Ultrafast dissolution and creation of bonds in IrTe$_2$ induced by photodoping

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The observation and control of interweaving spin, charge, orbital, and structural degrees of freedom in materials on ultrafast time scales reveal exotic quantum phenomena and enable new active forms of nanotechnology. Bonding is the prime example of the relation between electronic and nuclear degrees of freedom. We report direct evidence illustrating that photoexcitation can be used for ultrafast control of the breaking and recovery of bonds in solids on unprecedented time scales, near the limit for nuclear motions. We describe experimental and theoretical studies of IrTe$_2$ using femtosecond electron diffraction and density functional theory to investigate bonding instability. Ir-Ir dimerization shows an unexpected fast dissociation and recovery due to the filling of the antibonding $d_{xy}$ orbital. Bond length changes of 20% in IrTe$_2$ are achieved by effectively addressing the bonds directly through this relaxation process. These results could pave the way to ultrafast switching between metastable structures by photoinduced manipulation of the relative degree of bonding in this manner.

INTRODUCTION

The study of interactions among different degrees of freedom strongly coupled to the lattice is a crucial key for elucidating and manipulating material properties (1). The mechanism of structural phase transitions with the modulation of the electron density and the associated periodic lattice distortions (PLDs) represent an especially challenging issue for elucidating cooperative phenomena (2–5). IrTe$_2$ is of particular interest to survey the relationship between structural phase transitions and orbital ordering in the presence of strong spin-orbit coupling (6–12). IrTe$_2$ is a quasi-two-dimensional layered system, which undergoes a first-order structural transition between two crystalline phases at 260 K (12). The conduction electron density becomes modulated in a complex way, and modifying forces among the ions and generating PLDs with the bond lengths shortened: Ir-Ir and Te-Te bond lengths in the low-temperature (LT) phase decrease by 20 and 10%, respectively, compared with those in the high-temperature (HT) phase (13–17). This is due to bond formations, observed as the formation of in-plane Ir dimers and/or polymerization of Te chains (12, 13, 15) and accompanied by orbital/charge ordering observed by core-level photoemission spectroscopy (18, 19).

According to angle-resolved photoemission spectroscopy and density functional theory (DFT) studies (13, 16), the electronic structure of IrTe$_2$ near the Fermi level ($E_F$) shows a multi-orbital system consisting of Ir 5d and Te 5p and preserves its metallic properties in both LT and HT phases. In the LT phase, the density of states (DOS) at the bottom of the conduction band has a large contribution from Ir $t_{2g}$ orbitals, and the $d_{xy}$ orbital is expected to play an important role in the structural phase transition and stabilization of the LT phase (13, 17). Dimerization in IrTe$_2$ is quite a special example among phase transitions exhibited in transition metal dichalcogenides, in contrast to the well-known charge density wave (CDW) type transition, resulting in an energy gap formation at $E_F$ in many other transition metal dichalcogenides and rare earth tellurides (20–22). Although there is no clear evidence of the CDW gap in IrTe$_2$ below the transition temperature (10, 15, 16), the suppression of DOS (pseudogap) is observed, similar to that in high-$T_c$ cuprate superconductors (15, 16, 23). The phase transition toward LT in IrTe$_2$ has been suggested to originate in intralayer Ir-Ir dimers, which compete against the interlayer Te-Te bonds (9, 12). Besides, strong spin-orbit interactions appear to destabilize Ir dimers and possibly influence the structural phase transition temperature in IrTe$_2$ (11, 13, 18). These experimental results suggest that the orbital and/or charge ordering in IrTe$_2$ is different from that in the conventional CDW induced by Fermi surface nesting and momentum-dependent electron-phonon coupling (16).

Femtosecond time-resolved techniques “light up” the various active degrees of freedom by abruptly modulating the electronic distribution while mostly preserving the energy transfer mechanism and coupling strengths among electron, spin, and lattice subsystems (24, 25). While extensive experiments in IrTe$_2$ have been performed (6–19), time-resolved experiments have not been demonstrated as yet. Here, we investigated the structural dynamics of PLD in 20–100-nm-thick, free-standing slices of single-crystal IrTe$_2$ (see the Supplementary Materials). The present ultrafast pump-probe experiment operates on the natural time scale of strongly coupled electronic and lattice degrees of freedom in IrTe$_2$ and allows an unprecedented insight into the physics underlying these complex orderings.

RESULTS

We performed femtosecond electron diffraction (FED) experiments in the transmission geometry along the c axis in both HT (300 K)
and LT (at ~200 K) phases. Figure 1 shows the background-subtracted electron diffraction pattern on 40-nm-thick IrTe$_2$ in the HT and LT phases, respectively. In the HT phase, the obvious electron diffraction patterns with the sixfold symmetry of the trigonal structure are observed. In the LT phase, the sequence of four weak superlattice peaks (SLs) highlighted by the arrows is visible between two Bragg peaks (BPs).

