Shining Light on Charge Density Wave Order

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(Dated: December 22, 2022)

Liquid crystals have both continuous and discrete spatial symmetries. Systems with such symmetries may be realized in solutions of organic molecules, but also in other systems. For example in solids charge density waves may break some but not all spatial symmetries from continuous translations and rotations to discrete translations and rotations. A recent experiment [Nature Physics **16**, 159 (2020)] found that shining an intense ultrafast laser pulse on LaTe$_3$ drove the system from a smectic liquid crystal charge density wave order to a crystalline charge density wave order. Here we discuss liquid crystal ordering, electron scattering and these experiments. This change in ordering can be understood by a Landau-Ginzburg free energy with two scalar fields whose coupling decreases when illuminated.

I. INTRODUCTION

Liquids have continuous rotational and translational symmetries, while crystals have discrete rotational and translational symmetries. In between these it is possible to find systems that arrange as liquid crystals with some continuous and some discrete spatial symmetries. For example, a nematic liquid crystal in three dimensions has continuous translational symmetry but breaks rotational symmetry so that there is only one axis of continuous rotational symmetry (oriented along the director). Breaking one more translational symmetry, one arrives that the smectic liquid crystal. In two dimensions, a smectic has one continuous and one discrete translation symmetry, and no continuous and one discrete rotation symmetry. The density of two-dimensional smectic can be written as

$$\rho(x,y) = \rho_0 \sin\left(\frac{2\pi}{\lambda}y\right) + ...,$$

where higher order terms in the Fourier expansion of the density are truncated. λ is the real-space period of the smectic. Here there is continuous translational symmetry in the x direction and discrete translational symmetry in the y direction.

Systems that realize the structure of a smectic liquid crystal include long organic molecules that arrange into smectic order where ρ is the mass density, and less traditional systems. A less traditional system that realizes the smectic order are charge density waves in solids where ρ is the charge density.

II. RARE EARTH TRITELLURIDES

The rare earth tritellurides, RTe$_3$ are bulk three dimensional materials comprised of two dimensional layers. Each unit cell contains six layers van der Waals bonded together: four monolayers of tellurium and two covalently bonded bilayers of the rare earth and tellurium. The structures have box shaped lattices with in-plane crystallographic axes a and c that are nearly equal, with stacking along the b axis. The precise lattice constants depend on the rare earth. This structure is relatively easy to cleave and exfoliate leading to the formation of exposed tellurium monolayer surfaces.

It has been known for about twenty years that these materials exhibit charge density wave ordering on the cleaved surface at low temperatures. The rare earth tritellurides are notable since "low" temperatures can substantially exceed room temperature for some of these materials, for example ~ 650 K for LaTe$_3$. All of the materials exhibit a smectic charge density wave order with only discrete translational symmetry along the c direction, while systems with rare earths from Tb onwards exhibit a second charge density wave order at lower temperatures where

$$\rho(x,y) = \rho_a \sin\left(\frac{2\pi}{\lambda_a}x\right) + \rho_c \sin\left(\frac{2\pi}{\lambda_c}y\right) + ...,$$

which is a "checkerboard" charge density wave order which breaks all continuous rotations and translations down to discrete symmetries forming a crystal. Again we truncate to the leading Fourier components.

III. PEIERLS INSTABILITY

The Peierls instability is the result that "a one-dimensional equally spaced chain with one electron per atom is unstable." This result may be derived using perturbation theory on a non-interacting electronic system: first take the Hamiltonian for the whole system and then perturb it by by moving every other atom an amount δa so that the chain dimerized: pairs of atoms alternate spacing between $a + \delta a$ and $a - \delta a$. Such a perturbation necessarily results in "level repulsion" where the bands in the halved (folded) Brilluoin zone (doubled the unit cell) don't overlap at the zone edge. This perturbation results in lower energy states for the bands filled with electrons and consequently a lower energy configuration for the whole system. Hence in one dimension at one electron per atom the equally spaced configuration is unpreferred over dimerization.

Now this dimerization of atomic positions is precisely a charge density wave: the charge density oscillates sinusoidally in space. If a two dimensional material is quasi-one-dimensional in one direction–for example if it is comprised of atomic wires that are weakly coupled together, then the Peierls instability gives rise to a smectic charge density wave order at one electron per atom.

In general this picture of weakly coupled wires doesn't hold, for example in the rare earth tritellurides, but an extrapolation of this idea does hold. This extrapolation is Fermi surface nesting, which is when substantial areas of the Fermi surface (in two or three dimensions) are separated by the same momentum. In one dimension, Fermi surface nesting is perfect because the Fermi surface is two points which are necessarily separated by some momentum. In higher dimensions if parts of the Fermi surface are like parallel planes, as is approximately the case in the rare earth tritellurides, Fermi surface nesting occurs.

