**Figure 1.** GC-MS spectra of (A), authentic 2-phenyl(2,2-H$_2$)ethylamine (B), and authentic 2-phenyl(2,2-$^2$H$_2$)ethylamine (C). Enzymatic product from DBM/CHDEA-$d_2$ reaction.

Autooxidation of 1,4-cyclohexadienes[15] as well as their reactions with organic free radicals[16] have been shown to proceed exclusively through a free-radical pathway, involving initial generation of the cyclohexadienyl radical, leading to formation of the corresponding

aromatic products. It has also been well-documented that peracids, known to carry out concerted oxygen-transfer reactions,[17] react with 1,4-cyclohexadienes to produce only the corresponding epoxides but not the aromatized products.[18] These facts suggest that DBM-mediated aromatization of CHDEA is indicative of initial abstraction of a hydrogen atom from a ring methylene, as opposed to a concerted two-electron process. Furthermore, the redirection of the specificity of DBM with CHDEA substrate—with the enzyme producing only aromatized product and not exocyclic allylic alcohol—is likely a consequence of the fact that initial abstraction of a hydrogen atom from a ring methylene of 1,4-cyclohexadiene is more favorable than abstraction of an allylic hydrogen atom from the exocyclic methylene.[19] Thus, our finding of DBM-mediated aromatization of CHDEA is best accommodated by a mechanism which involves initial abstraction of a hydrogen atom from a ring methylene by the activated copper oxygen species of DBM.

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## Scanning Tunneling Microscopy Investigations of a New Charge Density Wave Phase in Niobium-Doped Tantalum Disulfide

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Understanding the electronic and structural factors that determine metal/superconductor and metal/charge density wave (CDW) phase transitions is central to current research efforts in solid-state chemistry and physics.[1] Typical methods used to study such transitions (photoelectron spectroscopy, diffraction, etc.) generally provide information relevant to the average electronic and structural properties of materials. Many fundamental problems, however, such as understanding impurity effects are local in nature and difficult to address using these methods. The scanning tunneling microscope (STM),[2] which can provide atomic-resolution electronic and structural information, has been used to study superconducting[3] and CDW phases,[4-7] although few of these studies have probed local problems.[6,7] Herein we describe

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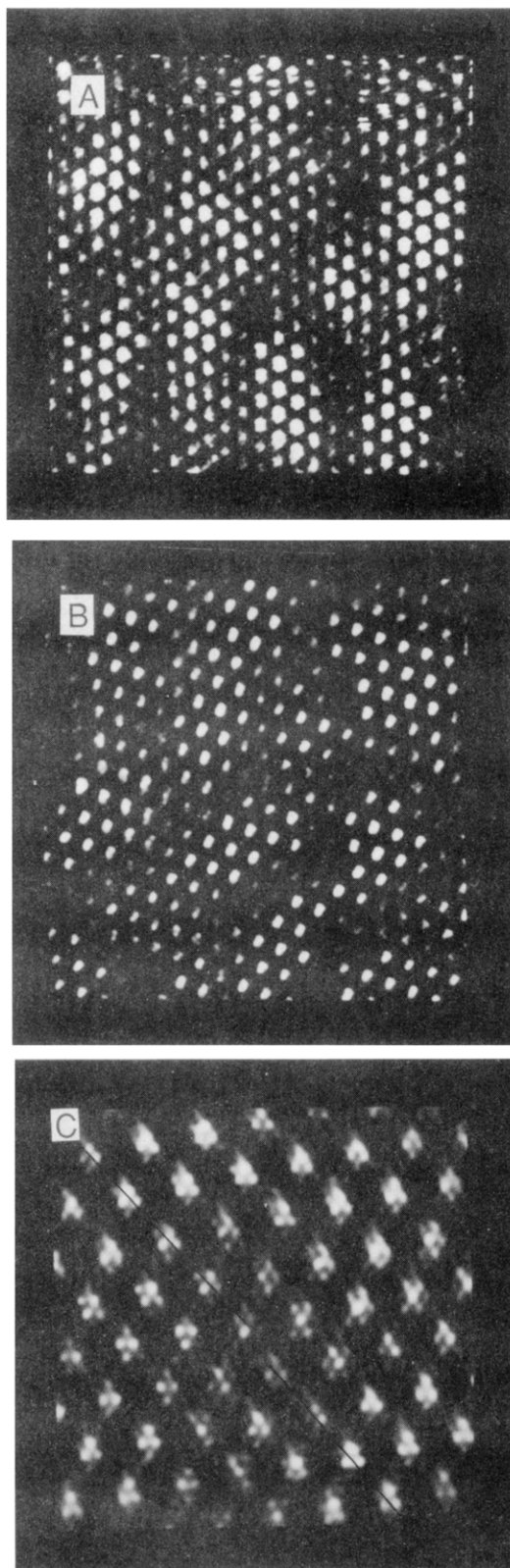
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**Figure 1.** Top-view images of $Nb_xTa_{1-x}S_2$ recorded with a tunneling current of 2 nA and a sample vs tip bias-voltage of 10 mV. (A) 225 × 225 Å image of a $x(Nb) = 0.02$ sample and (B) 205 × 205 Å image of a $x(Nb) = 0.04$ sample. The image data was low-pass filtered prior to display. (C) A 85 × 85 Å high resolution image of $Nb_{0.04}Ta_{0.96}S_2$. Lines through the CDWs in two domains show the phase-shift of one lattice period.

