POOLE-FRENKEL IONIZATION OF Ge:Hg
IN TERAHERTZ ELECTROMAGNETIC FIELDS

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Keywords: Far-infrared radiation, ionization of deep impurities, Poole-Frenkel effect.

Abstract. The ionisation of deep impurity centers in germanium has been observed with radiation in
the terahertz range where the photon energy is much less than the binding energy of the impurities.
It is shown that for not too high radiation intensities the ionisation is caused by the Poole-Frenkel effect.
Like in the well known case of dc fields, the electric field of the high frequency radiation
lowers the Coulomb potential barrier and enhances the thermal emission of carriers.

Recently the ionisation of deep impurities in semiconductors has been observed in the far
infrared where the photon energies are several factors of ten smaller than the binding energy of the
impurities [1]. In germanium doped with deep acceptors a photoconductive signal, rising
exponentially with incident power, has been detected in spite of the fact that the quantum energy was
much smaller than the ionisation energy. The experimental results gave evidence that the observed
phot ionisation of deep impurities is caused by phonon assisted tunnelling. The thermal emission of
the impurities is enhanced by tunnel ionisation in the impurity potential tilted by the electric field of
the high frequency radiation. As long as the the radiation frequency is smaller than the vibrational
frequency of the impurity, the adiabatic approximation applies and tunnelling takes place within one
period of the radiation field.

It is well known on the other hand, that the Poole-Frenkel electric field assisted ionisation [2]
leads to a current flow which increases exponentially with the square root of the applied electric
field. The Coulomb potential barrier is lowered in the presence of an electric field yielding an
increase of the thermal emission probability without tunnelling. The Poole-Frenkel effect has been
observed in the current-voltage characteristics under dc conditions in many insulators, semiconductors
and most recently also in porous silicon [3]. It is the dominant mechanism of electric
field assisted thermal ionisation at not too high field strengths before tunnelling of carriers sets in [4].

In this paper we report on the first observation of a Poole-Frenkel effect like mechanism of
impurity ionisation with terahertz frequency radiation. At low intensities, the far-infrared
photoconductive signal of germanium doped with mercury has been found to increase exponentially
with the square root of the electric field of the radiation as expected from the Poole-Frenkel effect [2].
At higher intensities the signal as a function of the electric field proceeds to the relation
known from phonon assisted tunnelling. In the whole range of intensities, the signal at constant
intensity does not depend on the photon energy for λ > 90.5 μm.

The measurements were carried out on p-type Ge:Hg, having a ionisation energy of
E_Γ = 90 meV. Samples with acceptor densities between 10^{14} cm^{-3} and 10^{15} cm^{-3} have been
investigated in the far-infrared. Ionisation of Hg impurities corresponds to a transition from a neutral ground state to a single charged state. The radiation source used was a pulsed FIR molecular laser, optically pumped by a TEA CO₂ laser. Using NH₃ and D₂O as active gases, 40 ns pulses with a peak power of 50 kW were obtained at wavelengths, \( \lambda \), of 90.5 \( \mu \text{m} \), 152 \( \mu \text{m} \) and 250 \( \mu \text{m} \). The corresponding photon energies of 13.7 meV, 8.2 meV and 5 meV, respectively, are much smaller than the ionisation energy of the impurity. The radiation was linearly polarised.

The Ge samples of thickness 1 mm were placed in a temperature variable optical cryostat and investigated in a temperature range between 20 K and 77 K where \( kT << < e_\text{T} \). The FIR absorption of the samples was unmeasurably small at all wavelengths and temperatures, therefore a heating of the samples due to radiation may be neglected. A series of cold and warm black polyethylene (1 mm thick), teflon and crystal quartz windows were used to transmit far-infrared radiation while rejecting near-infrared and visible light.

For all three wavelengths a photoconductive response was found which, as shown previously [1], is due to ionisation of Hg acceptors. The sign of the photoconductive signal corresponds to a decrease in the sample resistance. The decay time of the signal was about 50 ns which is somewhat longer than the laser pulse. Because the duration of the light pulses is shorter than the capture time of non-equilibrium carriers, recombination may be ignored during the optical excitation. Thus the determined relation \( \sigma_\text{i} / \sigma_\text{d} \) of the conductivities during irradiation, \( \sigma_\text{i} \), and in the dark, \( \sigma_\text{d} \), represents the ionization probability \( \sigma(E)/\sigma_0 \).

