Soft-mode driven dynamics in ferroelectrics - new insight from ultrafast terahertz and x-ray experiments

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Abstract. The coupled lattice and charge dynamics connected with soft-mode excitations are mapped by nonlinear terahertz spectroscopy and ultrafast x-ray diffraction. Sub-picometer lattice displacements induce electron relocations over 100 pm in polycrystaline aspirin and ferroelectric ammonium sulfate (AS). In AS, the electron motions induce a macroscopic polarization switching.

The concept of soft modes has been introduced in the context of ferroelectric phase transitions to describe low-frequency lattice modes which approach zero frequency at the phase-transition temperature and, thus, give rise to the formation of a new lattice structure [1]. Soft modes display a particularly strong coupling to the electronic system since their displacements are intrinsically coupled to spatial relocations of electronic charge. This coupling makes the soft-mode frequency and vibrational absorption strength susceptible to both local fields in the material and to correlation effects. So far, experimental insight into soft-mode dynamics, the nonlinear response of soft modes, and soft-mode induced charge relocations has remained very limited. Here, nonlinear two-dimensional terahertz (2D-THz) spectroscopy [2] and femtosecond x-ray diffraction [3] are applied to unravel the relevant microscopic interactions. Moreover, we establish a new link between transient microscopic charge densities and macroscopic electric polarizations.

Polycrystalline acetylsalicylic acid ($C_9H_8O_4$, aspirin) was studied by 2D-THz spectroscopy to map the nonlinear dynamic behavior of the soft mode at 1.1 THz which is connected with a CH_3 rotation in the molecular entities [4]. This mode couples strongly to the π-electron density in the crystal and, thus, forms a hybrid mode with electronic charge oscillations. Upon resonant vibrational excitation with a THz field strength on the order of 50 kV/cm, one observes a pronounced blueshift of the vibrational resonance from 1.1 to 1.7 THz in the pump-probe signals and non-instantaneous signatures in the rephasing photon-echo signal with a 2D lineshape distinctly different from a third-order response. The nonlinear response is in the nonperturbative regime of light-matter interaction and governed by a THz-induced dynamic break-up of the electron-phonon correlation which is mediated via the local Lorentz field in the crystal. The weakening of electron-phonon correlation shifts the vibrational resonance to higher frequency, representing the by far dominating
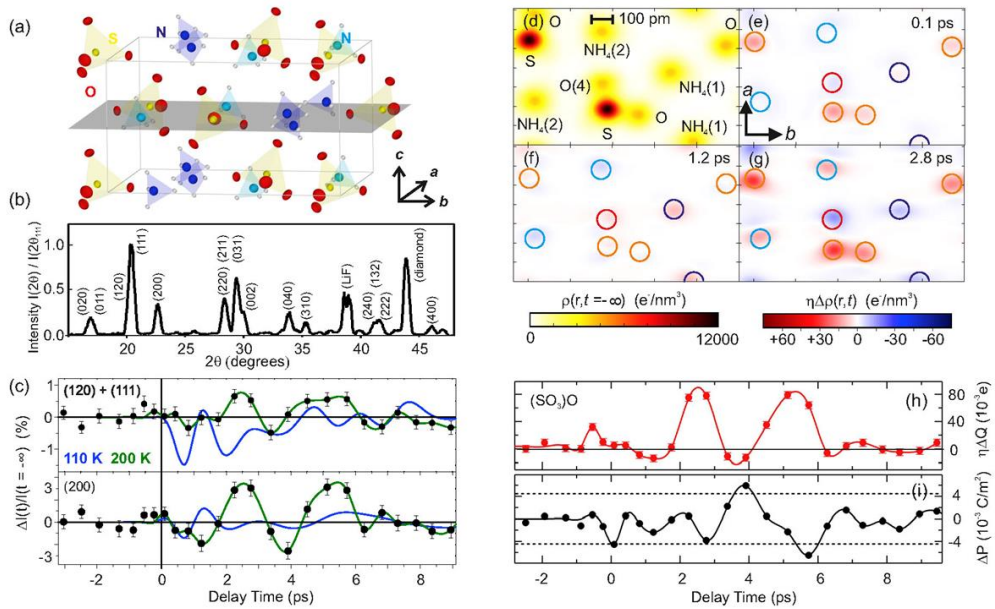
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Fig 1. (a) Equilibrium crystal structure of ferroelectric ammonium sulfate (AS). The grey area marks the lattice plane for which electron densities are plotted in panels (d-g). (b) Lineout of the equilibrium powder diffraction pattern of ferroelectric AS at 200 K. The x-ray intensity integrated over a particular Debye Scherrer ring is plotted as a function of the diffraction angle 2θ. (c) Transient changes of diffracted x-ray intensity for two reflections upon femtosecond excitation of ferroelectric AS at temperatures of 200 K (symbols, green lines) and 110 K (blue lines), the latter displaying a different time evolution. (d) Equilibrium electron density $\rho(\mathbf{r},t=-\infty)$ in the lattice plane marked in panel (a). The lettering gives the different molecular subunits. (e-g) Transient charge density maps $\eta\Delta\rho(\mathbf{r},t)$ for different pump-probe delays ($\eta\approx0.06$: fraction of excited unit cells). (h) Spatially integrated change of total charge $\eta\Delta Q(t)$ on the SO_3 subunits in the crystal structure as a function of pump-probe delay. (i) Change of macroscopic electric polarization ΔP as a function of pump-probe delay (dashed lines: amplitude of the stationary electric polarization of ferroelectric AS).

