kutierten Beiträgen zu der Zusatzsuszeptibilität klein. Diese Korrektur wurde von Bowers und Yafet[4] für InSb berechnet und ist im wesentlichen ebenfalls proportional zur Ladungsträgerdichte n.

IV. Schlußbemerkungen

Zusammenfassend kann gesagt werden, daß das Verhalten bei hohen Ladungsträgerdichten in beiden Arten der Untersuchungen auf den gleichen Grund zurückzuführen ist. Neben den Abhängigkeiten der effektiven Massen und der g-Faktoren von der Bänderform in der Landau–Peierls- und Pauli-Suszeptibilität der Elektronen treten zusätzliche Interbandterme, die proportional zur Ladungsträgerdichte sind, auf. Aus dieser Übereinstimmung folgt, daß die in den erwähnten Arbeiten verschiedener Autoren angewendete Aufteilung der Suszeptibilität in sich konsistent ist.

Die effektive Masse und somit der g-Faktor konnten für InAs auf eine empfindliche Art bestimmt werden.

Ein Teil der Resultate ist bereits in zwei Kurzberichten erschienen[23, 24].

Die Autoren danken Herrn Dr. E. Steigmeier für seine wertvolle Unterstützung bei der Auswertung der Hall-Effektmessungen. Ferner sind wir dem Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung für die finanzielle Unterstützung dieser Arbeit zu Dank verpflichtet.

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Intrinsic Optical Absorption in Germanium

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(Z. Naturforschg. **19 a**, 548—552 [1964]; eingegangen am 21. Januar 1964)

Dedicated to Prof. Dr. E. Justi *on the occasion of his 60th birthday*

The absorption constant of germanium beyond the first direct absorption edge has been determined up to energies of 2.5 eV by transmission measurements on very thin samples prepared from bulk single crystals. The results are discussed in terms of recent band structure calculations and previous reflection measurements. At low temperatures the observed structure gives evidence for exciton formation connected with direct transitions at a saddle point in the energy difference between conduction and valence bands.

The measurement of the optical constants at energies beyond the fundamental absorption edge is a very useful tool in determining the electronic band structure of semiconductors and insulators[1]. In detailed band calculations[2, 3] a few potential parameters are left adjustable in order to fit experimental values of vertical energy distances between valence and conduction band at certain points of high symmetry in k-space deduced from experiments. These calculations then in turn give the joint density of states of valence and conduction bands as a function of the vertical energy difference between both sets of bands. The joint density of states, on the other hand, is the essential factor determining the imaginary part ε_2 of the dielectric constant since it represents the number of initial and final states for direct interband transitions.

Reflection techniques have been most widely used in order to determine the optical constants n and k and hence the real and imaginary part $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2\,n\,k$ respectively of the dielectric constant at energies higher than the fundamental absorption edge. One technique uses a Kramers–Kronig analysis of the reflectance data of unpolarized light[4] and thus requires a measurement of the entire reflection spectrum or its most strongly contributing parts. The optical constants can also be calculated from the ellipsometry of reflected polarized light[5].

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[3] D. Brust, M. C. Cohen, and J. C. Phillips, Phys. Rev., Letters **9**, 389 [1962].

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The spectra determined by these techniques depend critically on the surface preparation and may not represent the bulk properties in detail. Direct measurement of the intrinsic bulk absorption requires extremely thin samples. It has been accomplished however, in thin films of a number of semiconductors including germanium prepared by vacuum evaporation [6, 7]. Although epitaxial growth has been observed on CaF_2 substrates these films do not represent single crystal samples and are probably not strain free due to different thermal expansion coefficients of the deposited material and the substrates. This paper is concerned with measurements on extremely thin single crystal germanium samples prepared from bulk material.

Sample Preparation and Measurements

Slices of 1 mm thickness have been cut, cleaned and annealed in vacuum at 850 °C for two hours. The grinding and polishing (Al_2O_3, grain size 0.05 μ) of one side was followed by another annealing treatment under the same conditions. Subsequently, the polished side of the sample was glued with a very thin layer of glycol phtalate of uniform thickness onto a plane parallel optically flat glass plate. Thus it was possible to get samples of highly uniform thickness of 3 to 10 microns by grinding and subsequent polishing. After dissolving the glue in acetone (24 hours at room temperature) the self supporting samples were brought onto quartz plates and etched in a 1 : 1 mixture of HF and HNO_3 in steps of a few seconds. A rough check on the thickness could be made by visual observation under a microscope. Below one micron thickness red light starts being transmitted and the etching treatment can be stopped at a desirable thickness.

