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III-6. Oscillatory Electro-Absorption Effects near the Direct Edge of Germanium*

Y. HAMAKAWA, F. GERMANO and P. HANDLER

Department of Physics, Department of Electrical Engineering and Materials Research Laboratory
University of Illinois, Urbana, Illinois, U.S.A.

The effect of an electric field on the optical absorption near the direct edge in germanium has been investigated in the temperature range from 300°K to 14°K with electric fields varying from 5×10^3 to 5×10^4 V/cm. The data for the field induced differential absorption coefficient $\Delta\alpha=\alpha(E, \omega)-\alpha(0, \omega)$ show a large exponential tail below the edge and many oscillations above the edge in qualitative agreement with the simple theory for the field induced change in the absorption coefficient on a parabolic edge. However, the magnitude of $\Delta\alpha$ is strongly temperature dependent. Also the first negative peak, observed close to the direct gap energy, is found to be larger in amplitude and narrower in width than predicted by the simple Franz-Keldysh theory. It will be shown that part of data can be explained by the simple theory, but a detailed fit of the data will require consideration of the effect of the exciton.

§ 1. Introduction

Recently it has been shown by a number of investigators that the electro-optical techniques can be used to determine the critical points in the band structure of solids. The electro-reflectance technique[1,2] has been especially fruitful for those critical points which lie above the fundamental absorption edge while the electro-transmission data have been useful in studying the fundamental absorption edge[3] and indirect absorption edges.[4,5] The simple theory of the effect of the electric field on the absorption edges of semiconductors predicts that the change in the absorption $\Delta\alpha=\alpha(E, \omega)-\alpha(0, \omega)$ will be exponential-like below the edge and oscillatory above it. While the exponential-like tail has been observed in some compounds[6,7] the oscillations have only been observed in the indirect edges of germanium and silicon[8,9] and in the direct edge of gallium arsenide.[10] Recently Frova *el al.*[3] have shown the portion of the first oscillation above the direct edge in germanium. The present paper introduces data containing several oscillations above the fundamental edge and allows a direct comparison of the line shape with theory. Duke and Alferieff[11] have just published the result of their calculation for the absorption coefficient of an exciton in an electric field. Their results indicate that the absorption due to the exciton will be broadened by the electric field and give rise to a low-energy exponential-like tail which has the same dependence as the change in the absorption coefficient of a parabolic edge without excitons, and that the apparent energy gap will be shifted to lower energy. Quenching of the exciton absorption at low fields in germanium has recently been observed by Vrehen[12] and suggests that the exciton plays a dominant role in $\Delta\alpha$. Unfortunately the exciton binding energy at the direct gap in germanium is less than a few millielectron volts and it is difficult to separate the effect of the exciton from those of the parabolic edge.

§ 2. Experimental

The samples were wide area indium alloy *p-n* junctions having windows less than twenty microns thick. They were abrupt junctions as determined from the capacitance-reverse bias voltage characteristics. The electric field at the junctions was determined from those characteristics. The samples were mounted on a thin germanium substrate to avoid strain effects at low temperatures and then set into a liquid helium optical dewar. A PbS detector was mounted on the liquid nitrogen shield directly behind the sample. In the present work we have used the electric field modulation technique employing phase sensitive detection described in previous

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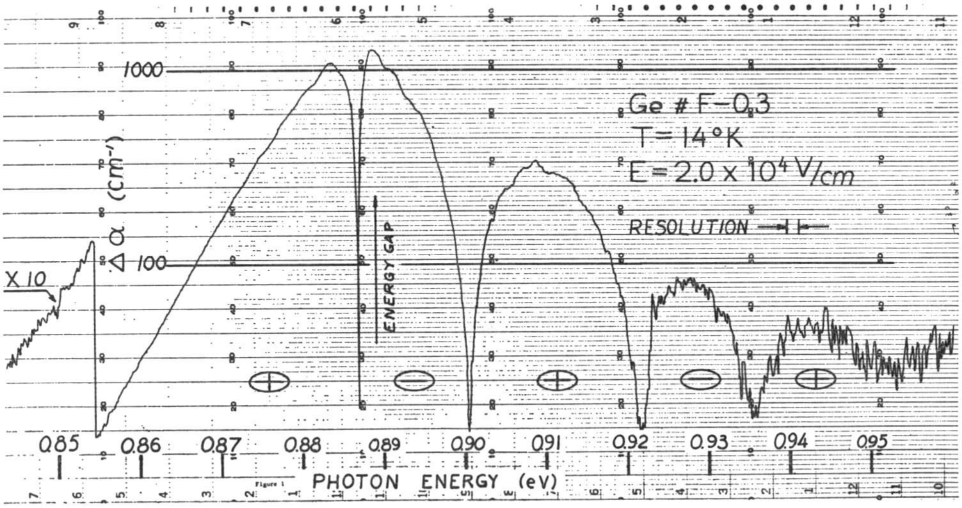

