Electroreflectance Spectra and Band Structure of Germanium

AMAL K. GHOSH
Itek Corporation, Lexington, Massachusetts
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The electroreflectance spectra of Ge were studied in detail in the region 1.5 to 6.5 eV. Structures are observed at energies which correspond to critical points in interband transitions. By varying the magnitude of the ac voltage which provides the modulating field at the surface of the sample, and by using different polarizations of the incident light, many overlapping structures have been resolved. Peaks at 2.05 and 2.24 eV are attributed to $L_{3'}$-L_1 transitions, the valence band being split by 0.19 eV at the $L_{3'}$ point because of the spin-orbit interaction. Structures observed between 2.7 and 3.3 eV are attributed to transitions between the doubly split valence band at $\Gamma_{25'}$ and the doubly split level at Γ_{15}. The splitting of the Γ_{15} level is 0.13 eV, as compared to the splitting of 0.29 eV for the $\Gamma_{25'}$ level. The $\Gamma_{25'}$-Γ_{15} transitions are found to overlap with the Δ_5-Δ_1 transitions around 3.13 eV. There are two overlapping structures around 4.4 eV, one of which is attributed to the Σ_2-Σ_3 transition; the other could be either a second manifestation of the same Σ_2-Σ_3 transition, or due to the X_4-X_1 transition. Structures observed at 5.85 and 6.18 eV are yet to be identified. Structures observed at 2.12 and 2.32 eV are attributed to the Λ_3-Λ_1 transitions, and those at 5.35 and 5.52 eV to the $L_{3'}$-L_3 transitions. Transitions at the Δ, X, and Σ points are found to have anisotropic electroreflectance spectra. The line shapes for electroreflectance spectra are in qualitative agreement with those predicted by Aspnes and by Seraphin and Bottka for critical points having M_0, M_1, and M_2 types of singularities, if Lorentzian broadening is included.

1. INTRODUCTION

ENERGY-BAND calculations[1–7] in conjunction with reflectivity experiments[8,9] have led to an understanding of the nature of interband transitions at energies greater than the band gap in Ge and other semiconductors. Although a vast amount of information on the band structure of Ge and Si now exists, our knowledge of structure away from the band edge is still incomplete.

Optical transitions occur at a critical point where there is a singularity in the joint density of states. Usually the critical points have high symmetry like Γ, X, Λ, L, Σ in Ge.[10] Brust[3] has shown that the important critical points in Ge have either M_0, M_1, or M_2 type of singularity.

With the advent of electroreflectance,[11] it was thought that many of the controversies about the band structure of Ge could be resolved because of the high sensitivity and resolution of the technique. The initial experiments, though showing great promise, were not successful in resolving most of the problems. With the aid of the techniques described in the present paper, however, the situation looks rather more promising.

Figure 1 is a sketch of the band structure of Ge. The $\Gamma_{25'}$-$\Gamma_{2'}$ transitions as measured by electroreflectance techniques[12,13] are at 0.8 and 1.09 eV. The two transitions are due to spin-orbit splitting of the valence band at $k=0$. Because of the masking effect of the Λ_3-Λ_1 transitions (2.12 and 2.32 eV), the $L_{3'}$-L_1 transitions in Ge have not been resolved until recently, in spite of strenuous efforts.[14] Using polarimetry techniques and measuring Brewster's angle, Potter[15] has obtained ϵ_1 and ϵ_2 (the real and imaginary parts of the dielectric constant) without measuring absolute reflectivities. In addition to the Λ_3-Λ_1 transitions and the $\Gamma_{25'}$-$\Gamma_{2'}$ transitions, he observes structures in ϵ_1 at 1.74 and 1.94 eV at room temperature, which he attributes to transitions from the spin-orbit split valence band at $L_{3'}$ to the conduction band at L_1. In our electroreflectance studies, structures at 2.05 and 2.24 eV are attributed to the $L_{3'}$-L_1 transitions.[16] To resolve the discrepancy between our results and those of Potter, we have carefully reinvestigated the spectra around 2 eV. The different theoretical values for the same transition are listed in Table I.

There is considerable controversy concerning the position of the triply degenerate state Γ_{15}. The different values quoted in the literature are summarized in Table I.