STM investigations of a new domain-like discommensurate (DC) CDW phase in a series of niobium-doped tantalum disulfide ($Nb_xTa_{1-x}S_2$) materials (i.e., systems that contain well-defined impurity concentrations). Notably, by using the STM we have characterized in detail the CDW amplitude, wavelength, and
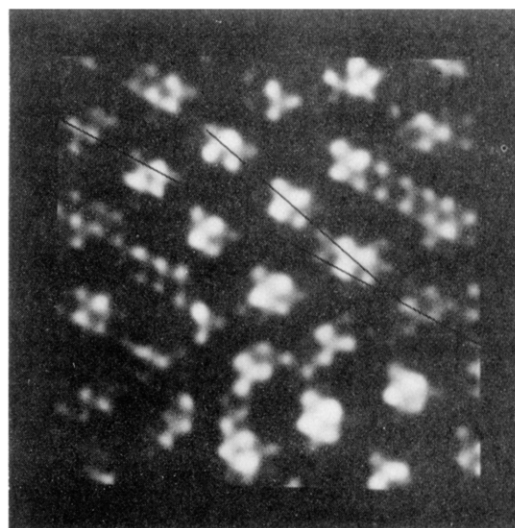


**Figure 2.** 60 × 60 Å top-view image of two CDW domains in $Nb_{0.1}Ta_{0.9}S_2$ recorded with a tunneling current of 2 nA and bias-voltage of 10 mV. The domains on the left and right side of the image are rotated ca. 14° with respect to the lattice. Solid lines indicating one CDW vector and one lattice vector highlight this rotation.

domain structure for the DC phase as a function of niobium concentration.

Single crystals of $Nb_xTa_{1-x}S_2$ ($x = 0–0.1$) were prepared via iodine vapor transport[8,9] and imaged in the constant current mode at room temperature by using an STM[10] that has been described previously.[5] Typical[11] grey-scale images of two niobium-doped samples are shown in Figure 1. Light areas in these images correspond to apparent surface protrusions, while dark areas indicate depressions. The CDW defines a regular hexagonal superlattice in the $x(Nb) = 0.02$ and 0.04 samples with the same average wavelength ± $1\sigma$ of 11.8 ± 0.3 Å. These wavelength values are consistent with previous diffraction measurements[12] and provide direct confirmation of the suggestion that substitution of $d^1$-Nb for $d^1$-Ta does not significantly perturb the size of the Fermi-surface.[8,12] A more interesting feature of the STM images is the domain-like structure of the CDW. These domains consist of clusters of high-amplitude CDW maxima separated by regions of substantially lower amplitude (5.2 ± 0.4 vs 2.3 ± 0.2 Å).[13] Although the domains are not strictly periodic, they are fairly regular and similar in size (containing 19 ± 3 CDW maxima/ domain for $x(Nb) = 0.02$ and 18 ± 4 for $x(Nb) = 0.04$). Since this new structure is reproducible,[11] we believe that the domains are intrinsic to these Nb-doped materials and are not due to surface contamination.

On the basis of previous diffraction, resistivity, and susceptibility measurements the CDW phase in the $x(Nb) = 0.02$ and 0.04 materials is expected to be nearly-commensurate (NC) at room temperature as in $1T-TaS_2$.[8,12] Our STM measurements show that on a local scale the CDW phase in the Nb-doped samples is domain-like and not NC. Several theoretical calculations have

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(9) Single crystal samples were grown over a 2–4-week period from prereacted powders of $Nb_xTa_{1-x}S_2$ using a 50–100 °C gradient. Following transport, the tubes were rapidly quenched into cold water to yield the 1T crystal phase. The stoichiometry of the crystals was confirmed by elemental analysis.

(10) Nanoscope, Digital Instruments, Inc., Santa Barbara, CA.

(11) These images are representative of those obtained on several independent samples using different tunneling tips. The images are independent of bias-voltage and tunneling current between ±100 mV and 1–6 nA, respectively. The values reported for the CDW amplitude and wavelength are averages of measurements taken from at least seven images.

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predicted that a domain-like DC CDW phase should be more stable than either a NC or incommensurate (IC) phase.[14] In these theoretical models the DC phase is predicted to consist of commensurate domains separated by low-amplitude regions in which the phase of the CDW changes. Because of this phase change the CDW in two adjacent domains should be out of registry by one atomic lattice spacing.[14a] Within the domains in $Nb_xTa_{1-x}S_2$ we observe the same array of atoms at each maxima indicating that the CDW is commensurate.[4c] To determine more rigorously whether the domains are commensurate we measured the angle between the CDW and the atomic lattice. This angle, 13.7 ± 0.9°, is nearly the same as the 13.9° angle required for a commensurate CDW.[15] The CDWs in adjacent domains are also out of phase by one lattice spacing as shown in Figure 1C. Finally, the average domain size is similar to that expected for $1T-TaS_2$.[14,16] Agreement of these results with theoretical predictions[14] strongly supports our suggestion that the CDW phase is DC.