This procedure provided us with samples of sufficient area for optical measurements and thicknesses of a few thousand Å. It should be noted that the preparation of the samples could be performed only from crystals with very low dislocation density. The structure of a thin sample was tested by electron transmission microscopy. The appearance of KIKUCHI lines in the diffraction patterns in Fig. 1 [*] implies that the sample is of nearly perfect crystallinity. The optical transmission measurements were performed with a Zeiss PMQ II double prism spectrometer. Its low scattered light level in connection with an intense source (Osram xenon arc XBO 450) and the use of gray filters when measuring the incident intensity made it possible to measure transmissions of less than one part in 10^5.

Results

Fig. 2 shows the absorption spectrum of a germanium sample of 2500 Å thickness at room temperature between 0.75 and 2.5 eV photon energy. It displays the edge due to direct transitions $\Gamma_{25'}^{3/2} - \Gamma_{2'}$ at 0.8 eV and a second edge due to transitions from the split-off valence band $\Gamma_{25'}^{1/2}$ at 1.08 eV. This second edge has been found by HOBDEN [8] previously. The thickness of our samples was determined by fitting the values of the absorption constant to those reported by HOBDEN between 0.8 and 1.25 eV. The optical density increases further towards higher energies to another doublet structure at 2.15 and 2.35 eV. The correspondent doublet has also been observed in reflection [9] and has been originally attributed to direct transitions at the L point [10] and more recently to $\Lambda_3 - \Lambda_1$ transitions (see Fig. 4). Transmission measurements on evapo-

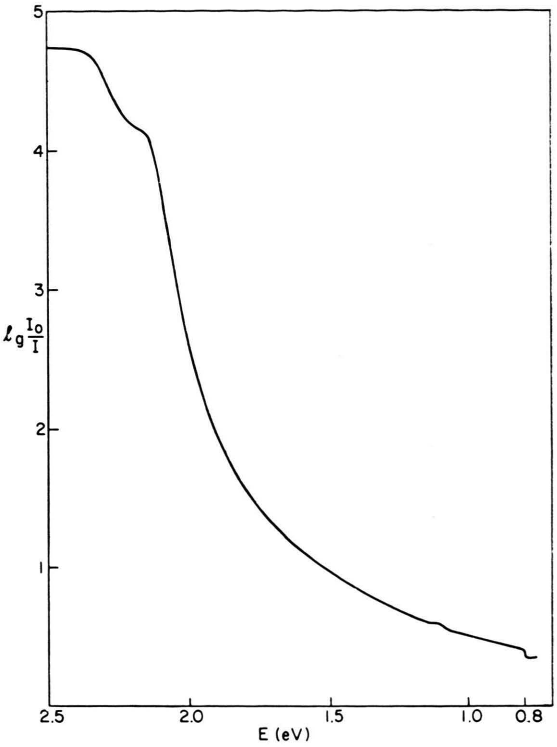

Fig. 2. Optical density of a germanium sample of 2500 Å thickness at 300 °K.

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[*] Fig. 1 on page 550 a.

[6] M. CARDONA and G. HARBEKE, J. Appl. Phys. **34**, 813 [1963].

[7] M. CARDONA, Phys. Rev. **129**, 69 [1963].

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rated films showed the doublet structure in a somewhat less pronounced form than the present data. At 77 °K the edge is shifted to higher photon energies and an absorption peak arises on top of it. This is shown in Fig. 3 in form of the absorption constant calculated from the measured transmission and the known reflectivity data[4, 9, 11] taking into account multiple reflection inside of the sample. The half width of this peak is about 0.03 eV. The existence of the peak is in contrast to the measurements on evaporated epitaxial films, where no such structure could be seen[6]. This must be due to the poor crystallinity of the films and strain effects. It should be noted that in our measurements also at low temperatures the sample is essentially strain free; it is attached to a quartz plate with a tiny dot of glue at one corner.

