sr}_{2.0}\text{MnO}_7$  [51], and single crystals of high temperature superconductors [51–53]. There is a general picture emerging from this limited data set based on the following two observations: (1) The spatial inhomogeneities seem to be pinned, in the sense that they do not move or fluctuate. As the temperature or magnetic field is changed, the inhomogeneities only change their size. (2) TMOs that have perfect stoichiometry and are either metallic or semiconducting do not exhibit spatial electronic inhomogeneities. For example, the images of  $\text{Sr}_2\text{RuO}_4$ , shown in Fig. 13 are like a normal metal. We have also achieved the same quality images of the double-layered material  $\text{Sr}_3\text{Ru}_2\text{O}_7$ . Kawai at the March 2000 APS meeting was the first to suggest that these data implied inhomogeneous stoichiometry on the nanometer scale [51]. In the case of the CMR materials, the inhomogeneity occurs in the concentration of the divalent and trivalent components, for example, La and Sr. For superconductors it may be the spatial variation in the oxygen concentration.

In Fig. 18 we show Shuheng Pan's *tour de force* [51,53]. On the left is an ordinary STM topographical image of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  while the plot of the right (b) shows a superconducting energy gap map of the sample [53]. Fig. 18(c) displays a histogram of the superconducting gap size revealing  $\sim 50\%$  spatial variation. These authors were able to show that there was a strong cross-correlation between the spatial variations in the superconducting energy gap  $\Delta$  and the local density of states (LDOS), both measured by the STM operating in the spectroscopy mode. Both the spatial variations in the LDOS and the superconducting gap  $\Delta$  occurred on a surprisingly short distance scale  $\sim 1.4$  nm, which is in fact shorter than the in-plane superconducting coherence length. The authors show that this is the appropriate length scale for the average spacing of O dopant atoms in the  $\text{CuO}_2$  planes. The picture that emerges from these measurements and models emphasize the role of *local physics* in high- $T_c$  superconductivity [53].

*What an exciting prospect.* Surface scientists will change the way the CMP community thinks.

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## References

- [1] C.B. Duke (Ed.), Surface Science, The First Thirty Years, North-Holland, 1994.
- [2] Nanotechnology: Shaping the world Atom by Atom, National Science and Technology Council, Committee on Technology (1999) <http://www.nano.gov/press.htm>.