Fig. 1. Typical experimental recording. The marks ⊕ and ⊖ express the sign of the differential absorption coefficient for each oscillation period.

papers.[3,8] The optical and electronic systems for measuring $\Delta\alpha$ were essentially the same as the ones used in ref. 3). The electric field modulating frequency was 1500 cps at room temperature and 500 cps at the lower temperatures to accommodate the response of the PbS detector.

Figure 1 shows a photograph of the data taken on a 2Ω cm n-type base p-n junction at 14°K. The output to the recorder is logarithmic so that both positive and negative changes in $\Delta\alpha$ are plotted positive. The signs within the circles in the figure show the true direction of thesignal. The effect is quite large immediately above and below the energy gap (0.889 eV) and the peak values correspond to almost a third of the total absorption of these points. Measurements were carried out on a number of samples having n-type base resistivities of 28, 21, and $2\,\Omega$ cm but for the purpose of this article only the data from the $2\,\Omega$ cm sample will be discussed.

§ 3. Discussion

A strong temperature dependence is observed in the amplitude of $\Delta\alpha$ as shown in Fig. 2 where $\Delta\alpha$ is presented for two different temperatures and the same electric field. The change in the absorption coefficient increases as the temperature decreases being about five times as large at 14°K than at 300°K. Such a large variation can be explained in part by thermal broadening which smoothes the absorption edge. The Franz-Keldysh effect theory for a direct edge is essentially temperature independent,[13] although some variation with temperature exists through the reduced masses of the electron-hole pairs and the energy gap. This variation, however, is less than 10% between 14°K and 300°K.

Figure 3 shows the change in $\Delta\alpha$ with photon energy, at room temperature, for three different fields. As can be seen in the figure the energy differences ($\Delta\varepsilon_n$) between the zeroes of $\Delta\alpha$ increases with the electric field. According to theory of the effect of an electric field on a parabolic edge[13,14] the $\Delta\varepsilon_n$ are proportional to the 2/3 power of the electric field. The constant of proportionality involves the reduced masses of the electron with the light and heavy holes.

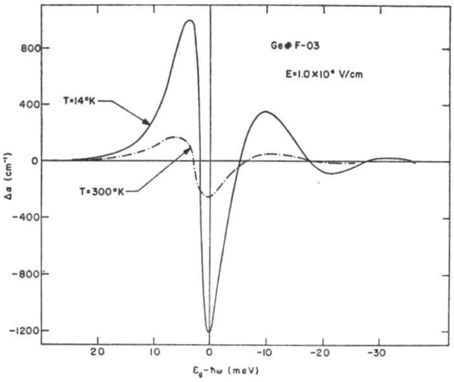

Fig. 2. Field induced change in the absorption coefficient near the direct edge of germanium at two different temperatures for the same electric field. ε_g is the direct energy gap as determined from the temperature measurements: 0.802 eV at 300°K and 0.889 eV at 14°K.

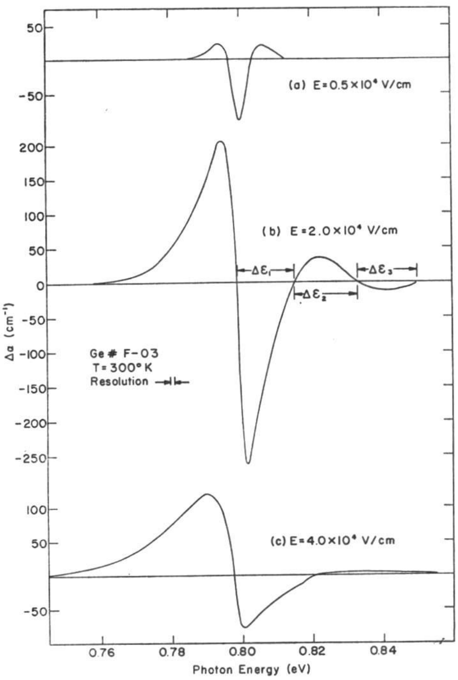

Fig. 3. Field induced change in the absorption coefficient of germanium at room temperature for three different fields.