Once Fermi surface nesting occurs then the same perturbation theory arguments for one dimension hold along the real space direction corresponding to the momentum space separation of the parts of the Fermi surface that are parallel. This leads to similar dimerization behaviors and the formation of charge density wave order. In the rare earth tritellurides there are two sets of parallel portions of the Fermi surface which are separated by a momenta in a and a momenta in c. Whether these dimerize and form charge density wave order ultimately comes down to the free energy.

IV. FREE ENERGY LANDSCAPE

It is observed that the c directed smectic is more robust than the a order. Physically this corresponds to perturbation that forms the c directed charge density wave gapping the Fermi surface in the planes perpendicular to the a axis. In Ref. [1] the authors argue that shining light on LaTe$_3$ locally melts the smectic order leading to the formation of dislocations. In the region of these dislocations the gap at the Fermi surface closes enabling the formation of a axis charge density wave order.

Rather than proceeding from the microscopic electronic structure, one may employ a Ginzburg-Landau free energy to illustrate the competition of a and c charge density wave order. The authors of Ref. [1] postulate the free energy

$$F = \int d^2x \left(\delta|\phi_a|^2|\phi_c|^2 + \sum_{i=a,c} \alpha_i|\phi_i|^2 + \beta_i|\phi_i|^4 + \gamma_i|\nabla\phi_i|^2 \right)$$

which has two competing scalar fields $\phi_a(x)$ and $\phi_c(x)$. The terms in the summation are the standard lowest order rotationally symmetric terms, while the cross term

$\delta|\phi_a|^2|\phi_c|^2$ is the lowest order rotationally symmetric coupling term between the fields that leads to competition between the fields. Let $\beta_c < \beta_a$ correspond to the the preference of the system to order in c directed smectics rather than a directed smectic order.

When δ is sufficiently large ($\beta_a\beta_c > 4\delta^2$), ϕ_c will be non-zero while ϕ_a will be zero, otherwise the cross term would raise the free energy. On the other hand if δ is sufficiently small ($\beta_a\beta_c < 4\delta^2$), then both ϕ_a and ϕ_c will be non-zero, otherwise the quartic terms would raise the free energy. In this free energy picture, the effect of shining light onto LaTe$_3$ is to lower the value of δ so that the system swaps from c directed smectic order to phase coexistence with smectic order in both a and c directions.

V. SCATTERING

Scattering probes the reciprocal space structure of materials. In reciprocal space, a smectic is two points corresponding to the $+k$ and $-k$ components of the sinusoid, while a rectangular crystal is four points corresponding to the other variation in density in both $\pm k_x$ and $\pm k_y$. These patterns are duplicated since momentum in a crystal is only defined modulo 2π.

Studying the electron scattering from LaTe$_3$ before illumination, Fig. 1(a), we see the presence of large red peaks corresponding to the atomic positions, and fainter horizontal "satellite peaks" in between these corresponding to the formation of c axis charge density wave order. This corresponds roughly to the real space STM probe of electron density illustrated in Fig. 1(b) which exhibits smectic order (note the dislocation defects). After illumination, Fig. 1(c), the satellite peaks are doubled corresponding to the coexistence of a and c axis charge density wave order. This corresponds roughly to the real space STM probe of electron density illustrated in Fig. 1(d) which displays crystalline order. Note that the intensity of the horizontal and vertical satellite peaks is different, which corresponds to the different amplitude of the a and c charge density wave orders.

