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 Marqusee 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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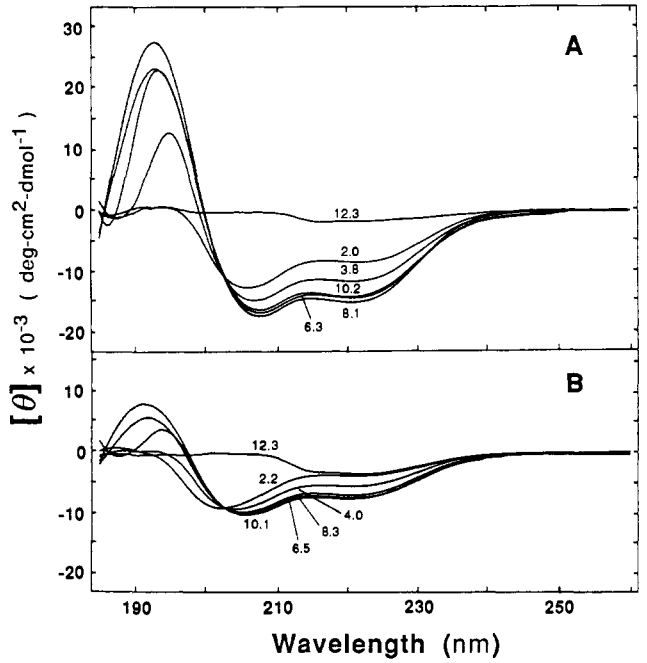

Figure 1. Circular dichroism spectra of peptides in 10 mM KF, 4 °C, at various pHs as indicated on the curves: (A) peptide I and (B) peptide II.

suggesting that ion pairing is a major component in stabilizing the helix in this molecule.

Peptide I was synthesized by the solid-phase method on an ABI 430A automatic synthesizer using *t*-Boc chemistry in the laboratory of P. S. Kim (Whitehead Institute, MIT, Cambridge, MA). Peptide II was made by F-moc solid-phase peptide synthesis on a Biosearch 9600 peptide synthesizer with dimethyl formamide as solvent and trifluoroacetic acid/dimethyl sulfide/dichloromethane (14:1:5) for deprotection. The C-terminal amide group in II was introduced by use of Biosearch PAL resin. Peptides I and II were succinylated and acetylated with succinic anhydride and acetic anhydride, respectively, in dimethyl formamide containing an equivalent of trimethylamine. The peptides were purified on a reversed-phase Deltapack 15 micron C_{18} HPLC column (Waters). Solvent A is 0.1% TFA in water, B is 0.1% TFA in 70% acetonitrile, with the detector set at 229 nm. The peaks corresponding to each peptide were rerun on HPLC, and FAB MS analysis (by Dr. Leonard Schronk, M-Scan, Inc.) of the products shows [M + H] = 2410 for I and 1718 for II, with additional ions corresponding to [M + *j*Na], j = 1, 2,...

Circular dichroism spectra were recorded on a modified Cary spectropolarimeter (Aviv DS60) in 10 mM KF solution titrated to appropriate pH values. Peptide concentrations were determined spectrophotometrically by a modification of the Lowry method.[11] The CD spectrum in the region of peptide bond absorption provides a test for helicity of a peptide; the characteristic spectrum of α helices exhibits a double minimum at 222 and 208 nm and a maximum at 190 nm.[12] The value of the mean residue ellipticity, $[\theta]_{222}$, for a perfect helix is about −35 000 at 222 nm, while that for a "coil" is estimated to be +3000.[12] The CD spectra of peptides I and II are shown in Figure 1, for several values of pH. Both indicate the presence of helix: we estimate that I contains up to about 35% α helix at 4 °C, while II has 16%. In both cases, an isodichroic point occurs at 203 nm in the spectra between pH 2 and 10, consistent with the presence of mixed helix and coil in these systems. Beyond pH 10, no isodichroic point occurs, and a different spectrum is seen. In both cases, the CD spectra are independent of concentration from 5–100 μM, consistent with

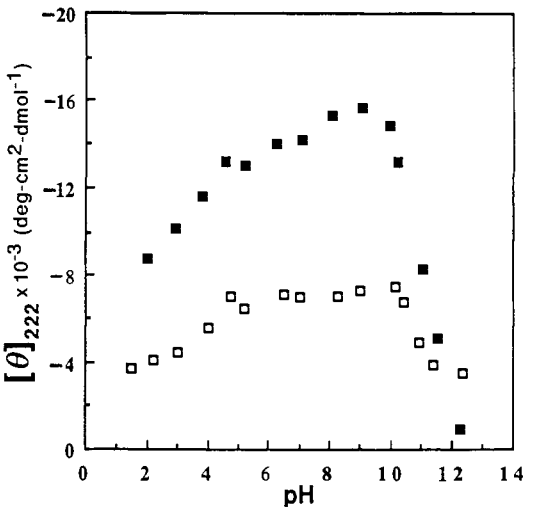

Figure 2. The pH dependence of the mean residue ellipticity at 222 nm, 4 °C, and 10 mM KF for peptide I (■) and peptide II (□).

intramolecular helical structure (see ref 8). Both peptides are highly soluble in water.

The dependence of $[\theta]_{222}$ on pH for these peptides is shown in Figure 2. As the pH approaches that of the pK_a for lysine side chains, the apparent helix content of both peptides diminishes, as has been seen for other helix forming synthetic and natural peptides.[6-8] Loss of helix in the case of I is nearly complete, much greater than that in II. Comparison of these data with those of Marqusee and Baldwin[8] suggests that there may be a roughly linear relation between loss of helix on titrating lysines near pH 11 and the number of potential bridges. Thus the alkaline titration of these two peptides provides suggestive evidence that ion pairing is in fact a major component in stabilizing them, since the charge distribution on titrating either the lysines or glutamates side chains still favors helix according to the results of Shoemaker et al.[7]

These models should make it possible directly to assess the thermodynamic effect of ion pairs on helix relative to the presence of alanine side chains or other specific helix stabilizing interactions.

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Observation of Gas-Phase Anionic Bismuth Zintl Ions

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We report in this communication the first observation of gas-phase anionic Zintl ions of bismuth. Laser-ionization time-of-flight mass spectra of mixed bismuth/alkali clusters produced by a gas aggregation source were investigated in our laboratory and found to exhibit maxima for clusters corresponding to reported Zintl ions. Bonding in homoatomic clusters is a topic of fundamental as well as practical importance. The electronic and geometric structure of metal clusters in particular is currently the subject of intense investigation among a great number of researchers. "Magic numbers" corresponding to particularly abundant gas-phase cluster ions are observed to depend on the identity of the metal or alloy and on the ionization conditions. Reasons for the exceptional stabilities of such "magic numbers" have been ascribed to preferred electronic and structural configurations for either the neutral or ionic species.

Figure 1 displays a typical distribution obtained for intermetallic clusters of bismuth and sodium. Each group of peaks represents clusters possessing a specific number of bismuth, and various

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