Designing disorder at the atomic scale

The crystal structures of solids can exhibit a vast array of different atomic arrangements, which may also change depending on conditions, temperature, pressure, etc. In new research, a team led by Dr Daniel Chaney, based at the European Synchrotron Radiation Facility (ESRF) in France, have used cutting-edge techniques to show for the first time how some materials display exciting new properties when they are prevented from adopting their preferred atomic arrangements. Their results could pave the way for many useful applications, but may also have a profound influence on the ways in which physicists view disorder within solid materials.

The orderly arrangement of atoms or molecules on a 'crystal lattice' is a common feature of many solid materials. When seeking to understand the physical properties of a material, and to predict how it will behave in different scenarios, it is crucial for physicists to measure the arrangement of the atoms as precisely as possible. To do this, studies carried out over the past century have measured how beams of radiation, most often x-rays, are scattered as they pass through crystals.

'Classical crystallography' techniques allow researchers to accurately measure the spacings between the atoms as they are arranged on the lattice – enabling them to successfully predict a wide variety of material properties. Yet as modern crystallography techniques become more and more sensitive, physicists are increasingly finding that the crystal structures of many solids are less orderly than once thought. In some cases, certain atoms can be shifted into unexpected positions, replaced with other types of atoms, or even removed entirely – introducing varying degrees of disorder into a material.

Furthermore, these features aren't always random: in some materials, clear patterns can emerge, giving rise to short-range correlations between disordered atoms. For Dr Chaney (European Synchrotron Radiation Facility (ESRF), France), this effect is crucial for materials physicists to consider. 'This phenomenon is known as "correlated disorder" and is responsible for many of the exotic properties found in promising new materials,' he explains. Through their research, Dr Chaney's team have revealed an entirely new form of correlated disorder, which could have important implications for our understanding of how solid materials behave and may be exploited when designing future advanced materials.

INDUCING POSITIONAL DISORDER

Crystals can display a diverse array of atomic geometries: from simple cubic lattices, to more complex hexagonal patterns and even arrangements with far less symmetry such as the orthorhombic structures. However, in many cases these arrangements are far from fixed: with variations in factors such as temperature and pressure, materials will always seek to possess the least amount of energy possible, by transitioning between different atomic arrangements.

In their latest study, Dr Chaney's team, including researchers from the University of Bristol, UK, focused on a particular effect named 'positional' disorder: describing points within a lattice where atoms can be found at some distance away from their expected positions.

To study this phenomenon, the researchers turned to a technique called 'epitaxial deposition', which allows for thin crystal films to be built up layer-by-layer on top of a substrate crystal such that the atomic structure of the film

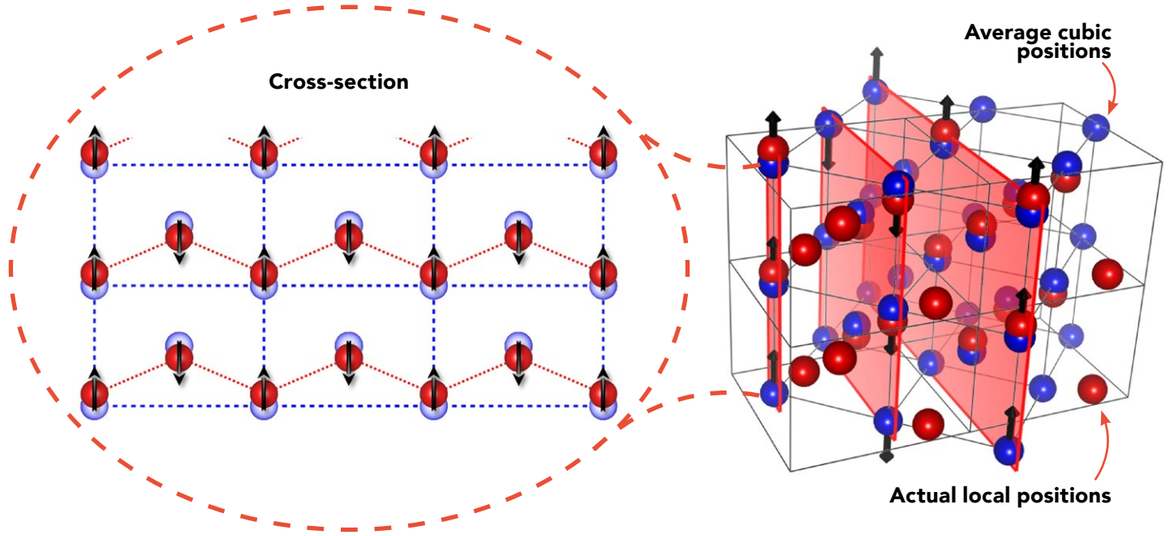

Figure 1. Right: The relationship between the average, cubic crystal structure (blue) and the actual, local crystal structure (red). To transition from the average to local structure the atoms within each red plane move together in the direction indicated by black arrows. Note that only three select planes are shown but every atom is displaced. Left: a cross-section perpendicular to the red planes highlighting the difference in atomic positions.

