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Order from Disorder

Dongbo Wang and Alejandro Fernandez-Martinez

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T (*4*), confirm the two modulation wave vectors, providing further details on the correlations and showing that below T_c, the applied field enhances the intensity of the scattering peaks (with the correlation length reaching 25 lattice spacings). Thus, it appears that the competing order responsible for the quantum oscillations has been detected, and details will likely soon be sorted out.

But this answer to the quantum oscillation problem leads to new questions. Although there has been a proposal regarding fluctuating charge modulations (*10*), many theorists believe that antiferromagnetic spin fluctuations play an important role in the mechanism of high-temperature superconductivity (*11*); however, the present charge modulations have no obvious connection with the observed spin modulations, especially the uniaxial spin modulations reported at lower doping (*12*). Have Ghiringhelli *et al.* detected a type of charge modulation that is universal among cuprates? Or does it depend on unique features of the $YBa_2Cu_3O_{6+x}$ structure? Do the indications of “conventional” electronic behavior revealed by the quantum oscillation experiments point to a hidden simplicity? Or do we still have to struggle with the challenging problem of strongly correlated electron physics? Whatever the answers, the work by Ghiringhelli *et al.* will surely stimulate more investigations in a fascinating field.

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MATERIALS SCIENCE

Order from Disorder

The repeat units of a crystalline material can be made up of disordered clusters.

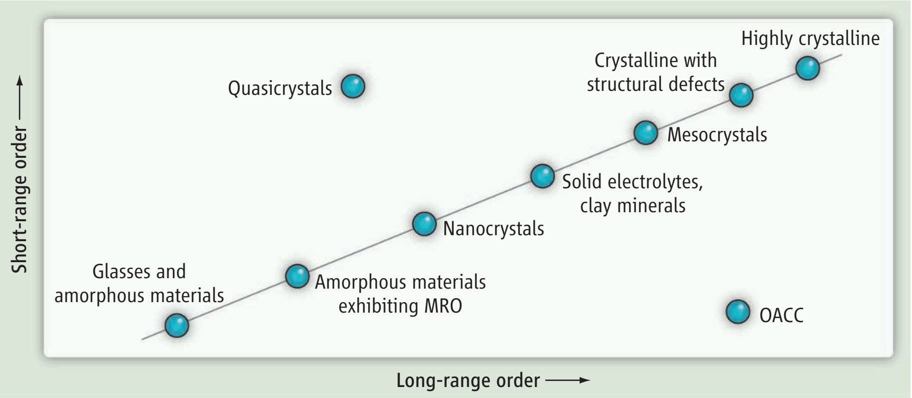
Dongbo Wang[1] and Alejandro Fernandez-Martinez[2]

Our understanding of the atomic structure of materials relies on our ability to describe structural characteristics such as the short-range order (in the case of liquids or amorphous materials) or the periodicity inherent to crystalline materials. On page 825 of this issue, L. Wang *et al.* (*1*) challenge our understanding of the inherent disorder that can be present in a crystal by presenting evidence for a crystalline material composed of amorphous clusters. They show that C_{60} molecules from the crystalline solvated fullerene phase C_{60}**m*-xylene undergo an order-to-disorder transition under compression at ≈35 GPa but keep their translational symmetry. A material can still possess long-range order even though its fundamental building blocks are disordered.

The resulting phase—a crystal composed of amorphous clusters or ordered amorphous carbon clusters (OACC)—showed both the x-ray diffraction reflections typical of a hexagonal close-packed (hcp) lattice and the broad oscillations of diffuse scattering typical of amorphous materials. Raman spectra indicate a high degree of disorder at the subnanometer scale of an amorphous component, and inelastic x-ray scattering (IXS revealed a transition from sp^2 carbon (that of native C_{60}) to sp^3 carbon. Together, these data provide strong evidence of a chemically heterogeneous and structurally disordered system, which could be termed amorphous. However, the *m*-xylene organic spacer that solvates the surfaces of the disordered carbon clusters is not highly reactive under the high pressures of the experiments and likely remains spatially ordered.

A simple classification of the degree of static topological order in solid-state materials can be established by quantifying their proximity to being crystalline or amorphous. The vast majority of materials exist within the continuum between these two end members (*2*, *3*). On one side, static disorder in crystalline materials has long been of interest because of the need to control defects in engineered materials for various applications. Crystallographic defects such as vacancies, interstitials, or stacking faults decrease the coherence of the crystal lattice, especially in crystalline nanomaterials, where a large number of atoms are at the interface resulting in surface relaxation effects that further reduce the size of their coherent domains (*4*).

Another example of crystalline solids showing a high degree of crystallographic disorder (i.e., disorder relative to a defect-free periodic lattice) is the cationic disorder. In solid electrolytes, such as AgS_2 or AgI, silver cations form a sublattice that exhibits a high degree of disorder, which results in a



Order up. Short-range order in most materials shows a strong dependence on long-range topological static order or disorder. Wang *et al.* show that the formation of OACC enlarges our current knowledge of this order-disorder diagram by expanding it to a region where amorphous clusters can be arranged in a periodic lattice, and it may serve as a conceptual end member to quasicrystals, which show substantial short-range ordering but little topological static ordering. In OACC, weak interacting solvent molecules of *m*-xylene act as spacers of the amorphous carbon clusters and hold the periodic structure.

