Controlling the type II multiferroic NiI_2 via orbital excitations

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Multiferroics are materials in which different ferroic properties – such as electricity and magnetism – are coupled. When taken to the two-dimensional (2D) limit, the strong light-matter interactions inherent to 2D systems are further enhanced by the magneto-electric interaction, enabling a direct coupling of the electric component of light to magnetic degrees of freedom [1]. This, in turn, makes 2D-multiferroics a particularly appealing platform for realizing highly efficient optical control of magnetism [2].

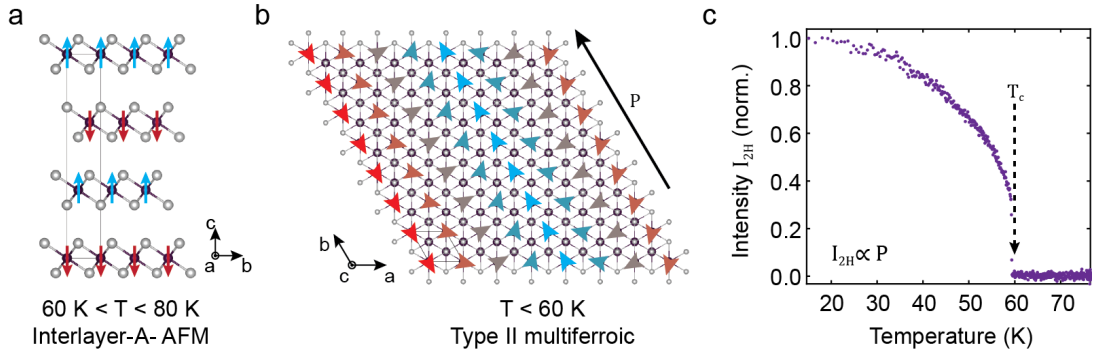

Figure 1. (a) NiI_2 crystal and magnetic structure in the antiferromagnetic phase. Interlayer exchange leads ferromagnetically coupled layers that are anti-aligned between each other, red and blue correspond to up and down magnetic moments, respectively. (b) The helical spin-spiral in NiI_2 in the multiferroic phase colors and arrows represent the in-plane component of the magnetic moment. The incommensurate spin-spiral has an approximate periodicity of seven unit cells. The ferroelectric polarization induced along the b-axis breaks inversion symmetry. (c) Second harmonic intensity as a function of temperature is proportional to the multiferroic order parameter P.

Recently, the type II multiferroic NiI_2 has gained significant interest for retaining its multiferroicity down to the monolayer limit [3]. NiI_2 is a quasi two-dimensional van der Waals material in which the Ni^{2+} ions sit on a trigonal lattice inside an octahedra of I^{2-} ions. Through interlayer exchange, NiI_2 becomes an antiferromagnet (AFM) at $T_N = 80$ K, here, spins ferromagnetically coupled within each layer, and anti-aligned between layers (Fig. 1a) [4]. In addition to interlayer exchange, a significant amount of geometric frustration arises from trigonal lattice of Ni^{2+} ions [4]. This frustration outcompetes interlayer exchange below 60 K, leading to the emergence of an incommensurate helical spin-spiral (Fig. 1b) approximately 7 unit cells (~30 nm) in periodicity. The spin-spiral is stabilized by the inverse Dzyaloshinskii-Moriya interaction (DMI), which – in combination with spin-lattice coupling – leads to an asymmetric shift of the I^{2-} ion positions [5]. This shift breaks inversion symmetry, resulting in ferroelectric polarization **P** and giving a rise to a multiferroic phase which can be probed optically using second harmonic generation.

To control the multiferroic phase in NiI_2, we tune femtosecond laser pulses to target *d-d* orbital excitations of the Ni^{2+} ions. These electronic excitations involve change in the orbital state of the magnetic Ni^{2+} ions and can affect the inverse DMI through spin-orbit coupling. Behaving similarly to conventional excitons, they can be either localized (e.g. Frenkel-like) or delocalized (Wannier-Mott-like), extending across multiple lattice sites. The localized *d-d* excitations have been previously shown to efficiently generate THz coherent spin dynamics in collinear Ni^{2+} based antiferromagnets [6]. In contrast to collinear AFM systems, we find that the localized $^3A_{1g} \rightarrow {}^3T_{2g}$ orbital excitation does little to perturb the non-collinear multiferroic phase of NiI_2. Instead, we find that the multiferroic phase can be resonantly quenched by delocalized $^3A_{1g} \rightarrow {}^3T_{1g}$ orbital excitations, which manifest as a sudden quench of the multiferroic order and the appearance of critical slowdown of the recovery dynamics (see Fig. 2a-c) [7]. The delocalized excitation distorts the electronic wavefunction over a distance larger than the periodicity of the spin-spiral (~30 nm), which likely quenches the inverse DMI more efficiently than localized excitations (Fig. 2c).

