In summary, we have clearly established that superconductivity in $(TMTSF)_2ClO_4$ is strongly affected by quenching from rather low temperatures (20–40 K). This phenomenon is reproducible and the relaxed state is fully restored by an annealing at 40 K followed by slow cooling. In the quenched state the critical temperature is reduced by 22% and only one-half of the electronic entropy is still involved in the superconducting condensation. The upper critical field is also reduced and the transition is broadened; we suggest that these modifications are related to a reappearance (induced by quenching) of the SDW state which mixes with the normal SC state.

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Reconstruction Mechanism and Surface-State Dispersion for Si(111)-(2 × 1)

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Pseudopotential total-energy calculations show that the π-bonded chain reconstruction of the Si(111)-(2×1) surface can be reached from the ideally bonded surface without increasing the total energy by more than 0.03 eV/(surface atom). Hence, the chain surface can be formed easily in the cleavage process. The minimum-energy chain geometry is determined, and the corresponding surface-state dispersion is in remarkable agreement with recent angle-resolved photoemission experiments.

The π-bonded chain model for the Si(111)-(2×1) surface was proposed by Pandey[1] mainly because of its ability to explain spectroscopic data. In this paper we show that the chain surface is an easily accessible final state of the cleavage process, and suggest a path in atom coordinate space by which the reconstructed surface may be reached.

The chain model requires that the bonding topology of the surface be changed from that of the ideal surface. It has been argued that this geometry, although lower in energy than the minimum-

energy geometry for the ideal-topology surface,[2-4] would not be realized because of an energy barrier which must be crossed to go from the ideal surface to a surface with chains. It has been proposed[5] that the observed cleavage energy[6] of 1.0 eV/(surface atom) is not sufficiently large to allow the chain surface to be formed. Since one must "break" 1.0 Si-Si bond per surface atom (on each surface) to form the chain surface, and the surface cleavage energy is only about 1.0 eV/ (surface atom), the chain model seems to require roughly 1.3 eV/(surface atom) more energy than the experimentally observed energy in order to be formed. This assumes a bond strength of 2.3 eV, i.e., $\frac{1}{2}$ of the cohesive energy of crystalline Si. However, this agrument is not appropriate since the energy required to change the topology of the surface atoms is estimated from bulk properties. To assess carefully the energetics of the formation of the chain model, we have performed a sequence of total-energy calculations for geometries which take the surface from a buckled surface to a chain surface. We start with a buckled surface only because it is a typical example of an ideal-topology surface. We find that the barrier separating the buckled surface from the chain surface is 0.03 eV/(surface atom).

The calculational scheme is based on the pseudopotential approximation within the local density functional formalism. The application of this method to the calculation of bulk, molecular, and surface structural properties of silicon has been discussed extensively in the literature.[2,3,7,8] We have used a norm-conserving pseudopotential[9]

and the Wigner interpolation formula to approximate the correlation energy in the exchange-correlation energy function. The same supercell method and convergence criteria discussed in Ref. 3 are used.

Starting from the minimum-energy buckled (paramagnetic) surface,[3] we have considered a sequence of eight geometries which take the surface from the buckled surface to the chain surface in small steps. The paths along which the atoms move are shown schematically in Fig. 1. The energies of these geometries, as a function of a generalized coordinate g, are shown in Fig. 2, where $g = 1.0$ corresponds to the buckled geometry, and $g = 7.0$ corresponds to a chain geometry. An increment of g by 1.0 corresponds roughly to displacements of the atoms in the first double layer by 0.25 a.u. All displacements occur in the two inequivalent (110) planes which intersect the surface at right angles. The energy of the surface must be increased by only 0.03 eV/(surface atom) to cross the energy barrier which separates the ideal-topology surfaces from the chain-like surfaces. We emphasize that we have not attempted to find an optimum path: The calculation gives only an upper bound on the energy required to reconstruct the surface. Indeed it may be true that there is no barrier at all for a path which takes the surface from the ideal surface (rather than the buckled surface) to the chain geometry. In any case, it is clear that the cleavage process supplies more than enough energy to effect the reconstruction, so that the chain model is not at all inconsistent with the observed cleavage energy of Si(111).