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diffraction pattern with both amorphous and crystalline characteristics (*5*). In clay minerals, cations occupy positions in the interlayer pores that compensate the negative structural charge generated by isomorphic substitutions randomly distributed within the solid framework (*6*).

On the other end, although amorphous solids do not typically show long-range order, they can sometimes show hints of medium-range order (MRO) at the nanometer scale, especially when strong interatomic interactions are present (i.e., covalent solids) (*7*). In some of these materials, the "stiffness" and stereochemical (or directed) character of the intramolecular bonds is translated into a certain pseudo-periodicity at the medium-range scale that is reflected by the presence of a prepeak or first sharp diffraction peak in the x-ray or neutron diffraction pattern. Possible origins for MRO include the presence of interstitial-void correlations, the formation of ring-structure topologies, cation-cation correlations, or density fluctuations [see Zaug *et al.* (*8*) and references therein].

How do the findings of Wang *et al.* integrate into our current understanding of statically ordered or disordered materials (see the figure)? Generally, highly crystalline materials form through crystal-growth processes near equilibrium in the absence of impurities, or they are annealed at high temperatures in order to reach low-energy topological configurations. Under these conditions, growth units attach without structural distortion. At conditions further from equilibrium or in the presence of impurities, structural distortions (defects) result in higher degrees of structural disorder but the materials is still crystalline.

However, amorphous materials are synthesized by introducing substantial levels of impurities or by rapid formation during a phase transition, commonly melt quenching or solution precipitation, under conditions far from equilibrium. When disorder is induced during a phase transition, it extends to the molecular or atomic scale and necessarily propagates to longer length scales. When such materials are formed, it is likely impossible to introduce structural coherency over longer length scales, resulting in materials with hints of MRO at best.

Another mode of building order is the recently reported formation of mesocrystals (*9*) and the occurrence of oriented attachment pathways (*10*, *11*). Under conditions far from equilibrium, nanoparticles nucleate but grow so slowly that they aggregate in a structurally coherent manner. However, long-range order is hindered by low-angle misalignment between nanoparticles. Another unusual mode of building materials is found in quasicrystals, where metals can precipitate with high degrees of short-range rotational symmetry ordering that lack translational symmetry, resulting in poor long-range ordering.

The formation of OACC generates partial disorder through a secondary process, in this case pressure-induced amorphization, where the C_{60} component is deformable but the *m*-xylene is not. This approach could be generalized to produce hybrid structures, where one component in a multicomponent system could be designed to deform and become amorphous. The presence of a weak interacting spacer molecule seems to be an important requirement in order to keep crystallinity in the final deformed system. This work opens the door for the synthesis of intercalated sp^3 amorphous carbon materials with the potential for a huge variety of physical properties. For example, if dopant molecules replaced the *m*-xylene space, it might be possible to combine the superconductivity in alkali metal-intercalated C_{60} (fullerides) (*12*) and the exceptional high hardness (*13*) in sp^3 three-dimensional polymers of C_{60}.

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CELL BIOLOGY

An Ancient Portal to Proteolysis

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The discovery in archaea of an alternative proteasome based on Cdc48 provides insights into the evolution of protein degradation machines.

Selective protein degradation in eukaryotes is mediated primarily by the ubiquitin-proteasome system, in which the small protein ubiquitin is covalently attached to a target protein to signal its degradation by the 26*S* proteasome (*1*). The ubiquitin-proteasome system may include as many as 1000 distinct gene products, thus constituting one of the broadest regulatory systems in nature. Recent work, including a report by Barthelme and Sauer on page 843 of this issue (*2*), has shed light on how this baroque pathway may have evolved and raises some unexpected possibilities for the mechanism by which proteins are delivered to proteasomes for their destruction.

Although no prokaryote has a bona fide version of the eukaryotic ubiquitin-proteasome pathway, various archaea and bacteria contain adenosine triphosphate (ATP)–dependent proteases that are of the same basic design (*3*, *4*). For example, many archaea have a proteasome-like complex known as PAN (*3*, *4*). PAN is composed of a hollow, 28-subunit proteolytic core particle (the 20*S* core particle), in which proteins are degraded, and a 6-subunit adenosine triphosphatase (ATPase) complex (the PAN cap). The PAN cap activates the core particle by opening up a channel and translocating in substrates while unfolding their globular domains. Ancestral variants of ubiquitin are also found in archaea, although the most prominent of these are not used to tag proteins for degradation (*5*). Nonetheless, ubiquitination-like protein conjugation systems linked to protein degradation have been found in archaea and some bacteria (*6*, *7*).

Among the curiosities of the eukaryotic ubiquitin-proteasome system is an ATPase complex known as Cdc48 (sometimes called p97 or VCP) (*8*). Its subunits form a six-membered ring, similar to the proteasomal

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