has a well-defined relationship to that of the substrate. More specifically, the team used a method named 'epitaxial matching.' Dr Chaney describes, 'with this technique, two different crystals with similar structures can be grown atop one another, such that they lock together like jigsaw pieces.'

This interlocking structure can produce a highly unique property: as the epitaxially-deposited crystal tries to transition from one form into another, sometimes it 'snags' on the crystal structure of the substrate below. Such that 'if one layer subsequently tries to adopt a different structure, this interlocking can frustrate the transition,' Dr Chaney explains.

The team used these epitaxial matching techniques to construct an alloy containing a mixture of uranium and molybdenum (UMo), on top of a niobium substrate. Measuring just 300 nanometres thick, the material was deposited at temperatures of 800 °C. Under these conditions, the uranium and molybdenum atoms are arranged on a highly symmetric cubic lattice – but would typically reorganise themselves into another, lower symmetry structure as the metal cools. In this case, however, the picture changed entirely.

RETAINING CUBIC ARRANGEMENTS

To understand what happened to the UMo alloy, it is first important to grasp the concept of 'metastability' in materials. As a simple example, we can think of a ball rolling down a roughly-textured hill, pulled downward by gravity. In some cases, the downward motion of the ball can fall into small valleys on the hillside, temporarily halting its downward motion. Yet if the ball's momentum allows it to roll just far enough uphill to get out of the valley, it will continue rolling down the hillside, until it reaches the bottom.

In this case, the rolling of the ball is comparable to a cooling alloy's continually changing crystal structure, and the smaller valleys on the hillside are like the atomic arrangements it adopts along the way. Although these structures may be stable momentarily, they will inevitably decompose after a certain time, until the material reaches its lowest energy state.

As a form of disorder that has gone undetected, this phenomenon could have profound effects on material properties that depend on the underlying atomic structure.

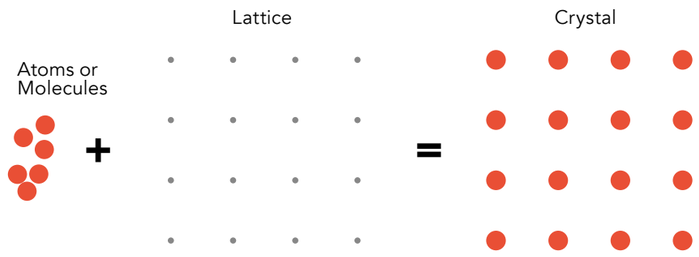

Figure 2. A crystal structure is formed when an atom, group of atoms or a molecule is added to every lattice position.

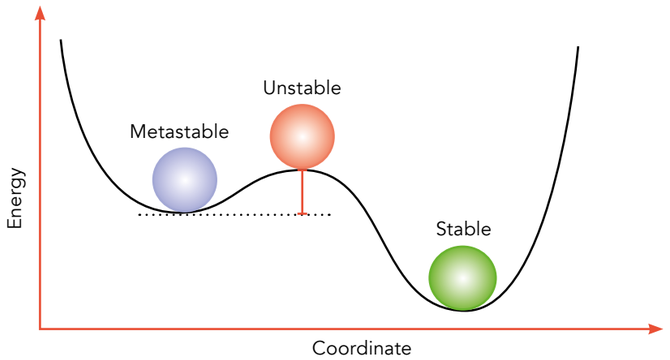

Figure 3. A general 'hill and valley' energy diagram showing stable, unstable and metastable states. The orange bar indicates the energy needed to move from the metastable to stable state.

As a result, these temporary valleys of stability are named 'metastable' states.

As Dr Chaney discovered, if a UMo alloy is epitaxially matched with a niobium underlayer, transitions between metastable states are prohibited from occurring – as if a ball had permanently come to rest in a small hillside valley. 'Instead of decomposing, interlocking forces the UMo alloy to retain its cubic structure as it cools, preventing uranium from adopting its preferred orthorhombic crystal structure,' he explains. As a whole, the atomic arrangement remains far more symmetrical than the alloy's uranium atoms would prefer at room temperature.