To illustrate the path by which the reconstruction may occur, we show, in Fig. 3, charge den-
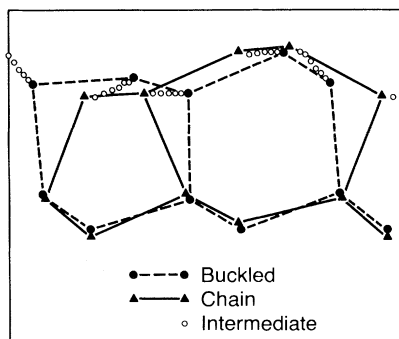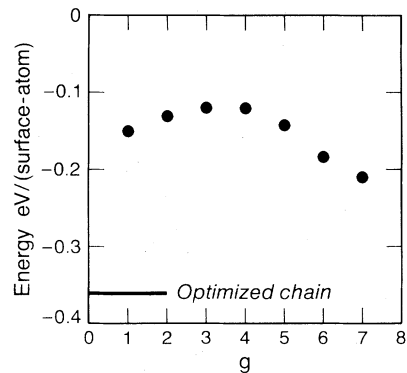

FIG. 1. Positions of surface atoms projected onto a (110) plane. The solid circles denote the positions of the atoms in the buckled geometry. The crosses denote the positions for the six intermediate geometries which take the surface to the chain topology. The positions of the atoms in the chain geometry are represented by triangles.

FIG. 2. Surface energy, relative to the ideal surface, as a function of g (defined in the text). The energy of the optimized chain surface is denoted by the solid line.
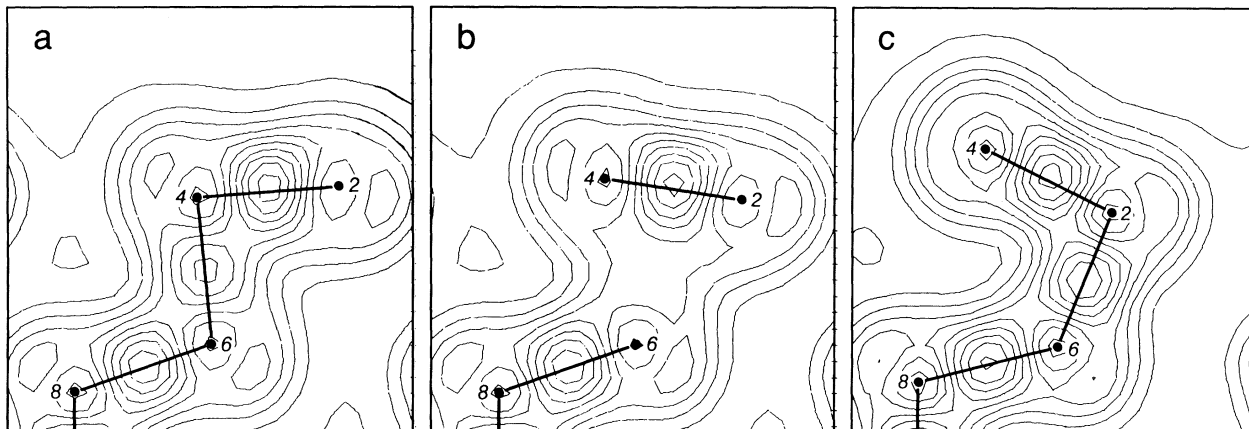
FIG. 3. Contour plots of the valence (pseudo) charge density for (a) the buckled geometry, (b) an intermediate geometry, and (c) the optimized chain geometry. The charge in the (110) plane intersecting the (111) surface at right angles is plotted.

sities for three of the geometries. The charge density for the (initial) buckled surface is shown in Fig. 3(a). In Fig. 3(b) we show the charge density for an intermediate geometry. Atom 4 has been moved away from atom 6, to which it was previously bonded. Atom 2 has been moved downwards toward atom 6, to which it will eventually be bonded in the chain geometry. In this intermediate geometry the bond charge which was previously between atoms 4 and 6 is much reduced. We may, therefore, consider this geometry to possess one less bond per two surface atoms than the buckled geometry. However, the total energy of this geometry is only 0.03 eV /(surface atom) higher than the buckled geometry. In Fig. 3(c) we show the charge density for the optimized chain geometry. Atom 4, which was previously in the second layer, is now part of the π-bonded chain of surface atoms, and atom 2, which was previously in the surface layer, is now in the second layer and is bonded to atom 6.

The optimum (i.e., lowest energy) chain geometry is determined by using the Hellmann-Feynman forces to predict geometries with successively lower total energy. For this chain geometry, the calculated dispersion of the dangling-bond surface states along Γ-J-K' is shown in Fig. 4(a). We find a surface resonance which disperses downwards from Γ to $0.5\Gamma J$. It then becomes a true surface state and disperses upwards rapidly by 0.8 eV from $0.5\Gamma J$ to J. From J to K' the occupied surface state disperses upwards slightly by 0.1 eV. The dispersion along Γ-J-K' observed by Uhrberg et al.[10] is also plotted. The shape of the calculated dispersion is

in remarkably good agreement with this experiment. (The position of the experimental points has been shifted upwards by 0.3 eV so that the experimental and theoretical energies are in exact agreement at J.) A qualitatively similar dispersion has also been observed by Himpsel, Heimann, and Eastman,[11] provided their results are interpreted in terms of a single band and the additional surface state observed near J is assumed to be extrinsic in origin. Hansson et al.[12] observed a dispersion of the dangling-bond surface state which is also consistent with these results.