The nearly parallel nature of the bands in the [100] direction indicates the possibility of more than one critical point having energies about the same as the

[1] F. Herman and J. Calloway, Phys. Rev. **89**, 518 (1952).
[2] F. Herman, Phys. Rev. **93**, 1214 (1959).
[3] D. Brust, Phys. Rev. **134**, A1337 (1964).
[4] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).
[5] M. Cardona and F. H. Pollak, Phys. Rev. **142**, 530 (1966).
[6] F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, in *Quantum Theory of Atoms, Molecules and the Solid State*, edited by Per-Olov Löwdin (Academic Press Inc., New York, 1966). This is also a good source of reference for both experimental and theoretical work.
[7] G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. **160**, 649 (1967).
[8] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).
[9] For detailed bibliography on both experimental and theoretical, see J. C. Phillips, Solid State Phys. **18**, 55 (1966).
[10] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).
[11] B. O. Seraphin, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1966).
[12] B. O. Seraphin, R. B. Hess, and N. Bottka, J. Appl. Phys. **36**, 2242 (1965).
[13] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Letters **23**, 37 (1966).
[14] G. Harbeke, Z. Naturforsch. **199**, 548 (1966).
[15] R. F. Potter, Phys. Rev. **150**, 562 (1966).
[16] A. K. Ghosh, Solid State Commun. **4**, 565 (1966).

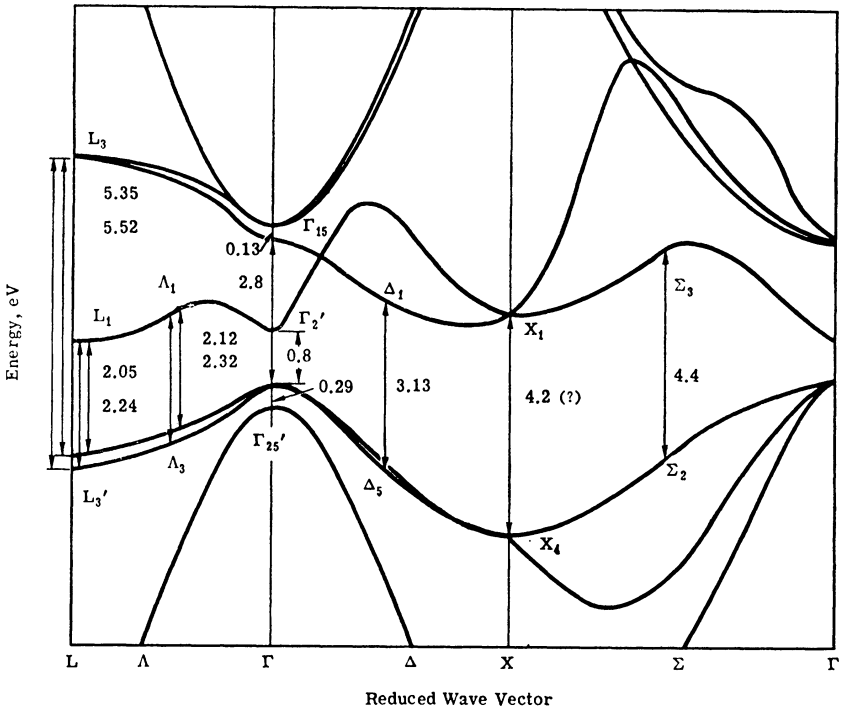

FIG. 1. Sketch of the band structure of Ge (based roughly on the structure reported in Ref. 6). No attempt has been made to draw the position and energies of the different transitions to scale.

$\Gamma_{25'}$-Γ_{15} transition. The value chosen for the $\Gamma_{25'}$-Γ_{15} transition has an important bearing on theoretical interpretation of ordinary reflectance spectra, electroreflectance spectra, piezoreflectance spectra, and photoemission spectra, particularly in the range between 2 and 4 eV. In the present work the spectra have been studied in more detail by varying the ac voltage and using polarized light. Some overlapping structures have been unmasked and the results have given a better insight into the nature of the transitions involved.

TABLE I. Experimental and theoretical values of different transitions (in eV) in germanium.

