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Photoinduced charge carrier dynamics in germanium

G. INZANI(1)(*), A. ESKANDARI-ASL(2), L. ADAMSKA(3), B. MOIO(1)(4), G. L. DOLSO(1), N. DI PALO(1)(4), L. J. D'ONOFRIO(2), A. LAMPERTI(5), A. MOLLE(5), C. A. ROZZI(3), R. BORREGO-VARILLAS(4), M. NISOLI(1)(4), S. PITTALIS(3), A. AVELLA(2)(6)(7) and M. LUCCHINI(1)(4)

(1) *Department of Physics, Politecnico di Milano - 20133 Milano, Italy*
(2) *Dipartimento di Fisica "E. R. Caianiello", Università degli Studi di Salerno I-84084 Fisciano (SA), Italy*
(3) *CNR–Istituto Nanoscienze - via Campi 213/A, I-41125 Modena, Italy*
(4) *Institute for Photonics and Nanotechnologies, IFN–CNR - 20133 Milano, Italy*
(5) *CNR–IMM, Unit of Agrate Brianza - 20864 Agrate Brianza, MB, Italy*
(6) *CNR–SPIN, UoS di Salerno - I-84084 Fisciano (SA), Italy*
(7) *Unità CNISM di Salerno, Università degli Studi di Salerno - I-84084, Fisciano (SA), Italy*

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Summary. — The light-induced injection of charge carriers from the valence to the conduction band of a solid, and their subsequent thermalization and relaxation, are fundamental physical processes. They allow dynamically altering the conductivity of a semiconductor, controlling its electro-optical properties with light fields. In this paper, we discuss the elusive photoinjection mechanism occurring during light-matter interaction, to then focus on the charge thermalization and relaxation processes in germanium.

An essential prerequisite to research and technological advancements in optoelectronics is the control of ultrafast electron dynamics in matter with light. Femtosecond (fs) light pulses allowed tuning the magnetic [1], electrical [2], and optical [3] properties of condensed systems on ultrafast time scales. They induce electron transitions across the Fermi level of a semiconductor, promoting charge carriers from the valence (VB) to the conduction band (CB). This process, called photoinjection, takes place during the pump pulse envelope, strongly affects the sample conductivity, and is followed by charge thermalization, relaxation and, eventually, recombination. Charge injection results from the simultaneous contribution of several physical phenomena taking place on the few- to sub-fs time scale, and could have significant future technological implications. Despite its importance, very few experiments investigated photoinjection with attosecond temporal resolution, and the role and interplay of the different mechanisms are still obscure.

(*) E-mail: giacomo.inzani@polimi.it

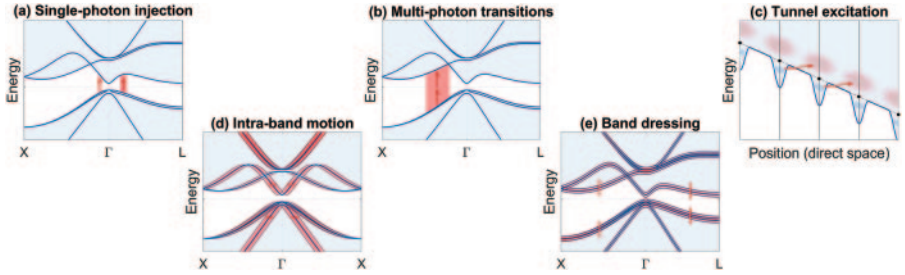

Fig. 1. – Sketches of the strong-field physical phenomena involved in photoinjection. Except for tunnel excitation, all representations are in reciprocal space.

Here, we discuss the elusive phenomena which unfold during the first femtoseconds of light-matter interaction, and we present an experimental investigation of the subsequent charge thermalization and relaxation mechanisms. This work sets the stage for an in-depth joint experimental and theoretical effort reported elsewhere [4], which investigates the first few fs of light-matter interaction with attosecond temporal resolution.

1. – Sub-fs light-matter interaction in germanium

Any relevant light-induced change in the electro-optical properties of a semiconductor, such as germanium, links to a modified distribution of the excited electrons in the band structure. Once the interaction with light is over, the initial non-equilibrium distribution of charges recovers through phenomena like thermalization, relaxation and electron-hole recombination, which therefore affect the electro-optical response of the material on the picosecond (ps) time scale. On a faster time scale, the optical response of the material to an intense ($\sim 1 \times 10^{13}\,\mathrm{W/cm^2}$) 10-fs optical pulse is instead determined by diverse phenomena, sketched in fig. 1.

Although attosecond experiments typically rely on intense pumping fields, the first physical process leading to charge injection is single-photon absorption [5] (fig. 1(a)). In regions where the local energy gap between an occupied VB state and an empty CB one matches the pump photon energy, vertical electronic transitions take place. Analogously, if the pump intensity is large enough, multi-photon excitation can occur every time the local gap equals an integer number of pump photons [6,7] (fig. 1(b)). When the minimum direct band gap is smaller than the pump photon energy, an intense enough light field can distort the bands so much that the CB minimum at one lattice site is almost at the same energy of the neighbouring-site VB maximum, eventually leading to tunnel excitation [8] (fig. 1(c)). Simultaneously, the large light field changes the band structure, both inducing intra-band motion along the field polarization direction [9] (fig. 1(d)), which can affect photoinjection [5], and dynamically dressing the bands, altering the energy gaps (fig. 1(e)).

