Free-Electron Laser Studies of Direct and Indirect Two-Photon Absorption in Germanium

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We succeeded in observing the two-photon absorption of germanium for both the direct and the indirect gaps, using the Vanderbilt free-electron laser. The two-photon absorption for the indirect gap was found to be 3 orders of magnitude smaller than the direct gap. The indirect-gap threshold position indicates that the two-photon absorption is assisted by an LO phonon, providing a long-delayed positive test of the Bassani-Hassan predictions.

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The broad-range wavelength tunability and high brightness provided by the newly available Vanderbilt free-electron laser (FEL) enables us to eliminate an important and long-standing gap in the knowledge [1–13] of nonlinear optical properties: the two-photon absorption of germanium. Specifically, no data were available on the two-photon absorption at the indirect gap, which is a three-particle process [1–3]. The last measurements of this type [5], performed in 1976 with conventional lasers, did not reach the direct gap; the fundamental interest of their results did nevertheless stimulate much theoretical work [1,2,13,14].

Two-photon spectroscopy has been for many years an important component of solid-state research because of its selection-rule complementarity with respect to conventional optical spectroscopy, and because of the many interesting and nontrivial features of two-photon absorption [1–14]. Originally treated by Göppert-Mayer [12], this spectroscopy could be practically implemented only after the invention of lasers [4], and became one of the basic tools of solid-state physics. Two-photon absorption in germanium, nevertheless, was never implemented comprehensively with conventional lasers. This might be due to the limitations of tunable sources in this spectral range prior to the FEL, specifically the low average power due to the low repetition rate.

The recently commissioned Vanderbilt FEL provides us with the necessary intensity and tuning range to finally overcome this obstacle. This instrument is an upgraded version of the Stanford University Mark III FEL [15]. The electron beam is produced by a 45-MeV radio frequency accelerator, operating at a frequency of 2.856 GHz. The source is tunable over the 2–10-μm wavelength range (first harmonic, down to 1 μm in third harmonic) with high output power and brightness. Pulses with 6 μs duration, 360 mJ energy, and 11 W average power (repetition rate 30 Hz) have been reliably demonstrated in tests conducted at the wavelength of 4.8 μm.

Our two-photon spectroscopy studies included two kinds of experiments: photoconductivity and photoluminescence. Both experiments were performed at low temperature, with the sample at $\sim$125 K in the first case and at $\sim$7 K in the second. The germanium sample used for photoconductivity measurements was the p^+-i-n^+ diode in an EO-817P North Coast Co. photodetector. The 4-mm-thick intrinsic region was made of high-purity, low-defect-density Ge, with a net carrier concentration (at room temperature) of 10^9–10^{10} cm^{-3}. A second sample composed of high-purity, dislocation-free Ge with net carrier concentration $p=2\times10^{11}$ cm^{-3} was characterized by single- and two-photon-induced photoluminescence and transmission measurements.

Figures 1(a) and 1(b) show the two-photon-induced photoconductivity spectrum in the energy region of the direct and indirect Ge gaps. We note immediately the presence of the indirect-gap two-photon absorption threshold in Fig. 1(b). The direct and indirect absorption edges cannot be seen on the same scale, because the latter is 3 orders of magnitude smaller, as discussed later.

The photoconductivity for Fig. 1 was measured after biasing the Ge p^+-i-n^+ structure at -300 V to fully deplete the intrinsic region; a transimpedance amplifier converted photoconductivity into a voltage change, ΔV, which in turn was measured by a boxcar integrator. A reference FEL intensity signal $V_{\rm ref}$ was provided by a Au-doped Ge detector which, due to Au impurity levels within the Ge gap, has broad spectral sensitivity dominated by single-photon absorptions. The reference signal was required to eliminate the effects of FEL intensity fluctuations (from 5% to 10% between macropulses). After testing the quadratic dependence of the absorption on the FEL intensity (see Fig. 2, to be discussed later), we plotted the data as $\Delta V/V_{\rm ref}^2$ versus double the photon energy, $2\hbar\omega$.

