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Unusually long carrier lifetime in a Mott insulator revealed by time-resolved Photoemission Electron Microscopy

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Abstract: Mott insulators display puzzling insulator to metal transitions under electric field. We study here the Mott insulator GaV_4S_8 using time-resolved Photoemission Electron Microcopy and reveal unusually long carrier lifetimes, supporting the mechanism of electronic avalanche. © 2020 The Author(s)

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The study in non-equilibrium conditions of an emblematic class of quantum materials, the Mott insulators, is currently developing into an active and fruitful branch of solid state physics. This research field opens up many perspectives by revealing unexpected physical properties based on new control parameters. Mott insulators excited either by ultrafast infrared or THz laser pulses [1,2], or by electric fields [3]display indeed non-trivial insulator to metal transitions (IMT's) which origin goes beyond the well-established bandwidth- and filling-controlled mechanisms [4]. Interestingly such transitions could be used to build up a new electronics based on Mott insulators, the so-called Mottronics, including breakthrough devices such as Mott memories [3] and artificial neurons for artificial intelligence [5]. A common feature of out-of-equilibrium IMT's in Mott insulators is that they are based on the massive excitation of electrons from the Lower (valence) to the Upper (conduction) Hubbard Band. For example, recent studies proposed that the multiplication of carrier in a Mott insulator placed under electric field occurs thanks to impact ionization and electronic avalanche [6,7]. However the efficiency of such mechanisms might vanish if carrier lifetime is too small, *i.e.* if electron-hole recombination due for example to defects is too fast. In classical semiconductors, the carrier lifetime varies from the millisecond in ultrapure silicon to the nanosecond in heavily doped silicon [8,9]. As usual purity levels of Mott insulators are far from the one of ultrapure classical semiconductors, one might naively expect very small carrier lifetime in the nanosecond range. Experimentally, the carrier lifetime in Mott insulators has been scarcely explored, partly due to the lack of appropriate technique to measure it. This situation has recently evolved, with the advent of time-resolved photoemission electron microscopy (tr-PEEM), a technique well-suited to determine carrier lifetime [10]. We report here a tr-PEEM study of the canonical Mott insulator GaV_4S_8.

GaV_4S_8 is a Mott insulator exhibiting a lacunar spinel structure (see Figure 1a) built from a NaCl-like arrangement of GaS_4 tetrahedra and V_4S_4 cubane-like units. In each V_4S_4 cluster, one out of the seven V 3d electrons is unpaired and lies on the threefold degenerate molecular t_2 level. In the solid, the three narrow bands deriving from these t_2 molecular levels are split by the on-site electron-electron repulsion, leading to an insulating state with a Mott-Hubbard gap of 0.3 ± 0.1 eV [6]. The application of electric field pulses in GaV_4S_8 leads to an IMT, opening the possibility to use this compound in memory applications [3]. We performed tr-PEEM experiments at room temperature on the KEK experimental setup [10] on a freshly cleaved GaV_4S_8 single crystal synthesized as described in Ref. [11]. Figure 1b provides a schematic description of the electron pathway in a pump-probe tr-PEEM experiment. A first pump laser, either 1.2 eV / 180 fs / repetition rate 500 Hz or 1.1 eV / 10 ns / 200 Hz, promotes electrons in the conduction band. A second laser, the probe, with a tunable delay with respect to the pump expels the excited electrons from the conduction band toward the vacuum level, where electrons are accelerated and detected. A typical tr-PEEM experiment presents the ratio of photoelectrons number detected with and without pump laser versus the time delay between the pump and the probe. Figure 1c shows the results of a first experiment carried out without any pump aiming at establishing the work function ϕ of GaV_4S_8 and performed by varying the probe energy between 4 and 4.8 eV. This curve displays a clear threshold effect consistent with a work function close to $\phi = 4.6 \pm 0.1$ eV. For the tr-PEEM experiments, we chose a probe energy of 4.47 eV slightly below the ϕ value, in order to detect only the excited electrons in the Upper Hubbard Band without any pollution by those in Lower Hubbard Band. A first tr-PEEM experiment performed with the 1.2 eV / 180 fs pump laser reveals a striking feature: there is no detectable relaxation of the signal shown in Figure 1d in the 0-100 ps time windows after the pump laser. To confirm this result, a second series of experiment was carried out using the 1.1 eV / 10 ns pump laser. Figure 1e-f shows that the relaxation indeed occurs over a much longer timescale, with a fair description of the relaxation as the sum of three exponential decay terms with $\tau_1 = 43$ ns, $\tau_2 = 270$ ns and $\tau_3 = 4$ µs. By comparison with classical semiconductors [8,9], the long carrier

