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# Recent developments in phonoconductivity spectroscopy of shallow bound states in semiconductors

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The invited talk was given by K. Laßmann.

The phonon emission spectrum of a superconducting Al-junction contains a sharp quasi-monochromatic lineup to the range of Debye energies tuneable by the bias. This is evident from steep phonon-induced conduction (PIC) thresholds due to excitation of carriers in semiconductors from shallow bound states to the neighbouring band. Information on phonon coupling to carriers and phonon propagation at extremely high frequencies in superconductors and semiconductors can be obtained from such experiments.

At low temperatures electrical conduction in semiconductors may be mediated by acoustic phonons activating carriers from localized states. Vice versa, trapping of non-equilibrium delocalized carriers is often determined by the conditions of energy and momentum conservation for phonon emission which may mean an important restriction. Since shallow states in semiconductors are extended in real space, i.e., confined in $k$-space the large wavevector of the high-frequency phonons involved in the transition often cannot be conserved.

A promising new possibility to investigate the relevant elementary processes is phonoconductivity, an analogue to photoconductivity. Superconducting tunnel junctions, evaporated onto the semiconductor substrate, are used as quasi-monochromatic phonon sources tuneable by the junction bias (see, e.g. ref. [1]). Sharp spectral features have been found in the phonon-induced conduction (PIC) corresponding to binding energies of carriers to shallow traps [2–10].

From these experiments information is obtained not only on the phonon coupling and the structure of the bound semiconductor states, but also on the superconductor phonon emission properties. In the special case of Al-junctions we got the remarkable result that the primary phonon spectrum as determined by the first step energy relaxation of the injected quasiparticles is essentially preserved well into the range of Debye frequencies, i.e., to wavelengths as short as some lattice constants. In this range of phonon frequencies there are many possibilities for a rapid decay of the generated nonequilibrium phonon distribution before being detected within the semiconductor: phonon down-conversion from reabsorption by Cooper-pairs, phonon-quasiparticle and phonon-defect scattering within the thin superconductor films, transmission loss through the non-ideal interface to the substrate, loss to the surrounding liquid helium (Kapitza anomaly) and anharmonic decay leading to small phonon diffusion lengths in the semiconductor because of strong isotope scattering.

All these processes can be investigated in principle with help of the phonoconductivity thresholds which may be a sensitive means of detection: a signal-to-noise ratio of about 10 (with an integration time of 300 ms) was obtained resulting from less than $10^7$ Sb-donors in Ge irradiated by less than 1 μW of nominal phonon power at 10 meV with a resolution of 100 μeV given by the modulation width of the Al-junction generator [10]. This nominal phonon power is an upper limit assuming that all of the junction power at the bias within the modulation width goes into the monochromatic line of the (differentiated) primary relaxation spectrum; it should be reduced not only within a realistic model of the relaxation spectrum [11], but also due to the aforementioned inelastic scattering processes. Apart from the basic questions concerning low-temperature electrical conductivity in semiconductors, lifetime of carriers and phonons in superconductors and semiconductors, there is an additional interest in the knowledge of the phonoresponse since it enables a qualification of semiconductor systems used as phonon bolometers, e.g. for particle detection.

An important difference for phonon interaction versus photon interaction with carriers in extended states in semiconductors is due to the fact that the sound velocity is roughly $10^5$ times smaller than that of light. The resulting much larger phonon density of states (dos) favours the electron interaction with the thermal phonon bath whereas the corresponding smaller wavelength $\lambda$, i.e., larger wavevector $q$ of the phonon leads to a reduction in the transition probability for states of extent $a^*$: due to the confinement of the bound state in $k$-space and the narrow steep dispersion of the free carriers the probability for conservation of the large phonon $q$ vector in a transition is reduced by a larger factor containing the product $(qa^*)^n$ approximately for $qa^* \gg 1$, where $n$ may be 6 or 8 depending on situation. For neutral donors in GaAs, e.g., the binding energy is about 6 meV and the Bohr radius of the ground state $a^* \sim 10$ nm whereas for LA-phonons at 6 meV we have $\lambda \sim 3$ nm (assuming linear dispersion) which means a reduction by more than $10^8$ for a transition from the donor ground state to the bottom of the conduction band (CB) which is at $k = 0$ in the Brillouin zone in the case of GaAs. If, however, the band consists of several equivalent extrema at large $k$, conservation of phonon $q$ may be possible by an interextrema scattering since the bound state is composed of contributions of the different extrema. For the Sb-donor in Ge the match is perfect: Its binding energy, $\sim 10$ meV, coincides with the energy of the TA-phonon at the X-point in the Brillouin zone (fig. 1). The corresponding $q$-vector is equivalent to the $k$-vector joining two L-points where the minima of the conduction band in Ge are situated (fig. 2). Thus in the transition from the ground state (i.e., a portion of it made up of wave functions belonging to one valley) to the CB (i.e., another valley of it) energy and momentum are ideally conserved. This together with the peak in the dos of this phonon branch at the X-point may account for the high detectivity with this donor. Fig. 3 shows the corresponding threshold in the PIC-signal at $\sim 10$ meV. For P and As with binding energies of $\sim 13$ meV and $\sim 14$ meV corresponding thresholds have also been found [7]. The smaller Bohr radius of these deeper donors relaxes somewhat the matching conditions. The stress dependence of threshold height and position, as discussed in ref. [10], ascertains the importance of the intervalley scattering in the transition; in the special case of Sb it shows that the threshold position is determined by the dos peak at the X-point overlaying the ionization response. The detection