	Experimental				Theoretical			
Transition	Philipp *et al.*[a]	Seraphin *et al.*[b]	Potter[c]	Cardona *et al.*[d]	Bruste[e]	Herman *et al.*[f]	Cohen *et al.*[g]	Dresselhaus *et al.*[h]
$\Gamma_{25'}$-$\Gamma_{2'}$		0.798 1.090	0.80 1.09	0.789 1.090	0.8	0.90	1.2	0.80 1.09
$L_{3'}$-L_1	2.1 2.3		1.74 1.94		1.78	2.05±0.1	2.0	2.08 2.27
Λ_3-Λ_1		2.109 2.322	2.13 2.32	2.12 2.34	2.01			2.11 2.32
$\Gamma_{25'}$-Γ_{15}	3.1		2.63 2.75 2.92 3.04		3.6	2.91±0.07	3.5	2.55 2.84 3.13
X_4-X_1	4.5			4.42	3.6	4.10	3.8	
Σ_2-Σ_3					3.8			4.12
$L_{3'}$-L_3	5.9 6.1				5.44	5.3	5.4	5.32 5.51 5.70

[a] References 8 and 20.
[b] Reference 12.
[c] Reference 15; R. F. Potter, Bull. Am. Phys. Soc. 12, 320 (1967).
[d] Reference 22.
[e] Reference 3.
[f] Reference 6, p. 381; F. Herman, R. L. Kortum, and C. J. Kuglin, in Slater Symposium Issue, Intern. J. Quantum Chem. (1967).
[g] Reference 4.
[h] Reference 7.

The strongest peak in the normal reflectance is around 4.4 eV for both Ge and Si. This peak has been attributed to an accidental coincidence of the X_4-X_1 transition and the Σ_2-Σ_3 transition.[3] This assignment has become questionable as a result of recent band calculations by Kane[17] and Dresselhaus *et al.*[7] They found that the main contribution to this peak seems to come from the Σ transition. The theoretical values calculated for transitions at both the Σ and X points are always lower than the corresponding experimental values. In order to resolve this region experimentally, we have carefully studied the details of the electroreflectance spectra using polarized light.

The X transitions have type M_1 singularity and the Σ transitions have type M_2 singularity. The shape of the electroreflectance structure for each type is different, and in addition, each varies with the angle between the applied electric field and the symmetry axis, as shown by Aspnes.[18] This means that structures due to $M_1(\|)$ are different from those due to $M_1(\perp)$ and similarly for $M_2(\|)$ and $M_2(\perp)$.[19] When these effects are coupled with the fact that X transitions (M_1) occur at critical points along the [100] direction and Σ transitions (M_2) occur at points along the [110] direction, one finds that the relative contribution to the electroreflectance spectra by X and Σ transitions can change as the polarization of the incident light is varied. These effects will be discussed later.

The structures due to the $L_{3'}$-L_3 transitions are found to be around 5.35 and 5.52 eV in electroreflectance spectra.[16] Similar doublet structure (Table I) attributed to these transitions has been reported in normal reflectance measurements.[20] The electroreflectance spectra are in agreement with the earlier interpretation that the doublet is due to spin-orbit splitting of the $L_{3'}$ level, the splitting due to the L_3 level being negligibly small.[20,21] Recent calculations by Dresselhaus and Dresselhaus[7] are not in complete agreement with such a view (Table I). The reason Cardona *et al.*[22] did not observe these structures in their electroreflectance spectra is not understood at present. We observe additional structures in electroreflectance at 5.85 and 6.2 eV which cannot be assigned at this time.

2. EXPERIMENTAL TECHNIQUE

The experimental technique is the same as that of Cardona and co-workers,[13] which is a modified version of the technique originated by Seraphin.[11] The sample was immersed in an electrolyte consisting of a 0.1N solution of KCl in distilled water. A Beckman uv cell was used to hold the electrolyte. A Pt wire or Pt foil was used as the second electrode; the position or configuration of the Pt in the electrolyte did not have any effect on the spectra. In most of our measurements the crystal was negatively biased; this was the blocking direction of the rectifying contact. It was found that in some cases after etching, the spectra could be recorded without any bias or with a positive bias. The crystals were etched with CP-4 before use. The peak-to-peak modulating ac voltage varied between 1 to 56 V and its frequency was 150 cps. The light from a 150- or 450-W Xe lamp, after being dispersed by a Bausch and Lomb 500-mm grating monochromator, was reflected from the sample and detected by an EMI/6255S or 9558Q photomultiplier. The ac output from the photomultiplier was sent to a PAR lock-in amplifier and recorded. The dc output was held constant by a servo system which controlled the gain of the photomultiplier by varying the high voltage fed to it. The resultant recorder plot is the ratio of the modulated signal to the dc signal ($\Delta R/R$). Glan Taylor prisms were used to obtain polarized light.