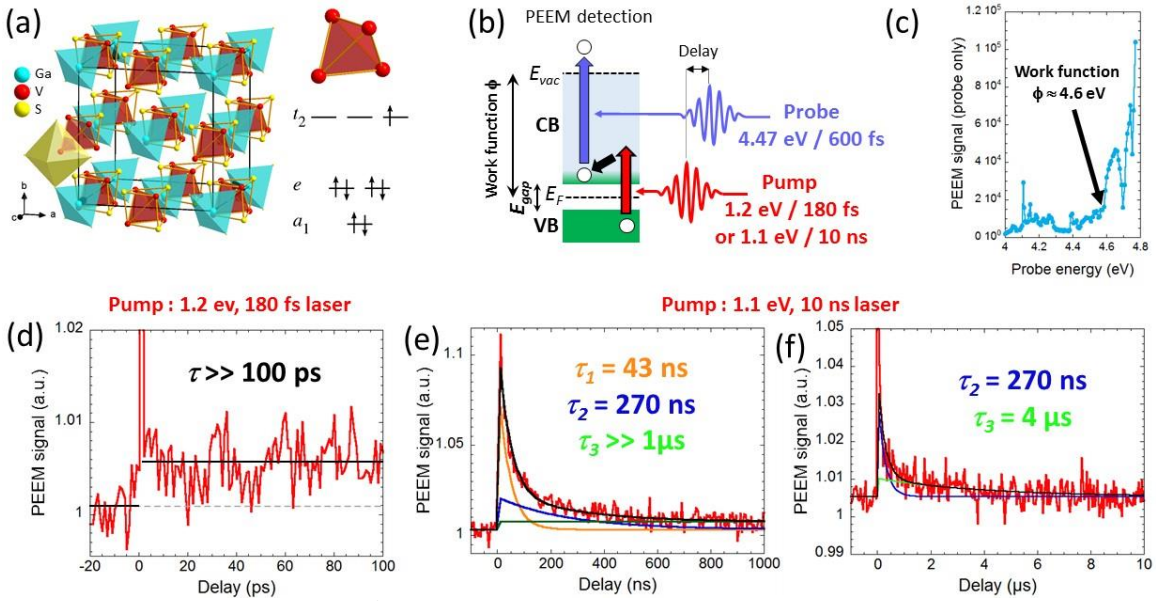


Figure 1 : (a) crystallographic structure of GaV_4S_8 and molecular orbital diagram associated to the V_4 tetrahedral cluster. (b) schematic description of the electron pathway in a tr-PEEM experiment. (c) PEEM energy scan of the probe laser without any pump on a GaV_4S_8 single crystal. (d-f) tr-PEEM signal vs various ranges of time delay between the pump and the probe in GaV_4S_8 at room temperature.

lifetime found here might look surprising in a Mott insulator possessing likely a high level of native defects. However, a comparison with other strongly correlated insulators might be more instructive to clarify its origin. Among the scarce studies of carrier lifetime in such compounds, extremely different values are observed, going from the sub-picosecond range in the Mott insulator 1T-TaS_2 [12] to 1-20 µs in the strongly correlated insulator VO_2 [13]. As proposed in Ref. [13], a possible clue is the difference of nature and symmetry of the valence and conduction bands states. In a "one-band" Mott insulator like 1T-TaS_2, the Lower and Upper Hubbard Bands derive from the same band and therefore display the same symmetries. In this case, the electron-hole recombination is permitted and hence very fast. Conversely, in a "three-band" Mott insulator like GaV_4S_8, the top of the LHB and the bottom of the UHB are most probably made of different and orthogonal V3d bands (see Suppl. Mater. of Ref. [14] and Figure 1a). This would result in a mostly forbidden interband transition and hence in a slow electron-hole recombination. Even if further theoretical and experimental work is required to confirm this conjecture, the possibility to tune the carrier lifetime in Mott insulators by more than six orders of magnitude is of prime interest for artificial intelligence applications. The carrier lifetime is indeed controlling the operating frequency of artificial neurons based on Mott insulators [5].

In summary, we have detected unusually long carrier lifetime in the multiband Mott insulator GaV_4S_8 using the tr-PEEM technique. This result is important since it supports the proposed mechanism of electronic avalanche [6,7] and will guide the future development of new hardware components in artificial intelligence.

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