Summary of Anatoli Melechko's thesis: Defect-Mediated Condensation of a Charge Density Wave:

The system being investigated is shown in the top of Fig. 1. It is a thin film (1/3 of a monolayer) of Sn or Pb on the (111) face of either Si or Ge. The structure is $(\sqrt{3}x\sqrt{3})R30^0$ and referred to as the α-phase, whose family of adsorbate-substrates has been studied by the surface community for ~20 years [1] It wasn't until 1996 that Carpinelli cooled the sample and discovered that there was a phase transition to a (3x3) structure [2]. Carpinelli discovered that for both Sn or Pb on Ge(111) that the low temperature phase was a CDW [2, 3]. The CDW phase results in a periodic lattice distortion which according to both x-ray [4] and LEED [5] studies is a vertical buckling of the Sn atoms. One atom in the unit cell moves up and the other two down (~0.3 Å vertical buckling), accompanied by an increase in the first to second double-layer spacing in the Ge substrate.

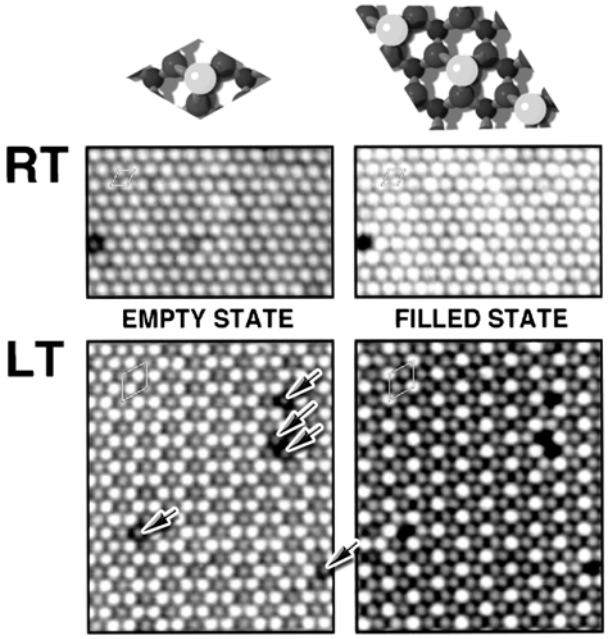

Fig. 1. Marble models (top) and STM images of the CDW transition in the α-phase of the Sn/Ge(111) system (1/3 monolayer). Arrows mard Ge substitutional defects.

Melechko's discovery that the defects were key participants in the CDW condensation dramatically changed the perspective of the scientific community. The following will describe his finding that there are two interlocked phase transitions—a first-order defect alignment and a second-order CDW condensation [6-8]. The arrows in Fig. 1 point to the defects in the Sn/Ge film. The vast majority of the defects are Ge substitutional atoms in the Sn overlayer (~10% of the defects are vacancies). Defects, both vacancies and substitutional Ge atoms, created temperature dependent exponentially damped CDW-like perturbations. The experimental observations lead to the construction the following ansatz to fit the experimental images;

$$I(\vec{r}) = f_{\sqrt{3}\times\sqrt{3}}(\vec{r}) + \sum_{n}^{N} A_n e^{\frac{-|\vec{r}-\vec{r}_n|}{l(T)}} \sum_{i}^{3} \cos(\vec{k}_i(\vec{r}-\vec{r}_n)+\phi_n). \qquad (1)$$

The first term is the intensity in the RT $\sqrt{3}x\sqrt{3}$ filled-state image (Fig. 1) and the second term describes the damped CDW waves. The first sum is over the three **k** vectors that describe the (3x3)-CDW phase, and the second sum is over all defects n. The only parameters are the phase of the wave at the defect ϕ_n and the decay length *l(T)*. The phase is determined by the nature of the defect. A Ge substitutional atom does not want to be at a charge maximum (Fig. 2a), so the phase is π. Experience showed that all of the STM images could be uniquely fitted with a single parameter *l*(T) [6].

Fig. 2b displays the measured inverse decay length 1/*l*(T) as a function of temperature for Sn/Ge(111) [8]. The length parameter diverges at T_1=70 K, leading to the prediction that the CDW phase transition from a single defect would occur at this temperature T_1. In fact the transition occurs at a temperature T_2~120 K, when the defects interact via the density wave and move to align themselves with the CDW domain (6, 8). This occurs when *l*(T) ~ l_{av}, where l_{av} is the average defect-defect spacing 1/ l_{av} is shown as the dashed line in Fig. 2b.

The speculation that the defects are dynamic participants in the CDW condensation has been proven using the variable temperature STM. The (3x3) unit cell in Fig 2b shows that there are three Sn atoms in each cell. This means that there are three possible CDW domains depending on which of the three atoms are negatively charged. Since Ge substitutional atoms do not like to sit on a charge maximum site, a random distribution of Ge defects would have, on average, 1/3 on unfavorable sites. Melechko and Braun performed a careful statistical counting of the defects to prove that the defects moved [8]. A sampling grid (80Åx80Å) slightly smaller than the average CDW domain size (100Åx100Å) was used to quantify the defect alignment on a large number of STM images at RT [6, 8]. If all of the defects were on two of the three lattices (avoiding the charge maximum lattice), the probability P_C was defined to be 1, and if they were equally distributed on three lattices, then P_C=0. Fig. 5c 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_2~120K the defects move to align themselves within each CDW domain. This indicates a first order, order-disorder phase transition with P_C being the order parameter. The transition temperature T_2 will depend on the defect concentration.

