News & views

Ultrafast spectroscopy

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Unveiling ultrafast disorder dynamics

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A pump–probe experiment utilizing the pair distribution function method characterizes ultrafast evolution of length-scale-dependent structural disorder in a crystal on a local level. This may have important implications for understanding ultrafast photoinduced transitions in solids.

Photoinduced transitions are thoroughly familiar to anyone who has ever sunbathed on a beach or observed paling of a formerly colourful toy long lost in a garden. Light-induced changes occur in individual molecules, their assemblies and in ordered crystalline lattices. Some of these effects are of great utility. Examples range from an old-style photographic film to fast optical switches in modern electronics. Understanding the microscopic mechanism of photoinduced transitions, especially those occurring on ultrafast (sub-picosecond) time scales, is key for harnessing their technological potential. The dynamics of ultrafast transitions is best characterized using the so-called pump–probe techniques. A femtosecond flash of light (the pump) induces a change in the material, and a time-delayed light flash (the probe) is used to study the material's properties. By varying the delay, one reconstructs the evolution of the system as the transition proceeds. The pump and the probe can have different photon frequencies. Terahertz to ultraviolet photons are used routinely. This energy range contains many of the electronic, magnetic and structural excitations relevant in solid state physics. Full understanding of the material, however, requires knowledge of its atomic structure. Structural information is obtained using photon wavelengths comparable to interatomic distances. This requires X-ray-based probes. Femtosecond X-ray pulses of the necessary brightness have recently become available at X-ray free electron laser (XFEL) facilities, enabling ultrafast structural studies of photoinduced transitions. This rapidly developing technique regularly produces breakthrough-type results. Writing in this issue in *Nature Materials*, Jack Griffiths and co-workers[1] study photoinduced structural changes in $CuIr_2S_4$. They observe ultrafast evolution of structural disorder using the atomic pair distribution function (PDF) extracted from diffraction of XFEL pulses. Unlike regular X-ray diffraction, PDF measurements characterize local structure. Now this is done on ultrafast time scales.

$CuIr_2S_4$ crystallizes in the cubic spinel structure, in which Ir atoms form a three-dimensional network of corner-sharing tetrahedra. At high temperatures, all the Ir atoms are equivalent, exhibit the $Ir^{3.5+}$ oxidation state and the compound is metallic. With decreasing temperature, an abrupt structural transition occurs at 230 K, at which the system becomes insulating and the Ir charges undergo ordering: one half of the iridium ions are now Ir^{4+}, and the other half Ir^{3+}. While all the electrons are paired in Ir^{3+}, each Ir^{4+} ion carries an unpaired electron of the $d_{xy/xz/yz}$ type. All the Ir^{4+} ions pair up forming Ir dimers. In each dimer, the two lone *d* electrons hybridize and form a state not unlike a chemical bond. As a result, the Ir^{4+} ions move closer to each other, making a structural dimer. The Ir dimers form an intricate order[2] consisting of weakly interacting chains[3] in which Ir^{4+} dimers are separated by two Ir^{3+} ions (Fig. 1). The dimers bond in two crystallographic directions, shrinking the structure and making it approximately tetragonal.

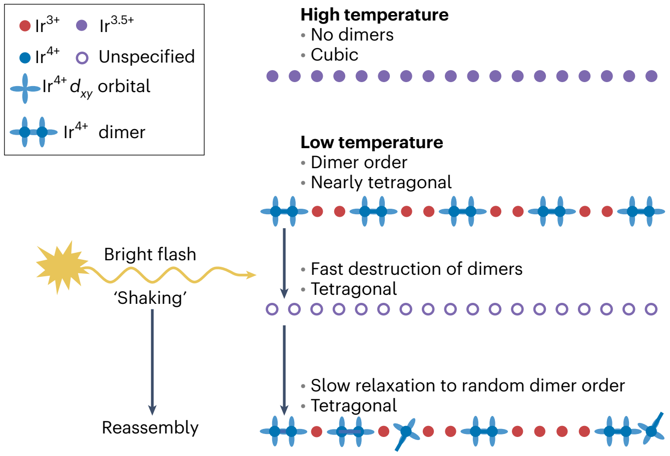

Fig. 1 | Iridium chains in $CuIr_2S_4$. All Ir ions are equivalent at high temperature. At low temperature, Ir^{4+} dimers order as shown. A flash of light destroys the dimers. Afterwards, the dimers reassemble effectively but not perfectly. In the bottom sketch, interchain dimers are present. The jigsaw puzzle is only partially recovered.

Intense light destroys the dimer order[4]. However, practically all the dimers remain in the crystal[5]. They gradually disorder with continuing irradiation, going through a state with incommensurate[6] correlations, and ending in what might be a complete disorder. Empirically, the process may resemble shaking of a box with closely packed hard spheres in which random close packing is eventually attained. The dimer bonds probably remain predominantly in the same plane because the crystal becomes truly tetragonal. It also becomes metallic. The microscopic states involved in the disordering process are unknown.

Griffiths and colleagues destroy the dimer order by an intense infrared flash (pump) and study how the structure evolves using XFEL X-ray pulses (probe). The key of their work lies in the X-ray diffraction methodology. Regular crystallography uses Bragg peak intensities. It measures the average structure and therefore cannot detect dimers in the disordered state. Local information can nevertheless be extracted from scattering data. For example, by taking the Fourier transform of a powder diffraction scan, one obtains the pair distribution function that gives the distribution of distances between pairs of atoms[7]. PDF 'sees' the local dimers directly and provides quantitative information on their bond lengths and concentrations. Measuring PDF requires taking high-quality diffraction data in a large range of scattering vectors. This is difficult. Griffiths and colleagues succeed in measuring time-resolved PDF on sub-picosecond scales. They observe true destruction of the dimers upon the flash. The unit cell remains tetragonal. Therefore, a previously unknown un-dimerized state is induced (the high-temperature structure is cubic). System relaxation is then observed, presumably leading to the disordered dimerized state (Fig. 1). The PDF method allows characterization of the relaxation process on different length scales, tracking the developing local structure in space and time.

Knowledge of time-dependent local structure is useful for understanding any photoinduced transition. For ultrafast transitions, it may be of key importance. System dynamics is commonly described using collective excitations, such as phonons. In ultrafast transitions, there may be not enough time for their full development. Substantial disorder can also occur. These phenomena are of obvious importance to such fields as nonlinear phononics[8], in which anharmonic vibrations are used to selectively modify the lattice, producing otherwise unachievable orbital and magnetic orders, superconductivity and topological phases. Pushing the X-ray PDF method into the true femtosecond scale may prove to be very beneficial for the future work on ultrafast transitions in solids.

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Competing interests

The author declares no competing interests.