VI. OUTLOOK

Theories comprised of low-order symmetry-allowed terms are powerful. As we have seen, they enable the analysis of the electronic problem of charge density wave formation as that of a smectic liquid crystal. Additionally the Landau-Ginzburg free energy can be used to explain phenomenology of phase competition and coexistence. From this viewpoint, illuminating matter with light to change coefficients in the free energy presents a powerful and tunable method to change between phase competition and coexistence as exemplified by the example of driving the charge density wave order in LaTe$_3$ from a smectic liquid crystal order to a crystalline order.
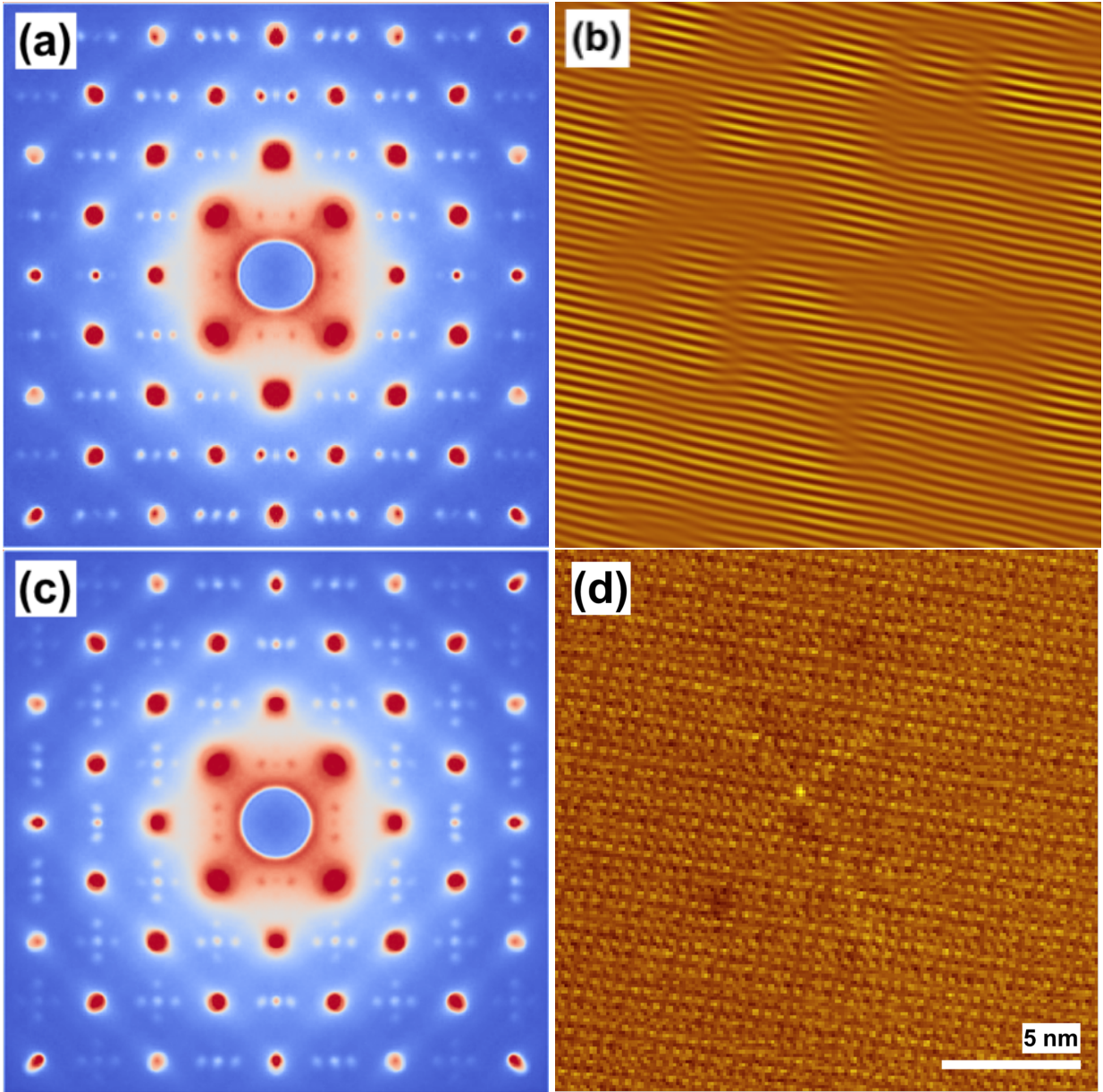
FIG. 1. Charge density waves (CDW) in the rare earth tritellurides. At high temperatures there is no CDW order, at intermediate temperatures there is smectic ordering along the c-axis, and at low temperatures there is crystalline CDW ordering. The rare earth tritellurides are layered two dimensional materials with *almost* square lattices in the layer. This slight anisotropy (0.1-1%) in the crystallographic a and c axes along with Fermi surface nesting leads to spontaneous smectic ordering along the c-axis below a transition temperature T_{c_1}. Some of the rare earth tritellurides form a checkerboard CDW below a temperature T_{c_2} whose charge density is that of *two* superimposed smectics aligned along the a and c axes; in combination these two CDW orders form a crystalline CDW that breaks all continuous translational symmetries. **(a)** In LaTe$_3$ at ambient temperature and pressure (300K/1 atm) a smectic CDW forms oriented along the c-axis of its crystal structure. This can be deduced from the intensity of elastically scattered electrons (incident energy 3 MeV): there are intense peaks corresponding to the atomic positions on the almost square lattice and weak peaks corresponding to the charge density wave order. The scattering peaks corresponding to CDW order only occur along the reciprocal lattice direction corresponding to ordering in c. Adapted from Ref. [1]. **(b)** ErTe$_3$ with 2% Pd doping at 1.7K exhibits a smectic CDW as shown in this STM image. While this is below T_{c_2} for this material, the disorder from the doping pushes it from checkerboard to smectic CDW order. Notice the presence of *defects* in this scan. This is the same structure we would expect for LaTe$_3$ in ambient conditions. Adapted from [2]. **(c)** Electron scattering from LaTe$_3$ at ambient temperature and pressure (300K/1 atm) 1800 fs after a 80 fs pulse of 800 nm laser light with intensity 5 mJ/cm^2 shows the formation peaks corresponding to a secondary charge density wave order along the a axis leading to the formation of a checkerboard CDW order. This corresponds to a rearranged free energy landscape following illumination with light. **(d)** STM of ErTe$_3$ with 0% Pd doping at 1.7K shows a checkerboard CDW order similar to what we would expect the post-illuminated structure of LaTe$_3$ looks like. Adapted from [3]. I couldn't find STM images of LaTe$_3$, hence the images of ErTe$_3$ instead.

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