

Field-induced dynamics of correlated electrons in LiH and NaBH₄

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Abstract: Femtosecond x-ray powder diffraction maps electron density in response to a strong electric field. In LiH, electron correlations lead to an electron transfer from Li to H while NaBH₄ shows a transfer from BH₄⁻ to Na⁺.

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OCIS codes: 260.7120

Field-driven physical processes play a key role for the electronic and optical properties of condensed matter and should allow for steering charge transport on the time scale of the optical cycle. To distinguish local electron displacements from a real-space electron flow, insight into the spatial electron distribution on ultrashort time scales is required. Recently, we have shown with the help of femtosecond x-ray diffraction that a strong non-resonant laser field induces transient optical polarizations which are connected with a spatial redistribution of electronic charge in the concomitant "virtual" or mixed quantum state [1]. In ionic crystals, the electronic states at the valence band maximum are typically localized on the negative ions and those at the conduction band minimum on the positive ions. When applying the external field, the simplest picture predicts a quasi-instantaneous, i.e. fully reversible, electron transfer from a negative to a neighboring positive ion. This picture is expected to break down whenever strong Coulomb correlations exist between valence electrons. Here, we demonstrate the strong influence of Coulomb correlations on the field-induced response of the model system lithium hydride (LiH), the most elementary heteronuclear solid. Electron density maps derived from femtosecond x-ray powder diffraction patterns reveal a net transfer from Li to H, in sharp contrast to the anticipated ionic behavior. Such results are in line with theoretical calculations of the bandstructure of correlated electrons.

In our experiments, we study crystalline powders of LiH and sodium boron-hydride (NaBH₄), both crystallizing in the rock-salt (NaCl) structure. In a pump-probe approach, the 800 nm excitation pulse provides a strong off-resonant optical field and the material's response is mapped by diffracting synchronized hard x-ray pulses (Cu K α , wavelength 0.154 nm) from the powder sample [2]. The pump wavelength of 800 nm is well below the bandgap of the materials and, on the other hand, above all vibrational transitions. The peak intensity corresponds to a peak electric field of 1 GV/m. Several Debye-Scherrer diffraction rings were recorded simultaneously as a function of the time delay between the pump and the x-ray probe in order to monitor the diffracted intensities changes of the different rings. The introduction of a chopper in the pump arm allows us to determine the relative change of the diffracted intensity of each individual ring and, moreover, reduces the source noise fluctuations down to the shot noise of x-ray photon detection.

We observed intensity changes on several Debye-Scherrer rings which occur in time around delay zero, i.e., when both the pump and probe beams are temporally overlapped. The angular positions of the rings remain unchanged. The diffraction ring which corresponds to the (111) reflection, shows a decrease of intensity on the order of 1% for LiH (Fig. 1.(a)), whereas the same reflection shows an increase of a few percent for NaBH₄ (not shown). The extracted structure factors $\Delta F_{hkl}(t)$ from the intensities changes $\Delta I_{hkl}(t)$ are used to reconstruct the temporal evolution of the electronic density $\Delta\rho(x,y,z,t)$ by means of the Maximum Entropy Method [3]. Surprisingly, the LiH results show a shift of electronic charge from the cation Li^{0.5+} to the anion H^{0.5-} [Fig. 1.(b)], whereas in NaBH₄ we measured a charge transfer from the anion to the cation (not shown). This unexpected result means that LiH becomes more ionic upon application of the external field, a behavior in contrast to NaBH₄ and the previously studied LiBH₄ [1].

The experimental result is reproduced by a theoretical analysis where the response to the external field is treated in the Coulomb-Hole-plus-Screened-Exchange (COHSEX) formalism [4,5]. In contrast to the simpler Hartree-Fock picture, the COHSEX formalism includes electron correlations beyond the single-particle level. By properly incorporating

the inhomogeneous screening of the electron-electron interaction, the COHSEX calculations predict the experimentally observed electron transfer from the cation $\text{Li}^{0.5+}$ to the anion $\text{H}^{0.5-}$ in LiH (Fig. 1.(c)), a behavior not reproduced by a Hartree-Fock calculation. Such findings underline the role of electronic correlations in LiH on the electron dynamics induced by strong optical fields and, vice versa, show that ultrafast x-ray diffraction represents a key method for investigating charge correlations.

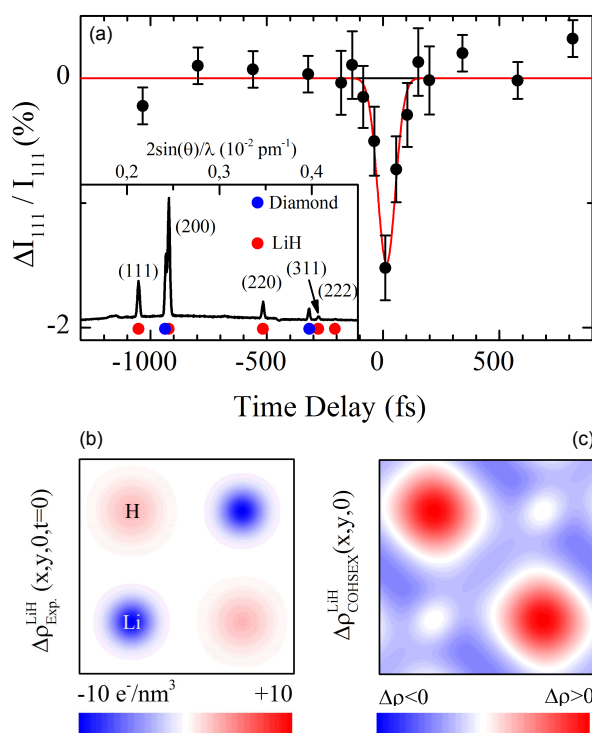


Fig. 1. (a) Relative change of the number of photons diffracted off the (111) plane as a function of the time delay between the 800 nm pump and the x-ray probe. Inset: Steady-state powder diffraction of lithium hydride. The diamond diffraction peaks arise from the sample holder. (b) Experimental electron density change at time delay zero in the lithium-hydrogen plane. (c) Calculated electron density change at time delay zero in the lithium-hydrogen plane as calculated within the COHSEX framework.

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