A NEW FORM OF DISORDER

To study the characteristics of their new metastable material in more detail, the researchers next measured the scattering of x-ray beams as they passed through the film. In itself, this crystallography technique presented a significant challenge: while x-ray scattering experiments are now very common, thin films are difficult to study since there is little material available to scatter the beam. Fortunately, the x-ray beam at ESRF was intense enough to overcome this challenge, allowing Dr Chaney and his colleagues to clearly identify the atomic arrangement of their alloy, despite the film thickness being just 1/70th the diameter of an average human hair.

Remarkably, their results revealed an entirely new type of correlated disorder. While the symmetry of the metastable cubic lattice was maintained on average, every atom in the alloy had actually been displaced from their expected positions – introducing correlated, short-range patterns of disorder. This meant that on an atomic scale, where only the arrangements of immediately neighboring atoms are considered, a lower-symmetry structure was actually recovered, reminiscent of uranium's preferred room temperature symmetry. Furthermore, the strength of the correlated disorder could be carefully tuned, by varying the amount of molybdenum present within the alloy.

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Now, there is an oft-quoted adage amongst physicists that 'structure drives function', that is, many of a material's properties are governed by the underlying arrangement of its atoms. Given this, the team set about to explore whether the correlated disorder evident on an atomic scale would manifest into an observable change in the macroscopic properties of the material. More specifically they used a technique called 'inelastic x-ray scattering' to probe how vibrations travel through the lattice. To further strengthen their results, Dr Chaney's team supplemented their experimental investigations with computer models based on the most advanced physical theories to date. These can make predictions of crystal structures in varying environmental conditions and then simulate their vibrational properties.

These efforts revealed that the correlated disorder, which exists only on an atomic scale, does indeed lead to large changes in the material's physical properties. 'By combining these scattering experiments with theoretical simulations, we showed that this exotic form of disorder strongly affects how the atoms vibrate,' Dr Chaney illustrates. 'In turn, it dramatically reduces the effectiveness with which these vibrations can carry thermal energy.'

DESIGNING FUNCTIONALITY

Overall, the correlated disorder uncovered by the team arises from a 'crystallographic conflict' between the preferred, atomic-scale symmetry of atoms within the alloy, and the higher symmetry of the lattice they have been arranged upon. Importantly, these effects are not confined to the specific alloy they studied, and instead may be expected in any material where such 'crystallographic conflict' can be produced. As a form of disorder that has gone entirely undetected so far, this phenomenon could have profound effects on any material properties that depend on the underlying atomic structure. 'This makes it an exciting tool for designing disorder and functionality into materials, and hints at a deep link between metastability and correlated disorder,' Dr Chaney concludes.

On one level, this success presents promising opportunities for physicists to engineer new, tuneable, and highly exotic materials – which could conduct heat and electrical current in unusual, and potentially incredibly useful new ways. Yet Dr Chaney also believes that the implications of his team's results could go deeper: arguing that the ability of a material to host correlated disorder could be the very property that allows many metastable systems to exist in the first place. If correct, this may call for physicists to take a closer look at many materials previously considered well understood and instead go hunting for unusual forms of disorder which may be significantly more prevalent than previously thought.

Behind the Research

Dr Daniel Chaney

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Research Objectives

Dr Daniel Chaney researches new behaviours arising from the disorder found in materials, as well as mechanisms by which to control such disorder.

Detail

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Bio
Daniel attended the University of Bristol, UK, from 2012 to 2021, first obtaining a masters degree in physics in 2016 before completing his PhD in 2021. He is currently in Grenoble, France, where he holds a postdoctoral scientist position on the ID28 beamline at the European Synchrotron Radiation Facility (ESRF).

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Personal Response

What opportunities could be presented by inducing correlated disorder in other materials?

"The most obvious avenue of exploration would be designing new types of materials within the class known as 'thermoelectrics'. These are incredibly interesting materials that generate electricity from a temperature gradient and vice versa. Importantly, the key factor in their efficiency is the ratio between a material's electrical conductivity and its thermal conductivity. We have demonstrated that this new form of correlated disorder can dramatically reduce the thermal conductivity mediated by atomic vibrations, however, as a metallic alloy the majority of the thermal conductivity in our samples is unfortunately carried by the electrons. If instead one could realise the same type of disorder in a semiconducting or insulating material, this would be an exciting avenue for designing new thermoelectric materials."