3. ELECTROREFLECTANCE SPECTRA

According to recent theories, electroreflectance depends on the influence of the low-frequency applied electric field on the energy band which causes an oscillating singularity at critical points. The relative change in reflectivity $\Delta R/R$ is related to the change in real ($\Delta\epsilon_1$) and imaginary ($\Delta\epsilon_2$) parts of the dielectric constant by the relation

$$\Delta R/R=\alpha\Delta\epsilon_1+\beta\Delta\epsilon_2,$$

where α and β are constants which vary with energy. To compute line shapes for $\Delta R/R$ at critical points having M_0, M_1, and M_2 type singularities, one has to know, apart from the α and β values, the line shapes due to changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ as a function of the electric field. Seraphin and Bottka[23] and Cardona *et al.*[22] have computed values of α and β as a function of energy for Ge. The former workers have also computed line shapes for $\Delta\epsilon_1$ and $\Delta\epsilon_2$ at M_0 and M_1 type singularities. The structures for both $\Delta\epsilon_1$ and $\Delta\epsilon_2$ at different critical points consist of a set of oscillations with energy, sometimes referred to as Franz-Keldysh oscillations. The oscillations at energies higher or lower than the critical point to which they are related are damped due to lifetime broadening.[23] Thus, the electroreflectance spectrum at a critical point is usually a structure consisting of a positive peak followed by a negative peak or a negative peak followed by a positive peak. Depending on the nature of the transition and the values of α and β, the critical point could be coincident with either the positive or the negative peak in the combination (or slightly displaced

[17] E. O. Kane, Phys. Rev. **146**, 558 (1966).
[18] D. E. Aspnes, Phys. Rev. **147**, 554 (1966).
[19] For an explanation of the distinction between the different types of singularities, see, for example, Ref. 3. The symbols ($\|$) and ($\perp$) refer to the components of the applied electric field parallel and perpendicular to the symmetry axis of the reduced mass of odd sign, respectively.
[20] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).
[21] J. C. Phillips and L. Liu, Phys. Rev. Letters **8**, 94 (1962).
[22] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967).
[23] B. O. Seraphin and N. Bottka, Phys. Rev. **145**, A628 (1966).

from these). If the wrong peak is chosen, the error in most cases will be about ± 0.1 eV.

Aspnes[18,24] has computed line shapes for all types of critical points. According to his results, the line shape for a transition at type M_1 and M_2 critical points is determined by the angle between the applied electric field and the symmetry axis defined by the direction of the reduced effective mass having the odd sign. The line shapes computed by Seraphin and Bottka[23] for a type M_1 singularity are for fields parallel to the axis of symmetry; for transverse fields the line shapes are different.

In analyzing our results we assume that the applied electric field is perpendicular to the reflecting surface. In general, the rate of variation of intensity of the peaks with applied electric field is different for the different structures. This could be due to the differences in the reduced effective masses at the different critical points and also due to differences in lifetime broadening. For the same critical point there could be differences between the effects of parallel and transverse fields for the same reason.[18,24]

4. RESULTS AND DISCUSSIONS

A. General

The electroreflectance spectra of 11-Ω cm p-type Ge are shown in Figs. 2 and 3, both for a (111) crystal face. Figure 2 is for -0.75 V dc and 38 V ac while Fig. 3 is for 0-V dc and 3-V ac. The structures in the spectra are opposite in sign to those reported by Seraphin and co-workers,[12] but have the same sign as those reported by Cardona *et al.*[13] We found that the samples which could be biased positively have spectra similar in sign to those reported by Seraphin *et al.* Comparing Figs. 2 and 3, one can easily find some similarities and some differences in structures. In general, there is a shift in peak positions to higher energies and an increase in half-width with increasing ac voltage. In Fig. 2 the negative peak around 2.04 eV is absent and the structures around 2.7 and 3.3 eV are better resolved. In the 4- to 5-eV region at high ac voltages, the structure is mainly a negative peak followed by a positive peak while at low ac voltages it is a positive peak followed by a negative peak. The negative peak around 5.5 eV appears to be split at low ac voltages. There are other differences between the two spectra. To understand these differences, each portion of the spectra was studied in more detail as a function of ac voltage and in many cases by using polarized light. Figure 4 shows a typical electroreflectance spectrum of a Ge thin film on a quartz substrate. The film was deposited at a substrate temperature of 500°C. The spectra of Ge films deposited at other substrate temperatures were also studied. The spectra of thin films generally are similar to those of Ge single crystals. The results of this study will be published later.