We have also investigated the effects of increased niobium concentrations on the CDW to characterize further the evolution of this new DC phase. It has been proposed previously that the CDW is IC at room temperature for $x(Nb) \geq 0.08$,[8,12] although at high resolution our STM images indicate that the CDW phase is domain-like (DC) for the Nb-doped materials. In a typical image of $Nb_{0.1}Ta_{0.9}S_2$ (Figure 2) there are small domains in which the CDW amplitude is 5.8 ± 0.7 Å separated by regions in which the vertical corrugation is lower 2.3 ± 0.5 Å.[17] This variation in the CDW amplitude is similar to that observed for $x(Nb) = 0.02$ and 0.04 samples. Within domains there is a similar array of atoms at the maxima and the CDW is oriented at a 13.5 ± 1° angle relative to the atomic lattice, indicating that the CDW is commensurate. The domains are, however, considerably smaller than those observed for $x(Nb) = 0.02$ and 0.04 (7 ± 3 maxima/domain), presumably due to the greater disorder in the lattice potential.[8,18]

In contrast to these results for the niobium-doped materials we have recently shown in $Ti_{0.1}Ta_{0.9}S_2$ that the CDW amplitude is uniformly low (1-2 Å) and that the CDW structure is randomly distorted (i.e., neither DC nor IC).[7] To understand the differences between the Nb- and Ti-doped materials we consider the energetics of forming an ordered state. The DC phase is favored by the electrostatic interaction between the lattice and commensurate CDW domains, and the magnitude of this interaction is proportional to the CDW amplitude.[14] Opposing this lattice-domain term are interactions between the CDW and the random impurity potential due to the Nb or Ti sites.[18] Our CDW amplitude measurements suggest that the DC phase in the Nb-doped materials is driven by the lattice–domain interaction. Because this electrostatic term is smaller in the Ti-doped systems (due to the uniformly low CDW amplitude), interactions with the random lattice potential lead to the disordered CDW structure. This study as well as future STM investigations should provide much needed data necessary to develop a better microscopic understanding of CDW and superconducting phases in low-dimensional materials.

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(15) The experimental error in these measurements is sufficiently large that we cannot conclusively rule out NC domains which should have a 12° orientation angle; however, we note that NC domains would not show the same trigonal array of atoms at each CDW maxima.

(16) This similarity is somewhat surprising in light of a recent STM study which found no evidence for a DC phase in $1T-TaS_2$ at 300 K.[6] We are currently investigating this point further.

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# The Role of Ion Pairs in α-Helix Stability: Two New Designed Helical Peptides

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Roughly 40% of the amino acid residues in known protein structures are α helical.[1] It is important in attempting to predict protein structures or design new proteins to understand the determination of this helical structure. Certain amino acids—alanine and leucine for example—have been identified as "helix forming" from host–guest experiments on synthetic polypeptides[2] and their frequent occurrence in helices within native proteins.[3,4] Others, most notably glycine and proline, destabilize helix. A number of neutral polar side chains, among them asparagine and serine, probably participate in nucleating and terminating helical structure via H-bonding interactions with groups of the backbone.[5]

Charged groups play a special role in regulating helical structure of proteins.[6-8] One mechanism involves an interaction between the charge and the helix dipole, arising from the oriented array of backbone peptide groups:[9] charge arrangements that oppose the helix dipole moment stabilize helical structure.[6-8] Thus negative charges tend to stabilize isolated helical structures if they are located near the N terminus and destabilize as they approach the C terminus. Positive charges display the opposite effect. A second mechanism involves ion-pair formation between oppositely charged side chains spaced at intervals such as $i, i \pm 4$.[10] Spacing of opposite charged side chains at these intervals tends to occur relatively frequently in helical sequences within proteins.[10] Presumptive ion pairs have been introduced into synthetic oligopeptides and found to promote formation of helical structure.[8]

Here we describe the synthesis of two peptides containing 18 and 15 residues, respectively, which exhibit significant α-helical structure in solution. Peptide I (Chart I) consists of two repeats

**Chart I**

peptide I:  succinyl-Ser-Glu-Glu-Glu-Glu-Lys-Lys-Lys-Lys-Glu-Glu-Glu-Glu-Lys-Lys-Lys-Lys-Phe-$CONH_2$

peptide II:  acetyl-Ser-Glu-Lys-Glu-Ala-Lys-Glu-Lys-Ala-Glu-Lys-Glu-Ala-Lys-Ala-$CONH_2$

of four glutamic acid residues followed by four lysines, allowing it to form eight potential ion pairs. Peptide II resembles molecules synthesized by Marquse and Baldwin[8] except that it contains two overlapping sets of possible ion pairs. Both peptides include a serine residue at the N terminus and are blocked at the chain termini to enhance a favorable charge dipole interaction.[6-8] On the basis of CD spectra, peptide I appears to lose almost all its helical structure on titrating the lysine residues near pH 11,

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