The time evolution of the relative intensity change of the diffracton signal is shown in Fig. 2 in the vicinity of BP and SL following photoexcitation by an optical pump pulse. Relative intensity changes from a BP and a nearest-neighboring SL are observed, as shown in Fig. 2 (A to D) (see also fig. S3). The corresponding lattice dynamics of the relative change in the Bragg peak ($\Delta I_{\text{Bragg}}/I_{\text{Bragg}}$), superlattice peak ($\Delta I_{\text{SL}}/I_{\text{SL}}$), and inelastic background ($\Delta I_{\text{BG}}/I_{\text{BG}}$) are plotted as functions of optical delay time in Fig. 2F. The intensity of SL is suppressed by ~13% on time scales of ~200 and 300 fs for 400- and 800-nm pump pulses, respectively, where the data are fit by two exponential decays. The decrease of $\Delta I_{\text{SL}}/I_{\text{SL}}$ and the accompanying increase of $\Delta I_{\text{Bragg}}/I_{\text{Bragg}}$ illustrate a cooperative behavior, indicating that the optically induced

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**Fig. 1. Static electron diffraction image of IrTe$_2$ obtained by ultrahigh acceleration voltage 128-kV electron pulse.** The upper panels are the electron diffraction obtained at 300 K (HT phase) and ~200 K (LT phase). The Miller indices (h k l) are also shown. Magnified view of the diffraction intensity (I) near the bright BP (see the white box in the upper panels) is also shown as an inset. The symmetry breaking, which corresponds to the presence of superlattices, is observed in the LT phase, as shown by arrows, and indicates the existence of a structural phase transition with modulation wave vectors $\mathbf{q}$ of (1/5, 0, 1/5) due to Ir-Ir dimerization and Te-Te polymerization (7, 9, 13). The bottom panels are the schematic illustration of IrTe$_2$ layers at the HT and LT phases. The HT phase observed at room temperature is formed by hexagonally arranged iridium (Ir) atoms, sandwiched by two tellurium (Te) layers coordinating the central Ir atom in an octahedral arrangement (7). In the LT phase, the structural change is associated with the phase transition at $T_s \sim 260$ K in combination with Ir-Ir (red line) and Te-Te (green line) dimerization with cooling from room temperature.
Fig. 2. Photoinduced time-dependent structural changes monitored by ultra-bright FED. (A to D) Differences of the diffraction patterns of the photoinduced and initial LT phases as a function of the delay time between the optical excitation and electron probe pulses, where the index at the HT phase is assigned. Note that red- and blue-colored scale denotes the increase and decrease of diffraction intensity after photoexcitation, respectively. (E) Wide view of the diffraction pattern subtracting of pump-probe and probe images after photoexcitation (+0.6 ps). (F) Relative intensity changes (ΔI/I) for selected BPs and SLs. The intensity of BP from the host lattice is multiplied by two to see more clearly, and the fast dynamical processes are shown in (G). The excitation fluence was ~0.55 mJ/cm². The sample was photoexcited by 50-fs, 800-nm optical pulses at a repetition rate of 1 kHz. (G) Fast dynamical processes taken by 400- and 800-nm pump pulses, as indicated. Exponential fitting takes into account the electron and pump pulse duration with an error function as a guide to the eye. For ΔMu/μL (ΔμBG/μBG), τ1,FED ~ 200 fs (230 fs) and 300 fs (500 fs) for 400- and 800-nm pump, respectively.

DISCUSSION

To obtain a better understanding of the process, we have used DFT to calculate the energy difference between the dimerized and nondimerized states (ΔE = E_dimer − E_nondimer) for several equilibrium temperatures. Because of fast electron-electron scattering, the electron system thermalizes rapidly, and we can approximate it with a Fermi-Dirac distribution with a certain elevated temperature from ambient. At LTs (region 1 of Fig. 3A), the system has two energy minima at the Ir-Ir distance of 3.1 and 3.9 Å, reflecting a stable state and a metastable state, respectively. The dimerized state has the lowest total energy (ΔE < 0); therefore, the system stays in the dimerized state. When the electron temperature exceeds 3 × 10³ K (0.26 eV), ΔE is reversed (ΔE > 0): Only one minimum remains in the potential energy at an Ir-Ir distance of 3.9 Å, reflecting that the nondimerized state is stable and the dimers break (region 2). Inclusion of spin-orbit coupling makes the dimerized phase slightly less stable (see the Supplementary Materials). Surprisingly, the dimerized state becomes stable again when the electronic temperature is increased further above 2 × 10⁴ K (1.72 eV), which implies the complexity of the occupation of the antibonding orbital and the filling of additional higher lying bonding orbitals in the excited states.