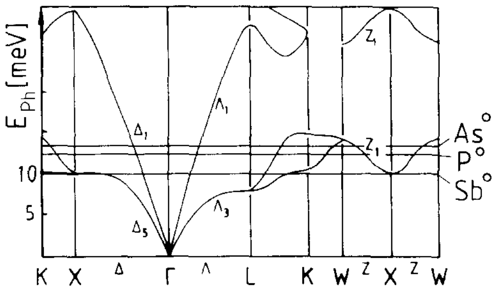


Fig. 1. Phonon dispersion and shallow donor binding energies in germanium.

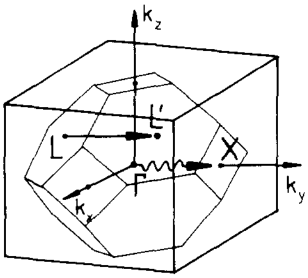


Fig. 2. Brillouin zone of fcc crystals visualizing the intervalley (inter-L-point) scattering by X-point phonons in Ge.

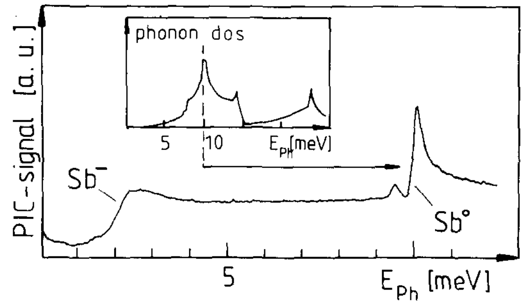


Fig. 3. Phonoconductivity response of Ge:Sb ($4 \times 10^{14}$ cm$^{-3}$). Inset: phonon density of states (dos) showing the coincidence of the peak of the TA-X-point phonon with the PIC threshold of the Sb neutral donor at 10 meV. The structure at ~9.6 meV is due to a small spectral precursor of the Al phonon source. The rise at ~1.5 meV is due to the detachment of electrons having been trapped by Sb-complexes (see text) after bandgap illumination.

zone is estimated to be within a depth of several μm from the superconductor–semiconductor interface corresponding to the small phonon diffusion length at these extreme frequencies. Since in the present experimental setup the change in resistance is measured across a 2 mm thick sample, of which only some μm change resistance due to phonoionization, much higher sensitivities may be expected with better adapted geometrics.

In contrast to donors no PIC threshold has been found corresponding to the ionization of the neutral acceptor Ga in Ge although its binding energy was shifted down under uniaxial stress from ~11 to ~8 meV. This is in accordance with the fact that the valence-band maximum is at $k = 0$ so that large $q$ transfer is not possible. Also, for donors in GaAs we got a negative result.