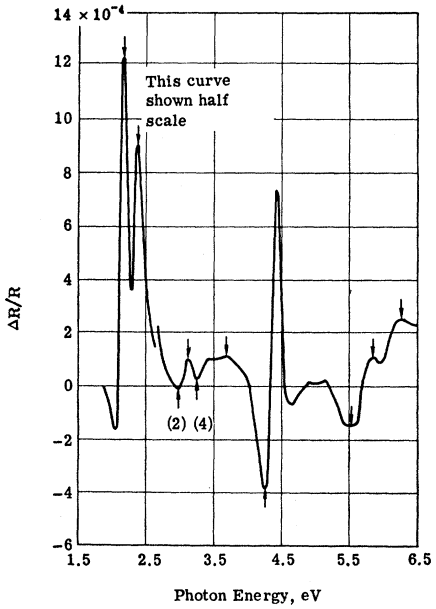

FIG. 2. Electroreflectance spectra of Ge at high ac voltage (0.75-V dc and 38-V ac).

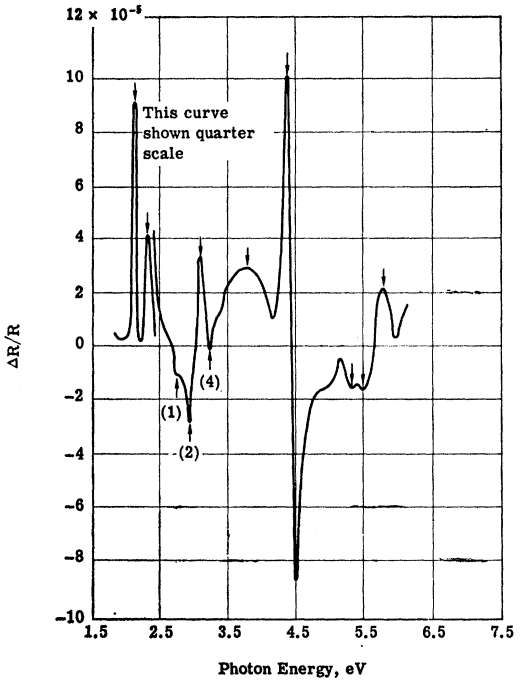

FIG. 3. Electroreflectance spectra of Ge at low ac voltage (0-V dc and 3-V ac).

B. Λ_3-Λ_1 and $L_{3'}$-L_1 Transitions

Around 2 eV $|\alpha| = |\beta|$, and the electroreflectance spectra are expected to be due to equal contributions from both $\Delta\epsilon_1$ and $\Delta\epsilon_2$. Careful study of structures in the

[24] D. E. Aspnes, Phys. Rev. 153, 972 (1967).

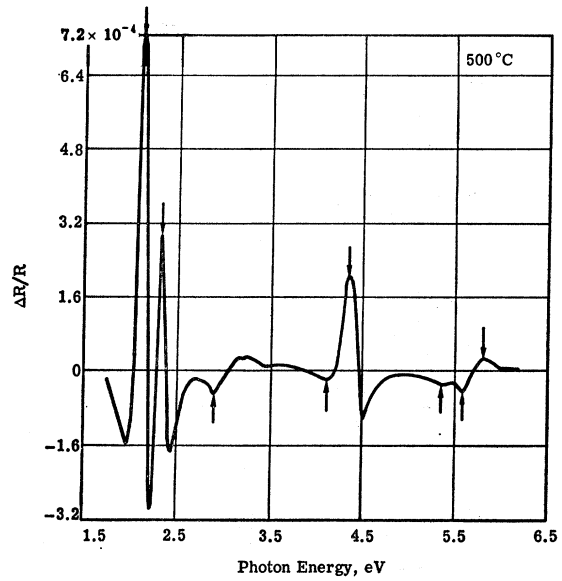

FIG. 4. Electroreflectance spectra of Ge thin film on quartz substrate (3-V ac and 0.13-V dc).

range 1.7–2.5 eV indicates the existence of several overlapping structures. Varying the ac voltage changes the relative magnitude of the different structures. Consistent interpretation of these results is obtained if the individual components of the overlapping structures are as sketched in Fig. 5. Curves (a_1,a_2) and (b_1,b_2) are attributed to an M_1 type singularity, (a) for parallel fields and (b) for transverse fields. For both types of fields, the critical points are expected to be roughly coincident with the position of the positive peak. It is known that Λ transitions are of the M_1 type with the critical points lying along the [111] axes. For any