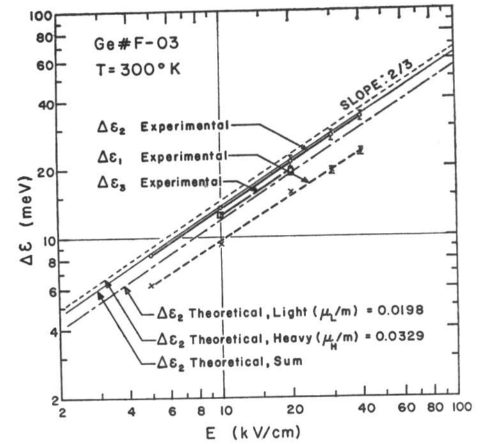

Fig. 4. Electric field dependence of the width of the oscillation above the gap.

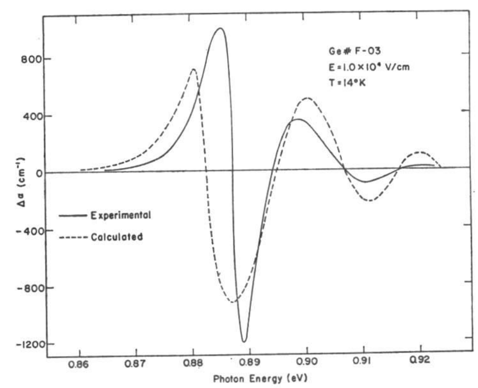

Fig. 5. Attempt of comparison between experimental data and the curve calculated from the simple parabolic edge theory. Thermal and electric field broadening were considered.

Figure 4 presents a plot of three of those energy differences $\Delta\varepsilon_1$, $\Delta\varepsilon_2$, and $\Delta\varepsilon_3$ (corresponding to the first, second, and third oscillations above the edge) against the electric field. The slope and magnitude of the $\Delta\varepsilon_2$ are seen to be good agreement with the theoretical values which are also inserted in the figure. Although $\Delta\varepsilon_1$ has the 2/3 slope, the width of the first oscillation is much narrower than expected from the theory. Similar results have been found in electro-reflectance measurements.[2)] At the lower electric field the positive peak below the edge becomes smaller relative to the first negative peak as seen in Fig. 3 (a). Most recently Vrehen[12)] has observed similar structures in germanium single crystals at electric fields up to 1000 V/cm. He finds that these structures are due to the excitons. At energies large compared to the exciton binding energy we might expect the data to be in good agreement with the theory of a parabolic edge without excitons.[13)] In Fig. 5 both calculated and experimental curve are presented. The calculated curve has been shifted so that the last oscillation of the two curves coincide. In the calculation of the theoretical curve the following numerical values were used: electron-hole reduced masses: 0.021 m and 0.037 m for light and heavy hole respectively; Lorentzian broadening parameters[15)] for thermal and electric field broadening $\Gamma_E=0.04$ meV and $\Gamma_T=0.2$ meV, that is, $\alpha(E)$ was broadened with $\Gamma_1=\Gamma_E+\Gamma_T$ and $\alpha(0)$ with $\Gamma_2=\Gamma_T$. We have neglected the influence of the field induced change in the refractive index.[16)] The error in neglecting this effect on $\Delta\alpha$ is estimated to be less than 1% over the range of our measurements. The reduced masses obtained from the slope of the exponential-like tail is found to be 0.024 m at 77°K and 0.022 m at room temperature which are close to the expected value of the electron light hole reduced masses 0.0214 m and 0.0198 m respectively. Analysis of this tail[17)] also suggests an effective gap lower than the true gap for this temperature. Thus both the high energy oscillations and the slope of the exponential tail suggest that our data are in qualitative agreement with the theory of Duke and Alferieff[11] for the effect of an electric field on the optical absorption of an exciton at a parabolic edge. The shift of the energy gap was also observed[3] for the indirect absorption edge in silicon where it was found that the effective gap was approximately five millielectron volts below the zero field indirect energy gap at that temperature. The shift to lower energies has also been observed in the indirect edge in germanium.[3,18]

In the case of the highest field in Fig. 3 the first negative peak has decreased relatively to the positive as has already been observed for the indirect edge in silicon.[3]

Acknowledgements

The authors wish to thank Dr. D. Aspnes, D. Blossey, and J. McNatt for a number of useful discussions and suggestions, and to E. Culver for his technical assistance. We also express our thanks to Mr. J. Swartz and the Delco Radio Co. for supplying the samples.