The data of Fig. 1(a) are from three different runs, and are consistent with several other runs. From the threshold, we estimated a direct-gap width $E_g^d=0.87\pm0.01$ eV. This evaluation was further tested by using Mahan's exci-

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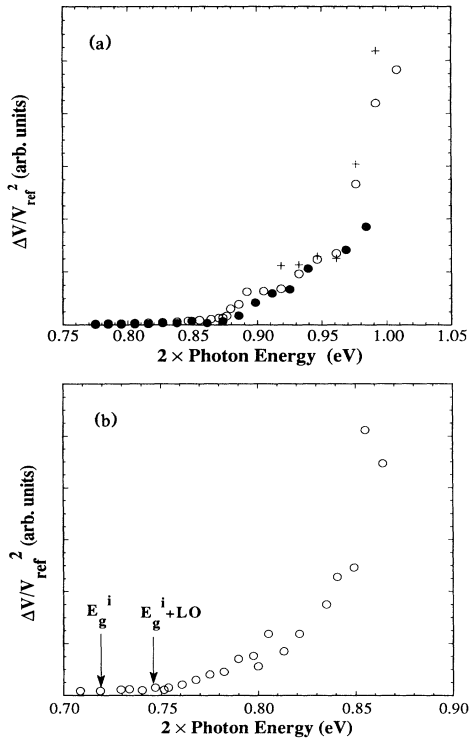

FIG. 1. (a) Two-photon-absorption-induced photoconductivity signal (normalized to the square of the intensity reference signal V_{ref}), as a function of double the incident photon energy. We note the direct-gap threshold, corresponding to the gap width of 0.87 eV at 125 K. (b) Similar data for the indirect gap. The vertical arrows mark the indirect-gap width, E_g^i, and the corresponding threshold for LO-phonon-assisted processes as predicted by Bassani-Hassan theory [1].

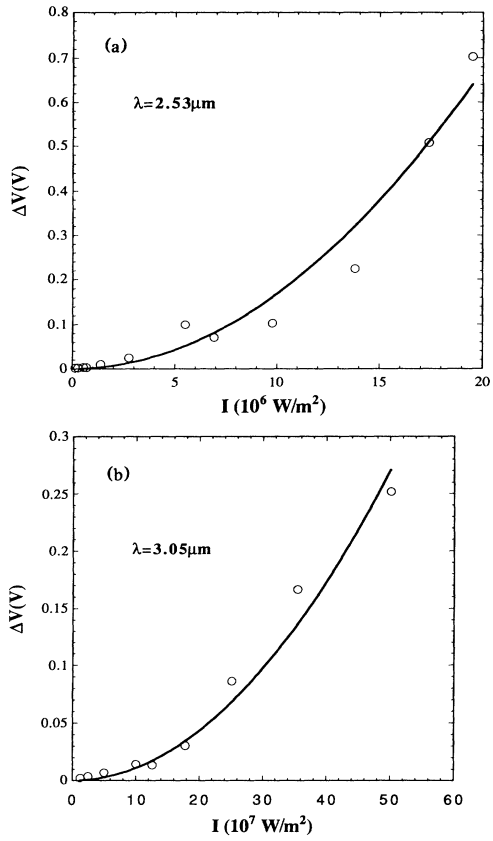

FIG. 2. (a) Dependence on the incident intensity of the relative magnitude of the induced photoconductivity signal. The data are for a photon energy of 0.490 eV (above the two-photon direct-gap threshold), and again for an estimated temperature of 125 K. (b) Similar data for a photon energy of 0.407 eV, between the direct- and indirect-gap thresholds. The solid lines indicate in both cases a quadratic dependence.

tonic theory [14], with E_g^d as an adjustable parameter, again obtaining 0.87 eV. This value is also reasonable considering the published value [16,17] and the estimated sample temperature: A gap of 0.87 eV corresponds to approximately 125 K.

The E_g^d value from this data analysis was then used to analyze the indirect-gap data. Specifically, we assumed that the difference between the gaps is independent of temperature (the published dependence [16,17] would in fact be negligible within our level of accuracy). From the indirect-gap width [16,17] at 77 K of 0.737 eV and the direct-gap decrease of 19 meV from 77 to 125 K, we derive an indirect-gap width $E_g^i = 0.718 \pm 0.01$ eV at 125 K. The position is shown by the left-hand-side arrow labeled E_g^i in Fig. 1(b).