nonlinearity which is fully reproduced by in-depth theoretical calculations.

Nonlinear THz spectroscopy maps the vibrational response but provides only indirect information on the electronic charge motions connected with nonequilibrium soft-mode excitations. The latter issue is addressed by femtosecond x-ray diffraction which allows for deriving the spatially and temporally resolved electron density from the transient structure factors of the different x-ray Bragg reflections [3,5,6]. First x-ray powder diffraction experiments with a 100-fs time resolution on aspirin suggest pronounced relocations of π-electrons on a 100 pm length scale which are induced by coherent few picometer displacements of the 1.1 THz soft mode.

X-ray powder diffraction was also applied to determine transient charge density maps of ferroelectric ammonium sulfate [$(NH_4)_2SO_4$, Fig. 1], a prototypical ferroelectric which undergoes a phase transition to the paraelectric phase at a temperature $T_C= 223$ K [6]. Upon 3-photon absorption by 70-fs pulses at 400 nm, we observe unchanged angular positions of the Debye Scherrer rings (Fig. 1b) with oscillatory changes of the x-ray intensity diffracted from the sample at a temperature of T=200 K, i.e., just below T_C (symbols and green lines in Fig. 1c). Such changes reveal oscillations with a 3-ps period, caused by coherent wavepacket motions of a 12-cm^{-1} phonon. The time-resolved x-ray diffraction patterns allow for deriving the transient charge density maps shown in Fig. 1(e-g) for the (ab) plane

of the crystal structure. As a striking hallmark of soft-mode driven charge dynamics, one observes strong charge relocations on the 100-pm length scale of interionic distances although the phonon displacements are less than 1 pm. This behavior strongly suggests a soft-mode character of the newly discovered 12-cm^{-1} mode.

The total change of charge on the different ionic entities in the crystal lattice is determined by spatial integration of the transient charge densities over appropriate sub-volumes. Fig. 1(h) shows the results for the SO_3 sub-unit of the $(SO_4)^{2-}$ groups displaying a strong oscillatory charge increase. The fourth apical oxygen atom of the $(SO_4)^{2-}$ units behaves in the opposite fashion and periodically looses electron density (not shown). The 3-ps oscillation period of the charge changes underlines again the prominant role of the soft mode for charge relocation. Due to the preserved symmetry of the ferroelectric crystal structure, these charge motions result in a net polarization solely along the polar c-axis, perpendicular to the (ab) plane shown in Fig. 1 (d-g).

As has been established by groundbreaking theoretical work [7], a variation of microscopic electron density as a function of an external parameter is required to derive macroscopic electric polarization differences from microscopic charge densities. The *time-dependent* electron densities determined here provide a new access to this problem and allow for calculating the macroscopic polarization along the *c*-axis of the crystal structure. The result presented in Fig. 1(i) displays oscillations of the macroscopic polarization (symbols, solid line) with an amplitude that slightly exceeds the stationary polarization in the ferroelectric phase (dashed lines). In other words, the soft mode excitation induces a periodic switching of the macroscopic polarization on a time scale of a few picoseconds, an unexpected behavior with a strong potential for applications, e.g., in electronic devices based on ferroelectrics.

In conclusion, different complementary aspects of soft-mode physics were addressed by nonlinear terahertz spectroscopy and ultrafast x-ray diffraction. Future x-ray experiments with terahertz pump pulses will provide information on electron relocations in the electronic ground state of ferroelectrics.

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