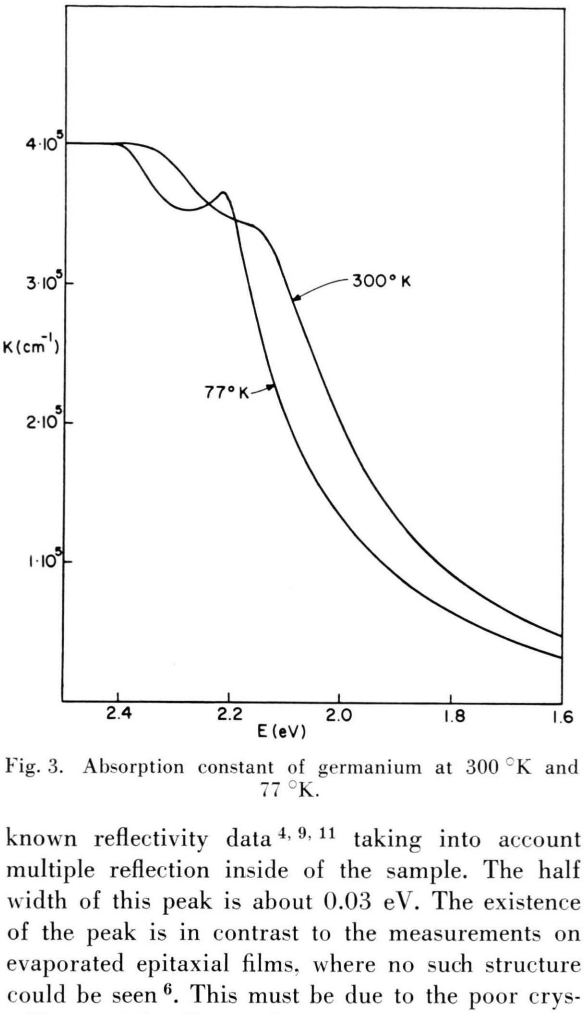

Fig. 3. Absorption constant of germanium at 300 °K and 77 °K.

It seems worth emphasizing that the peak has also not been found in the analysis of all previous reflectance data. However, the present results resemble the structure of the absorption constant or of $2\,n\,k$ at the correspondent absorption edge due to L- or Λ-transitions in more ionic zincblende semiconductors like InSb and CdTe[5, 6].

The edge itself is shifted without altering its shape in the range from 1.6 to 2.0 eV with a temperature coefficient of $-(4.4 \pm 0.3) \times 10^{-4}$ eV/°K. At 20 °K the edge is again slightly shifted to higher energies, however, the peak is not further sharpened. The splitting of the peak due to spin-orbit interaction is 0.18 eV in agreement with previous measurements[6, 9, 11].

Discussion

The band structure of germanium was first calculated by Herman[12] with the OPW method. This calculation gave information on the energy levels at some symmetry points in k-space. Based on this work the doublet structure at 2.15 – 2.35 eV was assigned to $L_{3'} - L_1$ transitions[10]. Recently the pseudopotential method as a scheme to interpolate between the levels at the different symmetry points demonstrated the existence of different van Hove[13] singularities characterized by the condition

$$\nabla_k (E_c - E_v) = \nabla_k E_{cv} = 0 ,$$

where $E_c(k)$ and $E_v(k)$ are the energies of states in the conduction and valence bands, respectively. If $E_{cv}(k)$ has a relative minimum at a certain energy we obtain a singularity of the type M_0. Saddle point structures of the first and second kind[13] are called M_1 and M_2 singularities. Fig. 4 shows the energy bands calculated by Brust, Phillips and

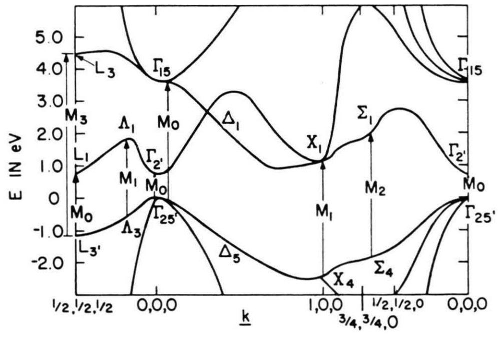

Fig. 4. Pseudopotential energy bands for germanium after Brust, Phillips and Bassani[2].