The defect-defect interaction can be modeled with a simple electrostatic interaction created by the damped CDW waves, which grows with decreasing temperature. Fig. 3 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 100K (determined by the activation barrier) there is a sudden alignment of the defects. The driving force for the Ge-Sn place exchange is the non-uniformity of the charge on the six nearest neighbors (to Ge defect) Sn atoms caused by the damped CDW wave from nearby defects.

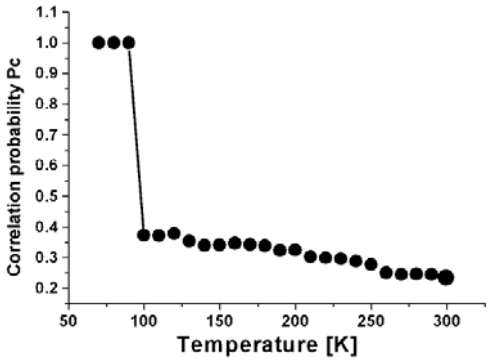

Fig. 3: Simulation of the order-disorder defect alignment phase transition

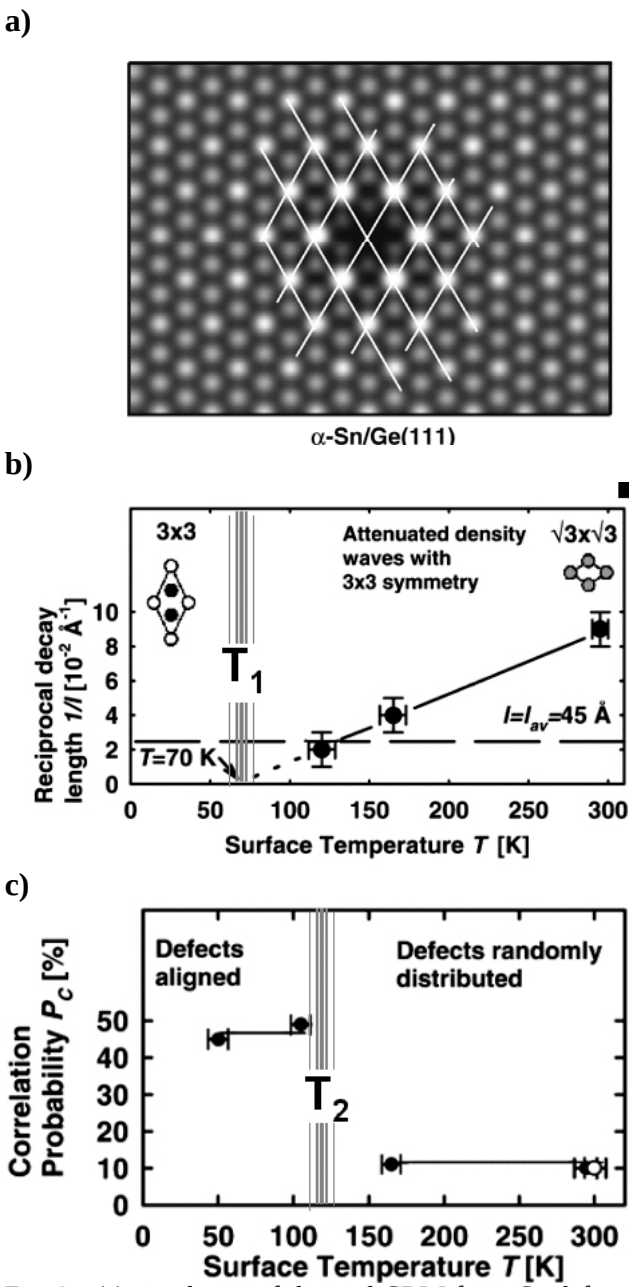

Fig. 2. (a) simulation of damped CDW from Ge defect. (b) inverse CDW decay length 1/l(T). (c) defect alignment correlation probability P_C vs. temperature.

It is crucial to point out a glaring failure of this model, based on the concept of temperature dependent damped CDW waves emanating from each defect (Fig. 5a). We cannot reproduce the STM images using Eqn. 1 when the temperature is low, i.e. after the condensation of the CDW. In this temperature regime the images consist of domains of the (3x3) CDW phase with very sharp domain walls [6-8]. Fig. 4 shows an abrupt domain wall for the Sn/Ge(111) system at 30K.

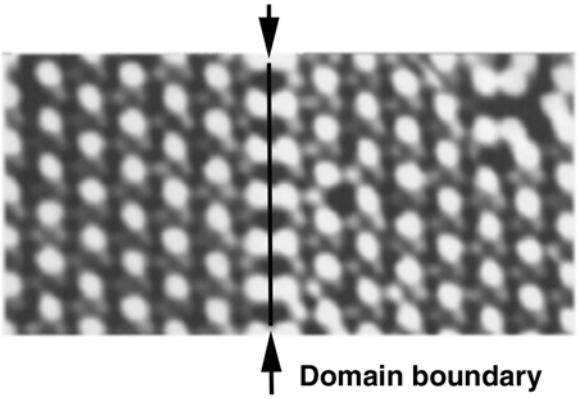

Fig. 4. STM image of sharp CDW domain wall for Sn/Ge(111) [6].

In his final paper on this subject Anatoli developed a model that could account for the observed characteristics of the STM images below the temperature of the phase transition [9]. This "charge-compensation model is based on four assumptions: 1) The charge on a lattice site is proportions to the sum of charges on its nearest neighbors; 2) The absolute value of a charge on any lattice site has a saturation value; 3) The charge on a defect site is fixed, and; 4) The total charge on the system is zero. Self-consistent solutions for this model as a function of the magnitude of the charge-compensation factor R(T) reproduce all of the salient features seen in the experiment [9].

- Anatoli Melechko's web site: http:/web.utk.edu/~melechko/alter.htm

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