There is, however, a class of shallow states where bandstructure is not of primary importance for wavevector conservation since for them $qa^* \sim 1$ at the binding energy of the carrier. These donor/acceptor-related states are analogues to the overcharged metastable $H^-$-ion. In semiconductors below roughly 10 K neutral donors and acceptors are most common shallow traps for non-equilibrium carriers. The metastable overcharged centers are readily produced by irradiating the sample with bandgap light generating electrons and holes or, alternatively, with FIR light to generate some majority carriers from the neutral impurities. They may also be produced by carrier injection or avalanche processes at higher field strengths. Within the hydrogenic model for single donors/acceptors the binding energy of the additional carrier is only 0.05 times that of the neutral state whereas $a^*$ due to the correlation of both carriers does not increase correspondingly. Such states have been first found by photoconductivity in the FIR range. It turned out that very sensitive detection is possible also by PIC. Binding energies have been thus obtained for the $A^+$-states of the acceptors B, Al, Ga, and In in Si [3] showing that the attractive central cell potential of the impurities is effective for the second, the outer hole, only in the case of the deep acceptor In where a binding energy of 5.9 meV is found instead of the hydrogenic value of 1.8 meV found for $B^+$, $Al^+$, and $Ga^+$. Another example for overcharged states is the signal rise near 1.5 meV in fig. 2. It is not due to carriers trapped by isolated neutral Sb in Ge since their binding energy as estimated from the hydrogenic model (neglecting many-valley effects) should be only 0.5 meV. A state with such a small binding energy is not very stable at the working temperature of 1 K. Instead, the threshold is due to the few carriers that are trapped with larger binding energies by, e.g., those pairs of Sb (so-called complexes) which according to the distribution probability at a total concentration of $4 \times 10^{14}$ cm$^{-3}$ are close enough. This interpretation is substantiated by fig. 4 where at the lower temperature of ~0.5 K the $P^-$-threshold at 0.6 meV is due to isolated $P^-$ whereas at 1 K only the few overcharged complexes with their distribution of larger binding energies contribute to the (much weaker) signal. The low-temperature curve, although having much better signal-to-noise ratio was obtained with much smaller phonon irradiation intensity. Analogous FIR-results have been discussed by Taniguchi et al. [12].

Unfortunately, to investigate the phonon intensity dependence there is no practicable way to vary in situ the tunnelling resistance of the junc-

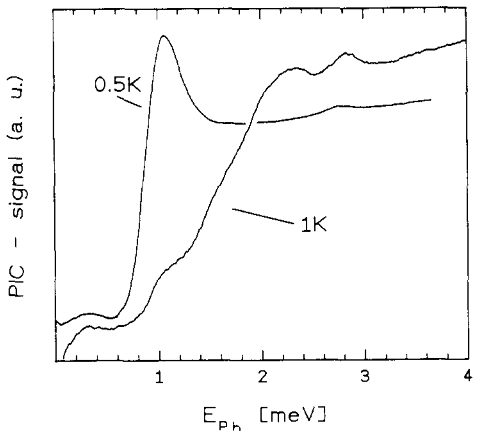


Fig. 4. Comparison of the PIC thresholds for Ge : $P^-$ ([P] = $1 \times 10^{14}$ $cm^{-3}$) at 0.5 K (dominated by the isolated $P^-$ metastable at this temperature) and at 1.0 K (dominated by the few more or less close overcharged pairs of P with their distribution of larger binding energies). The result at 0.5 K was kindly supplied by R. Schwinghammer (Universität Stuttgart, Diplomarbeit, in preparation).

tion and thus the injection current at a given bias. Instead one may use junctions with different tunnelling resistances in consecutive runs or look for the influence of additionally irradiated phonons from a second, a pump junction. From such experiments it is found [8] that the measured response may easily be influenced by the depopulation of the $D^-/A^+$-states by the phonons unless the rate of $D^-/A^+$-generation by light is high enough. As discussed in ref. [8] the spectral responsivity of a $D^-/A^+$-state can be approximated by deconvolution of the experimental phonoresponse (for low-intensity condition) with a more realistic emission spectrum of the Al-junction [11] than just the quasi monochromatic approximation. The resulting response may be rather narrow: for $B^+$ in Si, e.g., we obtain for a certain uniaxial stress [6] a halfwidth of 0.3 meV with maximum at 1.9 meV in good agreement with theoretical estimates [13] that take into account the stress dependence of the valence band structure and the $A^+$-state. Broader response may be obtained for higher D/A-concentration, but it may be shifted to or occur at higher phonon energies such as obtained for Si : $B^+$ (beyond 4 meV) or Si : $In^+$ (beyond 6 meV) [3], i.e., to energies where the phonon mean a free path is not very large. On the other hand in an epitaxial layer of slightly compensated n-GaAs a rather low-frequency band of responsivity around 0.2 meV has been found [4] corresponding to hopping conductivity. Such data are of importance also for a proper selection of the system as a phonon bolometer, e.g. for particle detection. A first application using Si : $B^+$ [14] showed that sensitive time-resolved detection is indeed possible.

In a number of experiments thin semiconducting layers have been used for phonon detection without, however, the knowledge of their spectral response. So far only few epitaxial layers have been investigated [4, 5] by phonon spectroscopy. It will be interesting to do more systematic work on their spectral phonoresponse, also to get information on the shallow electronic states effective for low-temperature conductivity in these layers.

In summary, from the results obtained so far it is evident that the combination of superconducting Al-junctions as high-frequency, high-resolution phonon emitters with the sensitive detection by phonon-induced conduction in semiconductors opens new possibilities for the investigation of phonon–electron interaction and phonon propagation at low temperatures.

## Acknowledgement

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