In Fig. 1 the experimentally determined dependence of \( \ln(\sigma_i / \sigma_d) \) on the square of the amplitude of the far-infrared electric field, \( E^2 \), at \( \lambda = 90.5 \, \mu\text{m} \) is displayed for two different temperatures, \( T = 47 \, \text{K} \) and 20 K. This plot shows that the ionisation probability \( \sigma(E) \) as a function of the electric field \( E \) follows the relation \( \sigma(E) \propto \exp \left( E/E_\text{c} \right)^2 \) at high fields. This behaviour of the photoconductive signal has been shown to be caused by phonon assisted tunnel ionisation of deep impurities [1]. The characteristic field \( E_\text{c} \) is determined by the tunnelling time [1, 5]. As it is seen from Fig. 1 at lower levels of the electric field, \( E < 1 \, \text{kV/cm} \), the dependence of \( \ln(\sigma_i / \sigma_d) \) on the electric field changes. The data for this range of the fields are plotted on the Fig. 2 in log-linear scale as a function of square root of the electric field. Fig. 2 shows that the probability of ionisation could be well described by the relation \( \sigma(E) \propto \exp \left( E/E_\text{pp} \right)^{1/2} \) in this

![Figure 1](image1.png)

![Figure 2](image2.png)
range of the field. The low electric field limit of the conductivity \( \sigma_i \) shown in this figure is given by the sensitivity of the photoconductive detection of free carrier generation. Finally we note that the ionization probability at constant field strength strongly rises with decreasing temperature.

In order to ensure reliable identification of the photoexcitation mechanism, we carried out power dependence measurements at longer wavelengths. These experiments showed that an increase of the radiation wavelength does not change the strength of the signal as function of the intensity in the whole available range of irradiation intensities. Thus, the probability of excess carrier generation is independent of the photon energy in the present spectral range. This is demonstrated in Fig. 3 where \( \sigma_i/\sigma_d \) is displayed in a log-linear plot as function of the square root of the amplitude of the radiation field for wavelengths 90.5 \( \mu \)m and 250 \( \mu \)m. In the range of electric field strength of Fig. 3 the curves for both wavelengths coincide within the accuracy of the measurement. This observation allows to rule out other nonlinear optical mechanisms like multi-photon absorption [6, 7], photon assisted tunnelling [8] as well as light impact ionisation [9]. The free carrier generation rate is determined by the strength of the electric field of the radiation.

The measurements shown in Fig. 3 have been carried out at 77 K. At this temperature the sample has a substantial dark conductivity which increases the sensitivity of detection across the 50 kOhm load resistor compared to lower temperatures. At this temperature a reliable recording of the photoconductive signal was possible at lower electric field strengths than those of Fig. 2. As at lower temperatures, the conductivity \( \sigma_i \) is proportional to \( \exp(E/E_{pp})^{1/2} \) in a certain range of the electric field. At very low electric field strengths \( \sigma_i \) saturates approaching ohmic conductance.

The field and temperature dependencies of the observed photoionization in the range of relatively small fields follows the well known behaviour of electric field enhanced conductivity in solids attributed to the Poole-Frenkel effect [2]. The Poole-Frenkel effect is usually employed to explain the effect of an electric field on thermal ionization of attractive Coulombic centers. For large distances from the center the potential is Coulomb like yielding shallow excited states. Close to the center the potential steeply drops generating one deep bound ground state.

In Fig. 4 the potential energy of a deep center is schematically sketched for the situation of a finite electric field strength. Under an electric field \( E \) the ionisation potential barrier is lowered along the direction of the electric field by an amount \( E_{pp} = \sqrt{E} \).
This Poole-Frenkel lowering of the potential barrier can take place only in the Coulombic region of the potential. The original Poole-Frenkel theory considers the emission of carriers only in the direction of the electric field. Then the ionization probability of thermal emission \( e(E) \) increases over the zero field value like

\[
e(E) \propto \exp \left( \frac{1}{kT} \sqrt{\frac{Z \alpha E}{\kappa}} \right)
\]

(1)

where \( Z \) is the charge of the center and \( \kappa \) is the dielectric constant. This expression yields the exponential increase of the photocurrent with the square root of the electric field, as shown in Figs. 2 and 3, but does not give full account for the conductivity \( \sigma_f \) as a function of the electric radiation field. The discrepancies are exactly those as observed in the case of dc electric fields [3, 10, 14]. The slope of \( \ln(\sigma_f/\sigma_0) \) is only about one half of that predicted by Eq. (1) and the photoconductivity saturates at low fields. These features of the photoconductivity at terahertz frequencies are in excellent agreement to published data of the enhanced conductivity in dc electric fields. They are also well described by more realistic theoretical approaches which consider the emission of carriers in three dimensions and in some cases taking into account carrier distribution statistics [4, 11, 12] or are based on the the Onsager theory of dissociation [12, 13]. These experimental and theoretical results additionally confirm our conclusion that the observed photoconducting signal at photon energies much less than the binding energy of the deep acceptors is due to the electric field of the high frequency radiation.

In summary the Poole-Frenkel ionisation of impurities in semiconductors has been observed with ac electric fields in the terahertz frequency range just as in the case of dc fields. The high frequencies have the advantage that the carrier emission process can be studied with very low dc bias fields avoiding injection at the contacts. Furthermore extremely high electric field strengths may be applied during a very short pulse without driving the sample into avalanche breakdown.

Acknowledgement. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References