- [3] Condensed-Matter and Materials Physics: Basic Research for Tomorrow's Technology, Committee on Condensed-Matter and Materials Physics, National Research Council, National Academy Press, Washington, DC, 1999, p. 10.
- [4] Complex Systems: Science for the 21st Century, Office of Science workshop, US Department of Energy, 5–6 March 1999, available at <http://www.er.doe.gov/production/bes/complexsystems.htm>.
- [5] J. Birgeneau, M.A. Kastner, Correlated electron systems, *Science* 288 (2000) 437.
- [6] J.S. Osborne, Correlated electron systems, *Science* 288 (2000) 468.
- [7] Y. Tokura, N. Nagaosa, Correlated electron systems, *Science* 288 (2000) 462.
- [8] J. Orenstein, A.J. Millis, Correlated electron systems, *Science* 288 (2000) 468.
- [9] S. Sachdev, Correlated electron systems, *Science* 288 (2000) 475.
- [10] P.W. Anderson, Correlated electron systems, *Science* 288 (2000) 48.
- [11] P. Ball, *Nature* 402 (Supp.) (1999) C73.
- [12] P.W. Anderson, *Science* 177 (1972) 393.
- [13] G. Gruner, *Density Waves in Solids*, Addison-Wesley, Reading, MA, 1994.
- [14] H. Mutka, Influence of defects and impurities on CDW systems, in: F.W. Boswell, J.C. Bennet (Eds.), *Advances in Crystallography and Microanalysis of CDW Modulated Crystals*, Kluwer Academic Publishers, Dordrecht, 1999.
- [15] I. Baldea, M. Badescu, *Phys. Rev. B* 48 (1993) 8619.
- [16] I. Baldea, M. Apostol, *J. Phys. C* 18 (1985) 6135.
- [17] B.I. Halperin, C.M. Varma, *Phys. Rev. B* 14 (1976) 4030.
- [18] T. Ichikawa, S. Ino, *Surf. Sci.* 105 (1981) 395.
- [19] J.M. Carpinelli, H.H. Weitering, M. Bartkowiak, E.W. Plummer, R. Stumpf, *Nature* 381 (1996) 398.
- [20] J.M. Carpinelli, H.H. Weitering, M. Bartkowiak, R. Stumpf, E.W. Plummer, *Phys. Rev. Lett.* 79 (1997) 1859.
- [21] J.S. Pedersen, R. Feidenhans'l, M. Nielsen, K. Kjaer, *Surf. Sci.* 189/190 (1987) 1047.
- [22] R.V. Coleman, B. Giambattista, P.K. Hansma, A. Johnson, W.W. McNairy, C.G. Slough, *Adv. Phys.* 37 (1988) 559.
- [23] A.V. Melechko, J. Braun, H.H. Weitering, E.W. Plummer, *Phys. Rev. Lett.* 83 (1999) 999.
- [24] A.V. Melechko, J. Braun, H.H. Weitering, E.W. Plummer, *Phys. Rev. B* 61 (2000) 2235.
- [25] H.H. Weitering, J.M. Carpinelli, A.V. Melechko, J. Zhang, M. Bartkowiak, E.W. Plummer, *Science* 285 (1999) 2107.
- [26] A.V. Melechko, Ph.D. thesis, The University of Tennessee, 2000.
- [27] L. Ottaviano, M. Crivellari, G. Profeta, A. Continenza, L. Lozzi, S. Santucci, *J. Vac. Sci. Technol. A* 18 (2000) 1946.
- [28] R.I.G. Uhrberg, H.M. Zhang, T. Balasubramanian, S.T. Jemander, N. Lin, G.V. Hansson, *Phys. Rev. B* 62 (2000) 1.
- [29] L. Ottaviano, A.V. Melechko, S. Santucci, E.W. Plummer, *Phys. Rev. Lett.* 86 (2001) 1809.
- [30] L. Li, C. Tindall, O. Takaoka, Y. Hasegawa, T. Sakurai, *Surf. Sci.* 385 (1997) 60.
- [31] X. Tong, Y. Sugiura, T. Nagao, T. Takami, S. Takeda, S. Ino, S. Hasegawa, *Surf. Sci.* 408 (1998) 146.
- [32] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fugita, J.G. Bednorz, F. Lichtenberg, *Nature* 372 (1994) 532.
- [33] R. Matzdorf, Z. Fang, Ismail, J. Zhang, T. Kimura, Y. Tokura, K. Terakura, E.W. Plummer, *Science* 289 (2000) 746.
- [34] M. Imada, A. Fujimori, Y. Tokura, *Rev. Mod. Phys.* 70 (1998) 1039.
- [35] M. Izumi, Y. Konishi, T. Nishihara, S. Hayashi, M. Sinohara, M. Kawasaki, *Appl. Phys. Lett.* 73 (1998) 2497.
- [36] N. Okawa, H. Tanaka, R. Akiyama, T. Matsumoto, T. Kawai, *Solid State Comm.* 114 (2000) 601.
- [37] Y. Maeno, *Physica B* 281/282 (2000) 865.
- [38] M. Braden, et al., *Phys. Rev. B* 57 (1998) 1236.
- [39] I.I. Mazin, D.J. Singh, *Phys. Rev. Lett.* 82 (1999) 4324.
- [40] W.E. Pickett, R. Weht, A.b. Shick, *Phys. Rev. Lett.* 83 (1999) 3713.
- [41] C. Bernhard, et al., *Phys. Rev. B* 59 (1999) 14099.
- [42] A. Moreo, S. Yonoki, E. Dagotto, *Science* 283 (1999) 2034.

- [43] S.A. Kivelson, E. Fradkin, V.J. Emery, *Nature* 393 (1998) 550.
- [44] J.M. Tranquada, et al., *Phys. Rev. Lett.* 79 (1997) 2133.
- [45] M. Uehara, S. Mori, C.H. Chen, S.-W. Cheong, *Nature* 399 (1999) 560.
- [46] M. Fathe, S. Freisem, A.A. Menovsky, Y. Tomioka, J. Aarts, J.A. Mydosh, *Science* 285 (1999) 1540.
- [47] B.J. Sternlieb, J.P. Hill, U.C. Wildgruber, G.M. Luke, B. Nachumi, Y. Moritomo, Y. Tokura, *Phys. Rev. Lett.* 76 (1996) 2169.
- [48] W. Bao, C.H. Chen, S.A. Carter, S-W. Cheong, *Solid-State Commun.* 98 (1996) 55.
- [49] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Moritomo, Y. Tokura, *Phys. Rev. Lett.* 80 (1998) 1932.
- [50] Y. Moritomo, Y. Tomioka, A. Asamitsu, Y. Tokura, Y. Matsui, *Phys. Rev. B* 51 (1995) 3297.
- [51] Symposium on STM Imaging of Transition Metal Oxides, March APS meeting, 2000.
- [52] T. Cren, D. Roditchev, W. Sacks, J. Klein, *cond-mat/0006039*, 2 June 2000.
- [53] S.H. Pan, J.P. O'Neal, R.L. Badzey, C. Chamon, H. Ding, J.R. Engelbrecht, Z. Wang, H. Eisaki, S. Uchida, A.K. Gupta, K.-W. Ng, E.W. Hudson, K.M. Lang, J.C. Davis, to be published.