The actual two-photon indirect-gap threshold of Fig. 1(b) is clearly shifted with respect to E_g^i, even considering the experimental uncertainty. As shown by the arrow labeled E_g^i+LO, the shift is consistent with a process assisted by the emission of a 30.4-meV LO (L_6^-) phonon [17]. The two-photon indirect threshold is therefore, as predicted by Bassani and Hassan [1] in 1972, primarily an LO-assisted process, as opposed to the one-photon mechanism which can be assisted by several different types of phonons [2,16].

The absolute value of the two-photon absorption coefficient β was measured by several authors [5–7] above the direct gap, obtaining values in the 0.34–2.5-cm/MW range. Note that β is defined [4,5,11] by the relation $(dI/dz) = -\beta I^2$, where $I(z)$ is the intensity as a function of sample depth. We used our data to estimate the change in value on going from the direct to the indirect gap and found a decrease of approximately a factor of 2×10^3 between $\hbar\omega = 0.490$ eV (above the two-photon direct-gap threshold) and $\hbar\omega = 0.407$ eV (between the indirect and the direct gap).

This estimate assumes that only two-photon absorption contributes to the photocurrent, consistent with the arlier evidence by Gibson *et al.* [5] that one-photon contributions are negligible for a crystal with the size and impurity concentration as well as beam intensities used in our

experiments. Note that the observed decrease is larger in magnitude than the corresponding decrease for one-photon processes [16] and is in the general magnitude range found, for example, for GaP [9,10]. This is slightly surprising, considering the different selection rules [2] that govern two-photon direct-gap processes for Ge and GaP due to their inversion symmetries.

The fits of Figs. 2(a) and 2(b) show that the near-threshold intensity dependence is essentially quadratic. This is reasonable, since the deviations from such a behavior [5] are expected to be small for our experimental conditions, due to the weakness of the two-photon absorption coefficient, the relatively moderate thickness of the specimen, and the relatively small incident intensity.

Note that the quadratic dependence implies a carrier lifetime longer than the transit time. This is consistent with the very high sample purity and with the low carrier concentration produced by two-photon absorption (estimated to never exceed 2×10^{9} cm^{-3} for the present data). There is also consistency with several other points: Saturation effects were not observed, the estimated free-carrier absorption is negligible with respect to two-photon absorption, and the laser intensity does not appreciably change over the sample's depth.

The photoconductivity measurements were complemented by photoluminescence measurements, performed by filtering the emitted photons with a standard single-grating monochromator, working at an estimated resolving power of 140 (due to the large slit width required because of the weak emission).

Figure 3 (lower curve) shows a typical emission spectrum, which clearly demonstrates two-photon excitation because the incident photon energy was 0.496 eV, above the two-photon direct-gap threshold. The spectrum is consistent with our own one-photon photoluminescence data on the same sample (upper curve) as well as with data [17,18] from the literature: The main spectral feature is due to an LA-phonon-assisted exciton recombination [18].

Measurements of the photoluminescence intensity versus the incident photon energy enabled us to observe the threshold due to the direct gap. The signal was too weak, however, to clearly observe the indirect-gap threshold in the photoluminescence data.

In summary, we measured the two-photon absorption spectra of germanium both for the direct and the indirect gap; relative measurements of the absorption coefficient revealed a decrease by approximately 3 orders of magnitude on going from the direct- to the indirect-gap spectral region. The spectra clearly show both thresholds, and the indirect-gap threshold appears due to an LO-phonon-assisted process as predicted by Bassani and Hassan [1].

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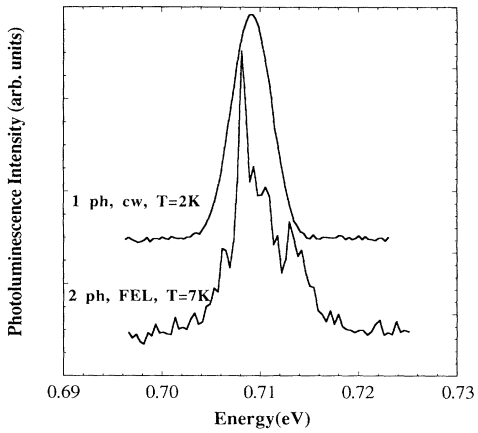

FIG. 3. Lower curve: photoluminescence spectrum excited by two-photon absorption at an incident photon energy of 0.496 eV. The sample was at a temperature of 7 K. A one-photon-absorption photoluminescence spectrum of the same sample is shown for comparison (upper curve).

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