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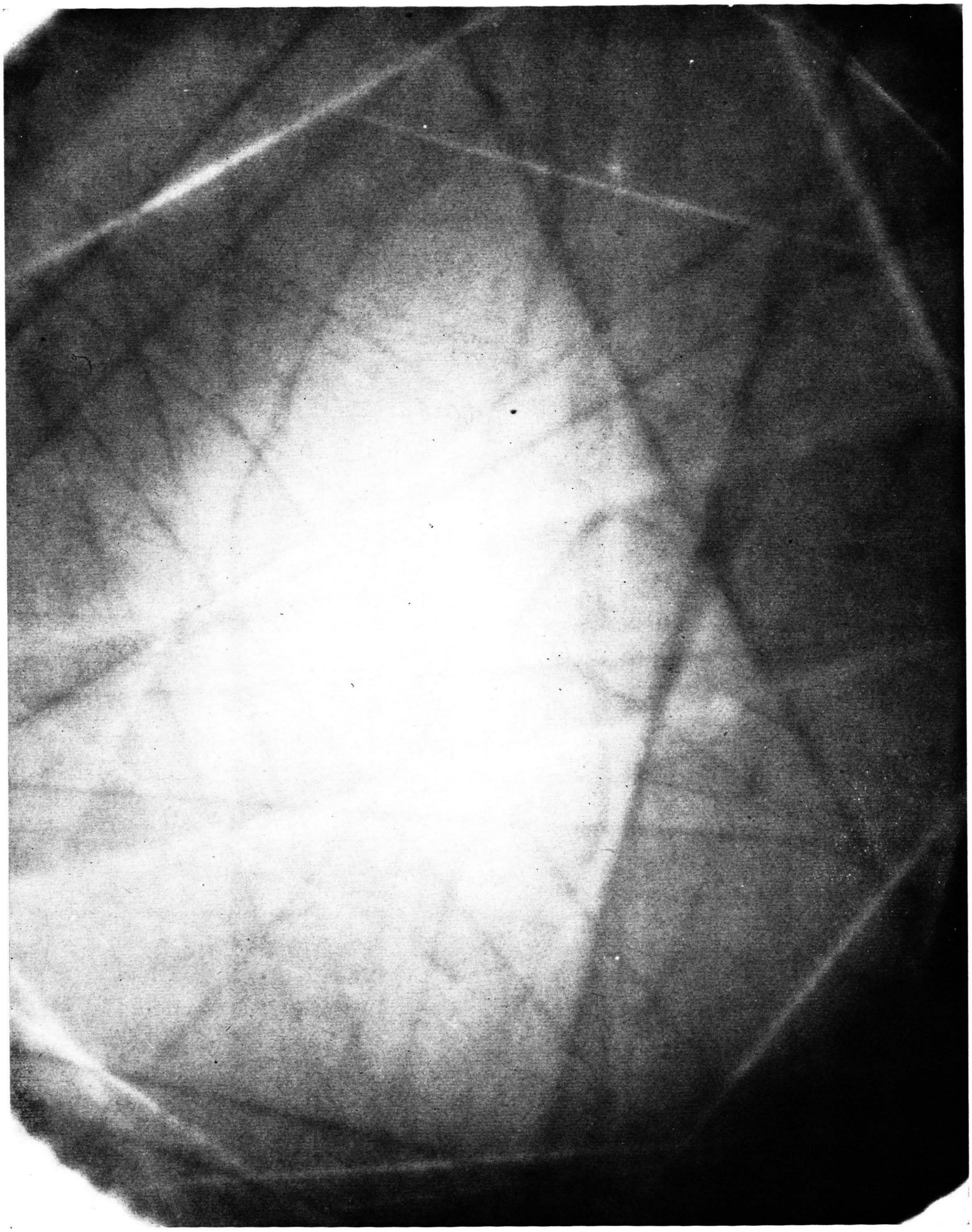

Fig. 1. Transmission electron micrograph of a germanium sample.