To strengthen this interpretation, we have also calculated the forces applied on the ions with fixed electron occupation. This calculation shows that when exciting electrons from the valence to the conduction band by adding 0.61 eV of energy, the Ir-Ir dimerized atoms move in opposite directions (Fig. 3B). This reflects dimer breaking in region 2. When looking at the DOS of those two atoms (see the Supplementary Materials), we observe that these electrons are mainly related to d orbitals that coincide with the above-mentioned dxy antibonding state. This is a rather intriguing result and illustrates complex light-induced chemistry driven by ultrafast changes in the occupation of antibonding and bonding d orbitals. This electronic temperature range (3 × 10⁻³ to 2 × 10⁴ K) also coincides with the width of the dxy antibonding band predicted in (13, 17).
The short decay time scale is attributed to the partially dissolved, while the intermediate decay time scale indicates energy transfer, implying that Ir 5d and Te 5p orbital orders (15) are state dynamics sensitive to the orbital occupations and DOS at E_pump-probe spectroscopy measurements, reflecting the electronic action between lattices and electrons. We have performed all-optical the electronic subsystem via optical spectroscopy to elucidate the inter-
tion on the 150-fs time scale, followed by a fast recovery with a decay time of \( \tau_{1,opt} \approx 200 \) fs and subsequent slower decay with a relaxation time of \( \tau_{2,opt} \approx 10 \) ps. The short decay time scale is attributed to the energy transfer, implying that Ir 5d and Te 5p orbital orders (15) are partially dissolved, while the intermediate decay time scale indicates.

Besides, when the electronic temperature is below \( 3 \times 10^3 \) K, the probability of dimer breaking due to the electronic contribution is rather small, leaving the thermal contribution dominating. In line with the previous discussion of initial excitation, and subsequent electron thermalization and coupling to the lattice, the superlattice demonstrates a two-step recovery process: \( \tau_{1,FED} \) that is mainly due to the electron occupation of the antibonding orbital and \( \tau_{2,FED} \) that mainly arises from the electron-phonon coupling. However, the fast recovery of the \( \Delta I_{\text{Bragg}}/I_{\text{Bragg}} \) is obscured by the simultaneous reduction of BP intensity resulting from the Debye-Waller effect at the same time scale of \( \tau_{1,FED} \). Note that a suppression of \( \Delta I_{\text{SL}}/I_{\text{SL}} \) on a long time scale (>10 ps) mainly comes from the Debye-Waller effect and thermally induced structural changes. Another plausible explanation is partial suppression/distortion from homogeneous thermalization of electrons. With the excitation used in the experiment (<1 mJ/cm²), the electron temperature is very low with a homogeneous thermalization. The electron temperature cannot reach the dxy antibonding state, and DFT calculation shows that with such an amount of electron temperature change, it is not enough to bring structural change toward the HT phase, and the forces applied to the dimerized ions are rather complex.

It is informative to compare the structural dynamics with those of the electronic subsystem via optical spectroscopy to elucidate the interaction between lattices and electrons. We have performed all-optical pump-probe spectroscopy measurements, reflecting the electronic state dynamics sensitive to the orbital occupations and DOS at \( E_F \) (26). The photoinduced reflectivity change (Fig. 4A) shows a rapid onset on the 150-fs time scale, followed by a fast recovery with a delay time of \( \tau_{1,opt} \approx 200 \) fs and subsequent slower decay with a relaxation time of \( \tau_{2,opt} \approx 10 \) ps. The short decay time scale is attributed to the energy transfer, implying that Ir 5d and Te 5p orbital orders (15) are partially dissolved, while the intermediate decay time scale indicates...
that hot electrons release the energy to the lattice via phonon emission and the lattice temperature abruptly increases. Figure 4C shows a Fourier transform (FT) of the oscillation after subtracting the non-oscillating transient spectrum shown in Fig. 4B. Three distinct peaks at 1.5, 2.6, and 3.8 THz seen in the spectrum correspond to wave numbers of 53, 86, and 126 cm$^{-1}$, respectively. These frequencies coincide with Raman modes with $A_g$ and $B_g$ symmetry in the LT phase (27) that can be coherently excited by the pump pulse. The decay $\tau_{1,\text{opt}}$ matches quite well with the present FED results and indicates that the fast electronic contribution is due to the filling of the $d_{xy}$ antibonding orbital.