For germanium, where it exists a region of the Brillouin zone where the energy gap between the top of the VB and the bottom of the CB matches one infrared (IR) photon (1.55 eV), if the associated transition dipole moment is large enough, single-photon absorption should dominate charge carrier injection [10]. However, there are k-points in resonance with two or more pump photons, and their density is higher than that of single photon resonances. Since the probability for multi-photon absorption increases with pump intensity, we cannot *a priori* assume that this mechanism can be neglected

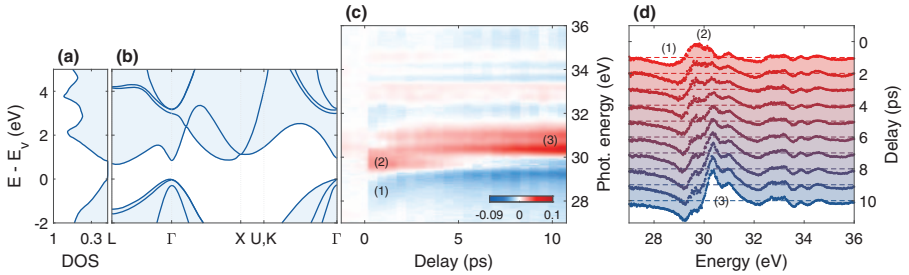

Fig. 2. – (a), Density of states and, (b), band structure of germanium [11]. The zero energy matches the valence band edge position from the $3d_{5/2}$ semi-core state. (c), Differential reflectivity of intrinsic germanium and, (d), cuts of the experimental trace for selected delay values.

when an intense few-fs pulse is shone onto the sample. In addition, the small direct band gap and the large density of states (DOS) at Γ could lead, depending on the experimental details, to tunneling [12], again influencing charge injection. We expect all these phenomena to contribute to both real or virtual carrier populations [13], dictating the subsequent charge thermalization and relaxation process which we will discuss in the next section.

2. – Charge thermalization and relaxation in germanium

One of the most widely-adopted techniques to investigate charge relaxation processes is transient absorption/reflection spectroscopy [14, 15]. In these all-optical pump-probe experiments, a pump pulse triggers the photoinjection process. After a given temporal delay, the probe pulse (or pulses) impinges on the sample, probing the empty states in the CB or VB. In attosecond experiments, the pump pulses have a duration of a few fs and are typically in the IR spectral region. Instead, the probing radiation usually spans the extreme-ultraviolet (XUV) and soft-x-ray range [15]. In our case, we measure normalized pump-induced variations in the sample reflectivity as a function of the pump-probe delay, τ, and of the probe photon energy, E. We define differential reflectivity as $\Delta R/R(E,\tau) = [R_p(E,\tau) - R_0(E)] \,/\, [R_0(E)]$, where $R_p(E,\tau)$ and $R_0(E)$ are the sample reflectivity with and without the IR pump, respectively.

Figure 2(c) shows a transient reflectivity measurement performed on intrinsic germanium. We reported details on the experimental setup elsewhere [16, 17]. An intense 10-fs IR pulse generates an excited electron population in the band structure (fig. 2(b)), according to the associated DOS (fig. 2(a)). This population changes the reflectivity of Ge at 66° angle of incidence around the $M_{4,5}$ absorption edge (29.2 and 29.8 eV), leading to positive and negative features in the differential trace (fig. 2(c)). The thermalization of the excited electron population, *i.e.*, its change from a non-thermal electronic distribution to a Fermi-Dirac one, and its subsequent relaxation and recombination, affect the measured signals.

We number the dominant features in figs. 2(c), (d). Feature (1) consists of an intensifying negative peak at ∼29.1 eV which blueshifts of ∼0.4 eV over a 10-ps time scale. By comparison with the band structure (fig. 2(b)), it corresponds to the VB region. Feature (2) is a broad positive feature at ∼29.7 eV, thus within the band gap region, decreasing to zero over a few ps. Feature (3), instead, is formed by two peaks (30.3 and 31.0 eV) within the CB that show a delayed growth. These features are consistent with those

already discussed by Kaplan and coworkers [18], and they are linked to the scattering processes involving holes in the Γ valley and electrons in the Γ, L and X valleys, together with the creation of phonons and the consequent band gap renormalization.

At variance with what was reported by Kaplan *et al.* [18], we observe for the first time features in the transient reflectivity up to $\sim$6 eV above the absorption edge. Their interpretation is based on the detailed structure of the electronic bands, and we will further discuss it elsewhere [4]. On such long time scales, they are linked to non-dispersive band structure regions (*i.e.*, peaks in the DOS) shifted by the phonon-induced band gap renormalization, resulting in a ps-lasting differential signal.

3. – Conclusions

In conclusion, we have shown that charge injection in germanium determines a vigorous optical response lasting for more than 10 ps and extending for several eVs both above and below the absorption edge. The initial charge distribution dictates the observed dynamics, in agreement with literature data [18]. Since photoinjection rules the charge carriers, achieving a detailed understanding of this process is of utmost importance for future applications. However, a comparison with the published literature does not allow a proper identification of the phenomena involved. Thus, the only way to understand photoinjection by a strong few-fs pulse in germanium is through advanced theoretical simulations combined with state-of-the-art experiments with attosecond temporal resolution, to be reported elsewhere [4]. The resulting, novel view on field-driven photoinjection will represent a significant step towards achieving control over charge excitation in solids, influencing the subsequent thermalization and relaxation dynamics.

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