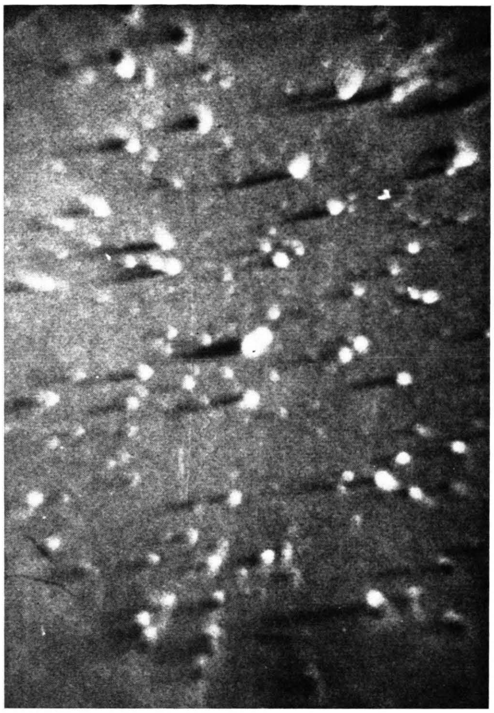

Abb. 4. Emissionsmikroskopische Aufnahme einer Schicht mit dem Strukturschema [Ag] — Cs_2O, Cs, Ag — Cs.

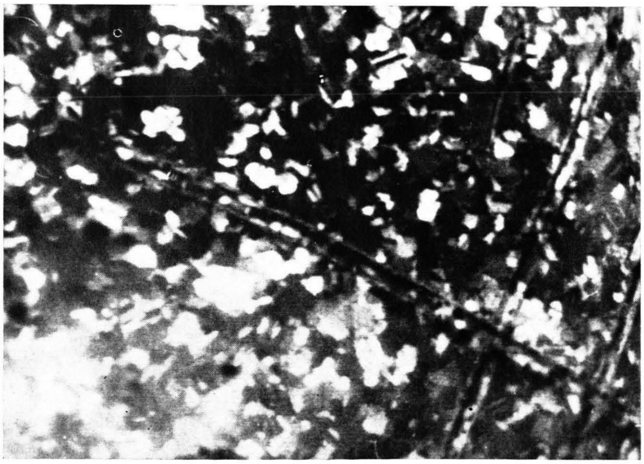

Abb. 6. Elektronenoptische Abbildung einer Nickeloberfläche unter Benutzung der Abtaströhre nach Abb. 5.

Bassani[2] with the pseudopotential method neglecting spin-orbit interaction. We notice a M_0 singularity for transitions $L_{3'} - L_1$ and a M_1 singularity for $\Lambda_3 - \Lambda_1$ transitions at $k = (0.17,\ 0.17,\ 0.17)$. The knowledge of $E_{cv}(k)$ makes it possible to determine $\varepsilon_2(E)$ since $\varepsilon_2(E) = \sum\limits_{c,v} f_{cv} \cdot N(E)$, where f_{cv} is the interband oscillator strength and $N(E)$ the joint density of states having the energy difference E. The oscillator strength f_{cv} varies very smoothly with E so that the characteristic structure comes from $N(E_{cv})$. The dashed line in Fig. 5 shows $\varepsilon_2(E)$ deduced by Brust et al. from the energy bands in Fig. 4. The curve is adjusted to get agreement in maximum values with the experimental ε_2 at 77 °K. Neglecting spin-orbit effects and some differences in the position of the maxima there is a gross agreement in line shape.

The sharp threshold 0.2 eV below the maximum position, however, does not show up in our results and there has been no clear experimental evidence for it up to now. According to Brust et al. the maximum in the theoretical curve is caused by the M_1 singularity $\Lambda_3 - \Lambda_1$ and the threshold is due to the onset of transitions at the M_0 singularity $L_{3'} - L_1$. In general, M_1 structures are dominating the ε_2 curves because of their very high density of states. However, $L_{3'} - L_1$ transitions in the neighbourhood of a M_1 edge have been found in reflection in GaAs, InSb, CdTe and ZnTe by Cardona and Greenaway (l. c. [14–16]). The band structure of these zincblende semiconductors is closely related to that of germanium [1, 17]. Assuming an energy difference of 0.2 eV[2] the absence of $L_{3'} - L_1$ structure in ε_2 of germanium can not be explained by lifetime broadening[2]. From the present results it can be seen that the lifetime broadening for $\Lambda_3 - \Lambda_1$ transitions at 77 °K is smaller than 0.05 eV (see Fig. 3). The lifetime in the L_1 conduction level should be longer than that in the Λ_1 level since there are no electron states of lower energy into which the electron could be scattered, and there is no reason for a strongly k-dependent lifetime in the $\Lambda_3 - L_3'$ valence band. From these considerations it must be concluded that the $L_{3'} - L_1$ transitions occur within 0.05 eV of the much stronger $\Lambda_3 - \Lambda_1$ singularity and cannot be resolved therefore. The energy region between 1 and 2.1 eV is governed by transitions in the neighbourhood of Γ and from Λ_3 to Λ_1 at points other than the singularity. This is also confirmed by the identical temperature coefficient of the edge in the range from 1.6 and 2.0 eV. The existence of the low temperature peak in absorption and consequently in the imaginary part fo the dielectric constant should be emphasized. Similar structure has been found in CdTe, InSb and other semiconducting compounds (l. c. [5, 18]). Cardona and Harbeke[18] invoked the effect of exciton formation connected with direct transitions in order to explain the structure. Marple and Ehrenreich[5] proposed a model with the L and Λ singularities having nearly identical energy in CdTe. This possibility seems to be ruled out by the recent reflectivity measurements by Cardona and Greenaway[16] showing an energy difference of 0.25 eV between the two singularities.