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COMMENT BY THE AUTHORS

The purpose of this note is to suggest that most, if not all the data observed by means of electroreflectance and electroabsorption techniques and previously interpreted as Franz-Keldysh effects are mainly due to the electric field quenching of the exciton absorption. The best demonstration of exciton quenching has been reported by Vrehen[1] on germanium at 77°K. The disapperance of the exciton peak is observed in both the absorption and the differential absorption. Also we have concluded, after an extensive effort to fit the line shape of the differential electroabsorption of the direct edge in germanium, that it is not possible to fit the observed data with the Franz-Keldysh (FK) theory.

Discussion of other data in the literature will be aided by consideration of Fig. 1(a), which shows a schematic description of the absorption coefficient for a direct parabolic edge with an exciton such as is found in germanium and gallium arsenide with and without a large electric field. Figure 1(b) shows the experimentally expected change in $\Delta\alpha=\alpha(E)-\alpha(0)$ while Fig. 1(c) shows the $\Delta\alpha$ expected for this edge from the Franz-Keldysh (FK) theory, suitably broadened as was $\alpha(0)$ in Fig. 1(a). Figures 1(d) and 1(e) show the expected change in reflection coefficient for the change in $\Delta\alpha$ due to excitons and FK theory. We note that the negative peaks labeled A and B precede the energy of the gap E_G by approximately the binding energy of the exciton. For electric field quenching of the exciton we would expect the points A and B to be relatively constant in energy as the electric field is increased, whereas in the FK theory these same points, now labeled A' and C will increase their distance from E_G as (electric field)$^{2/3}$. Figure 6 of Vrehen's data[1] shows that the A point is insensitive to the magnitude of the field. Data taken by Hamakawa, Germano, and Handler at temperatures from 14°K to 300°K also show that the A point is much less sensitive to field than predicted by the FK theory. In one case a change of $\sim$10 meV was expected, but almost none was observed. In addition they find that the position of the zero field energy gap lies at or above the A point rather than below it as is predicted by the FK theory. Figures 7 and 8 of the data of Frova, Handler, Germano, and Aspnes[2] (FHGA) show that the *A* peak is larger in magnitude than the first positive peak and that once again the *A* peak does not move with a change of almost five in the magnitude of the field. In gallium arsenide Paige and Rees[3] find that the *A* peak precedes the gap energy and is very close to the exciton energy. Their *A* peak is also *much larger* than all other peaks, contrary to FK predictions. In addition to the direct gap data, the experimental information available for indirect transitions where the exciton absorption is relatively weak also suggest that the FK theory is not applicable. Figures 4 and 6 of the paper by FHGA[2] show that the effective energy gap necessary to fit the data for indirect