Figure 5 summarizes the transient photo-driven cooperative processes in IrTe$_2$. The present FED study reveals a dimer dissolution due to the population of the $d_{xy}$ antibonding state. In IrTe$_2$, hot electrons excited to the $d_{xy}$ antibonding state induce the breakup of Ir-Ir dimers, which quickly recover because of the reduction of the electron density in the $d_{xy}$ antibonding state as the electrons thermalize and depopulate the antibonding state. Afterward, the electron-phonon interaction starts to dominate, and the lattice temperature increases near the HT phase. Thereby, the present study indicates that a specific lattice system is strongly coupled with the $d_{xy}$ orbital order. A recently published study using FED and time-resolved angle-resolved photoemission spectroscopy (tr-ARPES) has reported a similar dynamical process in In-In bonds on the Si surface (25). To further corroborate our findings, tr-ARPES would be helpful for understanding the non-equilibrium physics of materials with strong electron-phonon interactions (28).

The combined experimental FED and optical and theoretical DFT studies have uncovered surprising lattice dynamics reflecting nuclear motions strongly coupled with the electronic subsystem. The present work demonstrates that the ultrafast manipulation of orbital orders (namely, ultrafast switching between dimerization and nondimerization) and electronic control of the specific lattice subsystem are possible. This new insight can be used to control the degree of bonding, not as in the quantum control sense, but by explicit use of the localized changes in electron density to affect control over the lattice potential by photoexcitation to manipulate the material properties through change in bond order. It paves the way to the controlled breaking and creation of bonds by the applied pulse sequences. A more controlled excitation that can exactly fill in the antibonding orbital will also make the manipulation of the dimers more efficient. Switching between metastable structures with different bonding patterns, such as graphite-diamond, following this approach, would be particularly exciting. This straightforward experimental method will be extended for surveying the mechanism and control of interesting physical properties that holds potential to lead materials science to exploit metastable states as pathways to new material properties.

**MATERIALS AND METHODS**

Single crystals of IrTe$_2$ were fabricated by the self-flux technique. IrTe$_2$ thin films (20 to 100 nm in thickness) for FED were obtained from an IrTe$_2$ bulk sample using a microtome (the thicknesses were determined by the microtome). The thin films sliced from the bulk
sample were dropped into distilled water, picked up by a loop, and put onto a Cu mesh for transmission electron microscopy (TEM; see also the Supplementary Materials) to obtain a good thermal contact. The thin films of IrTe₂ on the Cu mesh were set on a sample holder made of oxygen-free Cu for both FED and optical pump-probe experiments. For both experiments, a sample temperature of 200 K was achieved using liquid N₂. We measured the sample temperature using a calibrated temperature sensor. The vacuum pressure was 10⁻⁶ Pa. We performed FED experiments using the fundamental (800 nm, 50 fs) output beam from a commercial Ti:sapphire laser system (Coherent). The fundamental laser pulse was split into two arms with a beam splitter for both pump and probe. A 266-nm laser beam was generated through the third harmonic generation and was directed onto a gold photocathode generating ultrashort electron pulses. Photoelectrons were finally accelerated to 128 kV by a dc electric field between the photocathode and anode plates. Discharged and directly transmitted electrons were focused with the magnetic lens onto a 1:1 fiber-coupled charge-coupled device camera (Quad-RO 4320, Princeton Instruments) coated with a P20 phosphor scintillator. To investigate the effect of optical excitation on the structural dynamics in IrTe₂, we demonstrated DFT calculation using the projector-augmented wave formalism for core-valence partitioning, as implemented in the Quantum Espresso code (29). Details of the DFT calculation are given in the Supplementary Materials.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/7/eaar3867/DC1

Section S1. Experimental methods
Section S2. Sample preparation
Section S3. Diffraction pattern of IrTe₂
Section S4. Dynamics on the Bragg and superlattice peaks
Section S5. Thickness dependence of lattice dynamics for Bragg and superlattice peaks
Section S6. Power dependence of lattice and electron dynamics
Section S7. DFT calculations
Section S8. Lattice temperature increases with the fluence of pump pulse
Fig. S1. Schematic diagram of the FED setup.
Fig. S2. Thin films and the TEM image.
Fig. S3. Delay time dependence of diffraction pattern.
Fig. S4. Lattice dynamics obtained from several BP's and SLs.
Fig. S5. Relative diffraction intensity change of IrTe₂ with different film thicknesses of 20 to 100 nm.
Fig. S6. Fluence dependence of FED and optical pump-probe experiments.
Fig. S7. Difference of electronic free energies of dimerized and HT structures as a function of electronic temperature, as calculated using DFT.
Fig. S8. Calculated forces on Ir ions after optical excitation.
Fig. S9. Calculated forces on the Ir ions in the dimerized structure after an instantaneous optical excitation.
Fig. S10. DOS contributions from the Ir ions.

REFERENCES AND NOTES


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