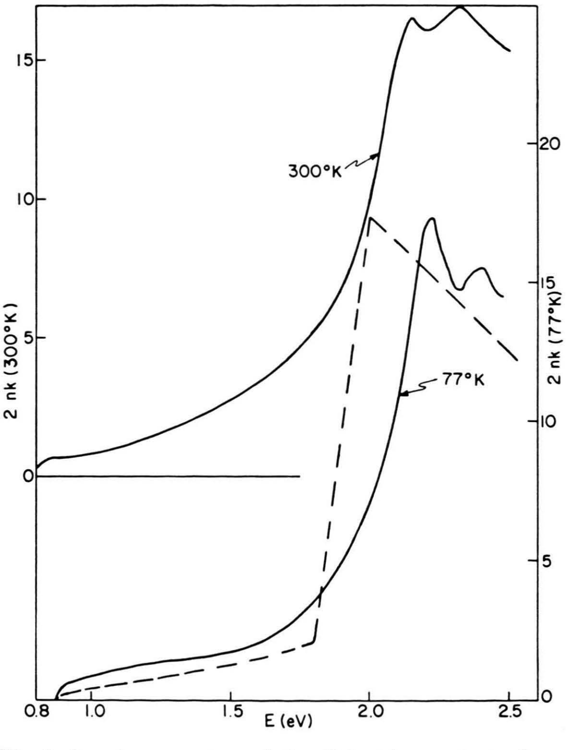

Fig. 5. Imaginary part ε_2 of the dielectric constant of germanium at 77 °K. Dashed line theoretical curve after Brust et al.[2]. Inset shows ε_2 at 300 °K.

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According to the present results, the situation could be given in germanium and would explain an additional threshold in ε_2 but not a sharp decrease at energies 0.03 eV higher than the threshold. Another possibility is interference with a nearby M_3 edge, that is, a relative maximum in E_{cv}. The detailed band structure calculations[2], however, do not give any evidence for this.

Moreover, the fact that these cusps connected with the $\Lambda_3 - \Lambda_1$ transitions have been found in many materials and now also in germanium favors the exciton picture, an accidental energy coincidence in all these semiconductors would be very unlikely. It should be considered that we are not dealing with hydrogenic excitons near parabolic energy bands.

Near M_1 or M_2 saddle points the concept of discrete, well separated bound exciton states is modified because of lifetime shortening. By cross scattering into band states of lower energy and slightly different k the lifetime can be shortened considerably. At any point in k space, however, where the condition $\nabla_k(E_c - E_v) = 0$ is fulfilled, i. e. at any critical point, electron and hole have the same group velocity and this gives rise to a strong Coulomb interaction between them. This interaction creates exciton like states near the bands and thus modifies the density of states at the critical point in a way which is reflected by the imaginary part of the dielectric constant in this region.

Thus we conclude that the structure observed at low temperatures is caused by exciton formation connected with direct transitions at a M_1 saddle point in the energy difference between the Λ_1 conduction and the Λ_3 valence bands. Phillips[19] estimated the binding energy of such saddle point excitons to be much larger compared to hydrogenic excitons near parabolic bands, namely of the order of 0.01 to 0.1 eV. Although the term binding energy might not be meaningful in this case the observed line widths fall within this range.

Acknowledgement

The painstaking efforts of Rudolf Zaum in preparing the thin samples are gratefully acknowledged. I would like to thank Manuel Cardona and David L. Greenaway for valuable discussions and M. D. Coutts for performing the electron microscopy work.

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