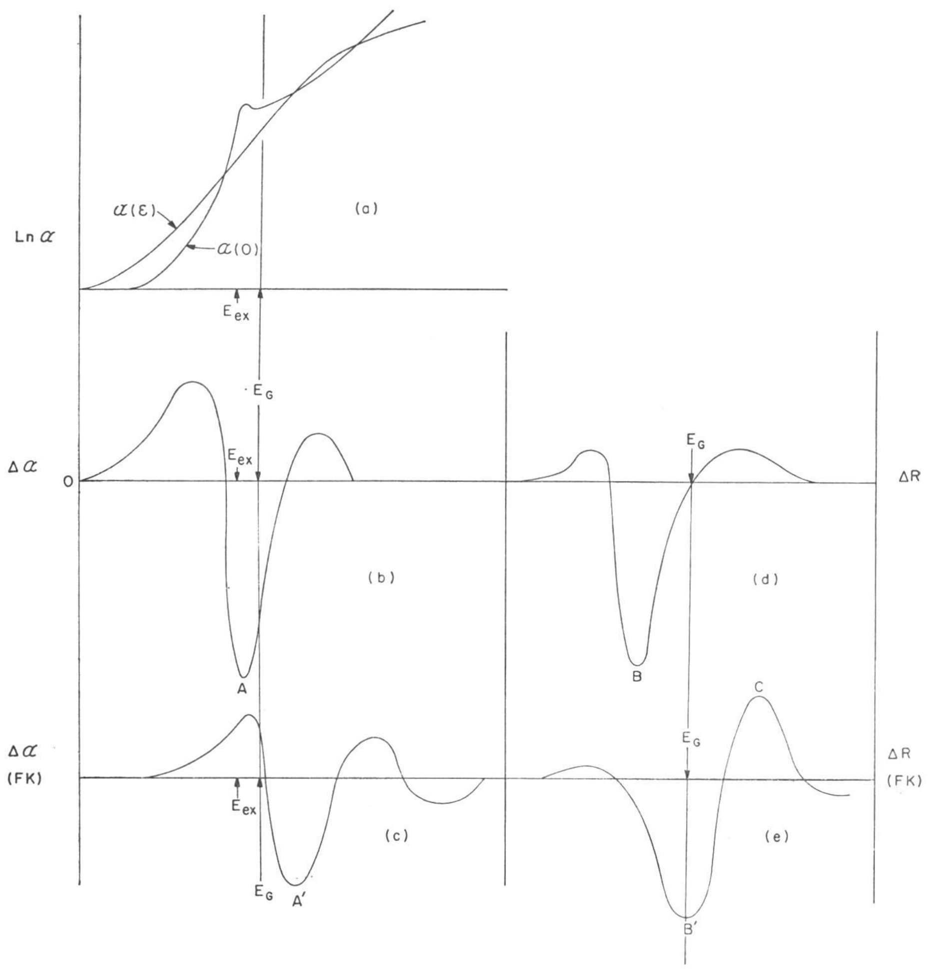

Fig. 1. Comparison of the change in absorption coefficient and change in reflection for a parabolic edge with and without excitons.

transition's germanium and silicon lies very close to the ground state of the exciton and more than five millielectron volts below the true gap. This same result is found for germanium in the piezotransmission data of Engeler, Garfinkel, and Tiemann.[4] Finally in CdS, Snavely[5] has observed a line shape very close to that found for germanium and gallium arsenide, which occurs at the energy of the exciton and far from a direct edge.

It will now be shown that the electroreflectance data on the direct edge in germanium and gallium arsenide are in agreement with the electrotransmission data. Unfortunately the electroreflectance data are difficult to interpret for a large number of reasons: the magnitude and uniformity of the field are unknown, the amount of field modulation is also unknown, the line shape changes with the magnitude of the field,[6] and it is not certain whether in a particular experiment the observed change in reflection is related to the change in the dielectric constant or to its derivative. Nevertheless the model presented in this letter suggests that lines at energies such as shown in Fig. 1(d) rather than that shown in 1(e) are to be expected. The most important difference between the two figures is that the FK theory predicts that the first negative peak B' will occur at E_G whereas inclusion of the exciton would suggest that B will occur below E_G. Seraphin in his paper on germanium[6] comments that the B peak "precedes slightly the fundamental edge". His line shape is very close to that shown in Fig. 1(d) and far from the FK prediction of Fig. 1(e). In the electroreflectance data on gallium arsenide both Seraphin[7] and Cardona[8,9] find that the dominant peak which they identify as the fundamental edge lies below the value of the energy gap as determined by Sturge[10] and thus the data for this line are in agreement with the electrotransmission work.[1~3]

If the above arguments with respect to the fundamental edge are correct, then another question has to be answered. Why are the line shapes for the Λ transitions in any given sample almost identical in form to that found for the fundamental edge in the electroreflectance data, (see figures in ref. 6)~9)) except for some increase in width and magnitude? The FK theory for saddle point edges is quite complicated[11] and the resultant line shape could take on any number of a large variety of forms, the most likely of which should not be similar to that observed at the fundamental edge. Also the FK theory predicts that the amplitude and period of the oscillations should vary with the reduced mass of the hole-electron pair in the direction of the applied field and with the orientation of the sample. Some differences in the motion of peaks with field are found by Seraphin[9] in gallium arsenide but the result does not discriminate between a FK theory and excitons. Thus in electroreflectance where the magnitude and modulation of the electric field are unknown, the only point that can be correlated is that the line shape of the higher transitions and the fundamental edge are similar. The fundamental edge line shape has been shown to be primarily an exciton effect in the electroabsorption data. Therefore in consideration of the above evidence the author believes that the electroreflectance lines, identified as Λ transitions, are associated with excitons and that all the higher energy transitions which also have line shapes similar to the fundamental edge, except for their widths, are also excitonic in nature.