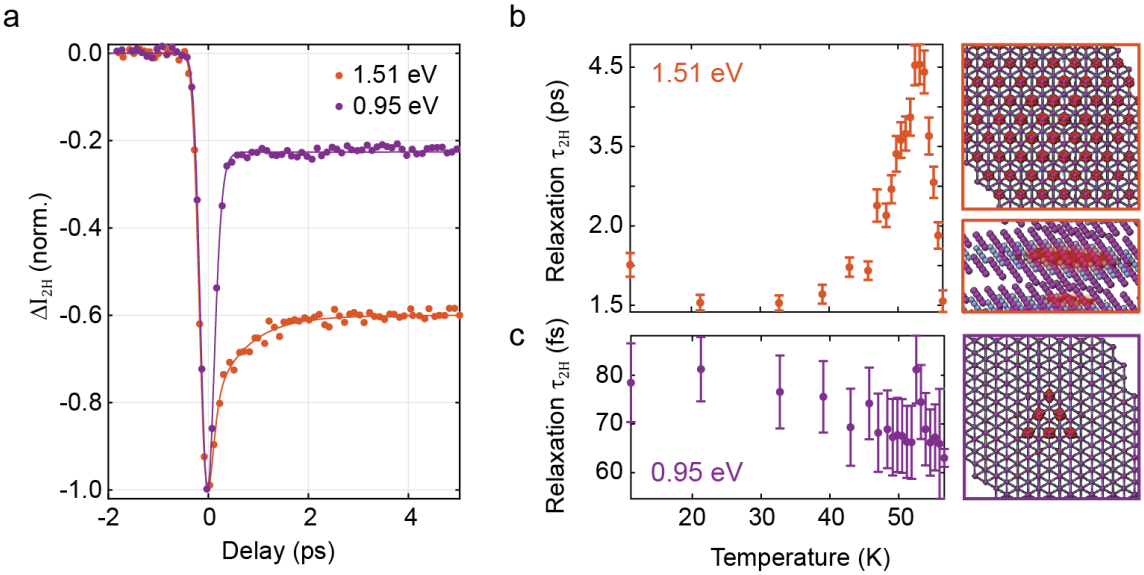

Figure 2. (a) The time-resolved ultrafast dynamics of the second harmonic (SHG) intensity in response to pump pulses resonant to the localized $^3A_{1g} \rightarrow {}^3T_{2g}$ orbital excitation (purple) and the delocalized $^3A_{1g} \rightarrow {}^3T_{1g}$ orbital excitation (orange). The quench in intensity is followed by a relaxation on the order of picoseconds and nanoseconds. Solid lines are fits to the data. (b) The relaxation timescale extracted from the fit of the orange curve in (a). A critical slowdown is observed for the delocalized $^3A_{1g} \rightarrow {}^3T_{1g}$ excitation. Right side shows the ab-initio calculation of the electron-hole wavefunction for the delocalized $^3A_{1g} \rightarrow {}^3T_{1g}$ orbital excitation, showing the extent of delocalization in the layer (top) and between layers (bottom). (c) The relaxation timescale extracted from the fit of the purple curve in (a). Right side shows the ab-initio calculation of the electron-hole wavefunction for the localized $^3A_{1g} \rightarrow {}^3T_{2g}$ orbital excitation.

Furthermore, our ab-initio microscopic DFT simulations show that the excitation affects wavefunctions in neighbouring van der Waals layer (Fig. 2b). This delocalization may lead to an enhancement of the interlayer exchange which favors the AFM phase of NiI_2 over the multiferroic phase stabilized by the inverse DMI. By tuning polarization, fluence, and wavelength, we aim to enable ultrafast optical control of ferroelectricity and magnetism in 2D vdW multiferroics.

References

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