The dispersion along J' to K' is shown in Fig. 4(b) and is qualitatively similar to that along Γ to J. Himpsel et al.[11] have observed a similarity in the dispersion for these two parallel directions with their two-dimensional imaging system. This similarity is characteristic of the one-dimensional nature of the chains; there is only a small coupling between atoms in different chains. Along Γ to J' we find a surface resonance which disperses downwards by 0.35 eV. Himpsel et al. observed a resonance dispersing downwards by 0.15 eV from Γ to J'. A small dispersion (less than 0.1 eV) has been observed by Houzay et al.[13] and by Uhrberg et al.[10] along $\Gamma J'$.

In view of the small amount of energy necessary to change the structure of the surface, one may speculate that the effect of contamination on the chain surface may be to induce a transformation to an ideal-topology surface. The relative energies of the ideal- and chain-topology surfaces may be reversed if an adsorbate is present. An adsorbate would saturate the dangling
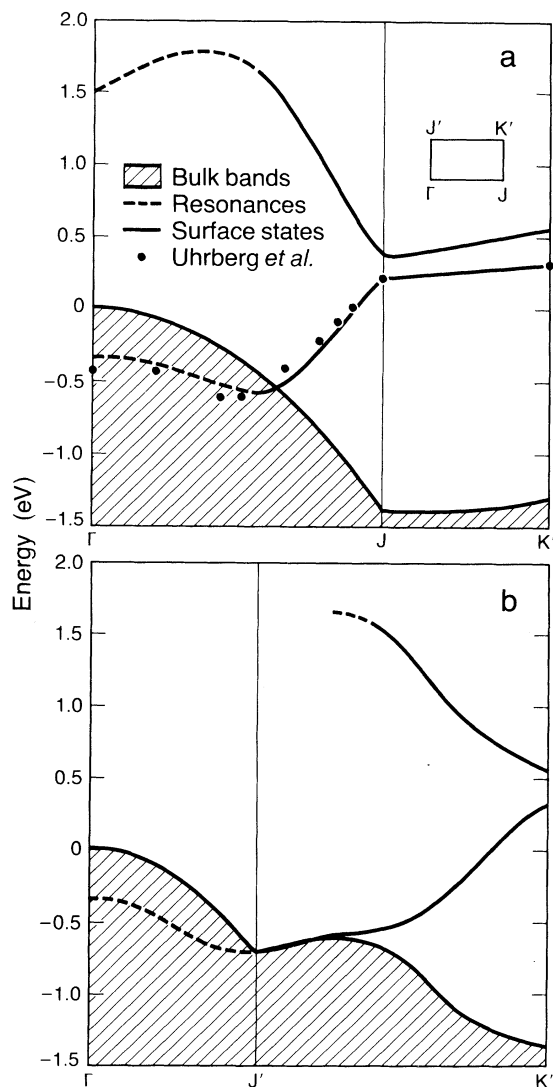
FIG. 4. (a) Calculated dispersion of the surface states and resonances along Γ-J-K'. The experimental points of Uhrberg *et al.* have been shifted upwards by 0.3 eV so that the theory and experiment are in exact agreement at the J point. (b) Calculated dispersion of the surface states and resonances along Γ-J'-K'.

bonds, thus eliminating the π bonding and removing this extra bonding mechanism which makes the chain structure more stable than the ideal-topology surface. This could explain the conver-

sion of the low-energy electron diffraction pattern to 1×1 as hydrogen is adsorbed on the surface.

A previous calculation[3] gave the energy of the nonbuckled antiferromagnetic insulating surface as -0.21 eV/(surface atom), which is about 0.10 eV/(surface atom) lower than the top of the calculated energy barrier separating the ideal topologies from the chain topologies. In addition, this surface was shown to be stable against the buckling distortion. This surface is, therefore, more stable against a transformation to the chain surface than is the buckled surface.

In conclusion, we have domonstrated that the chain model may be obtained easily during cleavage, and that for the optimized chain geometry the calculated dispersion of the surface states is in excellent agreement with experiment.

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