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DISCUSSION

Cardona, M.: 1) This first part of my question refers to the E_0 edge. I believe Dr. Handler has good evidence that the quenching of excitons has a large contribution to electro-optic effects near E_0. Franz-Keldysh type effects are, however, also observed at E_0 as evidenced by the large number of oscillations observed in several materials. Electric field shifts are also observed for these oscillations. We find for GaAs, after we carefully sort out impurity effects, E_0 gaps which agree with those of Sturge within experimental error. Also, Mavroides has reported E_0, piezo-reflectance gaps (0.797 eV) for germanium which agree with the electro-reflectance gaps. While exciton quenching could be important in electro-reflectance, they should not contribute to piezo-reflectance.

2) Higher transitions. The fact that $\Delta R/R$ has the same line shape at E_1 as at E_0 does not mean that $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$, the quantities related to the microscopic phenomenon, also have the same shape. We do not find in many materials the same shape for $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ at higher gaps as at E_0. Field dependence of peak positions close to estimates from Aspnes' theory is also found. In conclusion, I believe that the question of the exciton contribution to electro-reflectance at higher gaps is still opened, especially in view of the theoretical questionability of the existence of strong exciton effects at saddle critical points. Such exciton effects, should, in any case, be different at a saddle point and an extremum giving also different line shapes.

Handler, P.: I do not have anything to add besides that given above. I believe our difference can only be resolved by additional experiments.

Callaway, J.: Professor Handler is undoubtedly correct in maintaining that exciton effects are important and must be considered in any detailed comparison of theory and experiment concerning the effect of an external electric field on optical absorption. It is, perhaps, not so clear that the exciton effects must dominate the change in absorption in all cases. For example, in the experiments of Lambert, who studied the change in the optical absorption of GaAs in an electric field, (1) an increase in absorption was observed over a range large compared to the exciton binding energy, and (2) the degree of agreement between theory and experiment improves with increasing fields. Lambert reached fields about a factor of 2 larger than those of Handler. I would suggest that in order to obtain a reasonable comparison between the simple theory and experiment, rather large fields may be necessary.

Handler, P.: I refer you to the paper by Paige and Rees, Phys. Rev. Letters **16** (1966) 444, which includes measurements above the direct edge as well as below. They are the best available data and I believe they support the views printed above.

Paige, E. G. S.: The distinction between the bound and continuum exciton state should be made. Even when no clearly resolved exciton line is present the coulomb interaction of electron and hole produce a major contribution to the zero field absorption and this must be included in any quantitative theory. D. Rees has incorporated this interaction in some recent calculations (Thesis submitted to University of Cambridge). Incorporation of coulomb interaction leads to a lowest energy zero electro-absorption point which is field independent. This is observed experimentally in GaAs. Neglect of coulomb effects leads to field dependence of this point.

Handler, P.: Great ! !

Franz, W.: As the name of Keldysh and myself have during this conference several times been used, abused and objected to be used, I may make a short remark concerning idea, appearence and nomenclature of tunneling assisted optical transitions. Though Keldysh, I am sorry, is not present, I hope he would agree with that I am going to say. We did not invent the term Franz-Keldysh effect and do not know its exact definition. The definition may well be: tunneling assisted light absorption, as we were the first to calculate and predict such an effect. We do not claim anything being named this way, although we do not in general object. The essential idea of the theory is electron tunneling into the forbidden band before the optical absorption occurs. This means a broadening of absorption, not a shift. So a broadening of exciton lines by electric field is at least partly to be attributed to tunneling assisted absorption, a shift of exciton lines certainly is not. For an exponential band edge a broadening results in a shift only because the edge drops towards low frequencies. But this edge shift, caused by broadening, is, of course, entirely due to tunneling-assisted absorption.

Handler, P.: No matter how interpretations change I think that the names Franz-Keldysh will always be associated with photon assisted tunneling in solids.