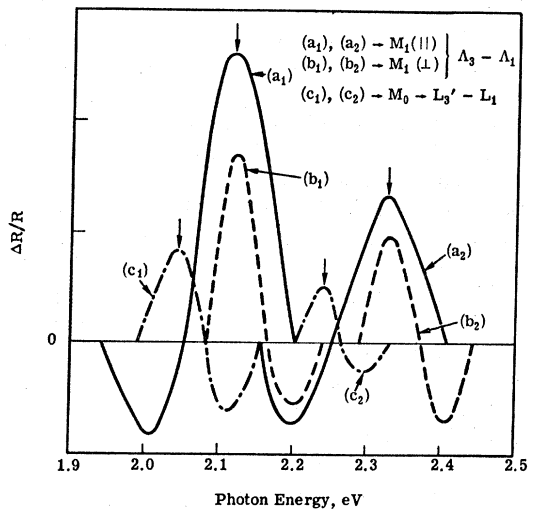

FIG. 5. Sketch of the overlapping structures believed to be present around 2 eV. The relative intensities are not drawn to scale. Some of the peaks are located approximately at positions where one observes structures in the electroflectance spectra.

electric field orientation there are, in general, four nonequivalent pairs of Λ critical points. Both parallel and transverse type electro-optic effects should occur at the Λ transition depending on the orientation of the field and the magnitude of the reduced masses at these critical points.[24]

Curves (c_1) and (c_2) in Fig. 5 are attributed to the $L_{3'}$-L_1 transitions which are known to occur at an M_0 type singularity. The positive peak of this structure is expected to be located near the critical point. For a spectrum recorded under certain specific experimental conditions, it is not possible to observe the details of each of the structures (a_1,a_2), (b_1,b_2), and (c_1,c_2) as sketched in Fig. 5. One sees only the superposition of all six structures. However, each component structure can be made more prominent relative to the others by carefully choosing the appropriate experimental conditions. For example, at high ac voltages (Fig. 2), the structures around 2 eV are mainly due to $M_1(\|)$, which corresponds to curves (a_1,a_2) in Fig. 5. The spectrum corresponding to curve (a_1) is observed but the negative peak associated with (a_2) is missing. This, we believe, is as a result of overlapping of structures due to broadening at high fields. With increasing fields there is a shift in peak positions to higher energies. In thin films (Fig. 3) the spectrum around 2 eV is due mainly to overlapping of $M_1(\|)$ (curves a_1 and a_2) and $M_1(\perp)$ (curves b_1 and b_2) structures. Because of the random orientation of crystallites, the structures due to both orientations are equally prominent. In crystals, both $M_1(\|)$ and $M_1(\perp)$ structures are present, but experimentally we find the $M_1(\|)$ character is dominant at high fields and $M_1(\perp)$ at low fields. Part of the M_0 structure [curves (c_1 and c_2), Fig. 5] can only be observed at low ac voltages (peaks at $\sim$2.05 and 2.24 eV, Fig. 6). It is weak and overlaps with the $M_1(\perp)$ structures. The positive and negative peak combination at about 2.12–2.175 eV (Fig. 6, spectrum for 1-V ac) corresponds to curve (b_1) and the 2.32–2.38 eV combination to curve (b_2) in Fig. 5. The peaks corresponding to curve (b_2) in thin films are at about 2.32 and 2.44 eV. In a crystal with a (110) face, the same peaks are at 2.29 and 2.35 eV. The other features of the (110) spectra are the absence of the weak shoulder around 2.05 eV and the presence of exponential tails with the 2.12- and 2.35-eV peaks. Hamakawa *et al.*[25] attribute the 2.35-eV structure to an M_3 type of singularity because of the exponential tail. As we have already stated, we attribute this peak to be part of an $M_1(\perp)$ structure. We feel that the exponential tail could be an accidental manifestation of the lifetime broadening effects. The absence of the weak shoulder at 2.05 eV in the (110) spectra could be a result of the difference in relative intensities of the overlapping $M_1(\|)$ and $M_1(\perp)$ structures for the two orientations. The same can be said for the absence of the 2.05 and 2.24 eV peaks in thin films. In single crystals, with in-

[25] Y. Hamakawa, P. Handler, and F. Germano (to be published).

creasing fields, the $M_1(\|)$ structures increase in intensity more rapidly than the overlapping $M_1(\perp)$ and M_0 structures. At high fields where $M_1(\|)$ structures predominate, the weak positive peaks at 2.05 and 2.24 eV and the negative peaks at 2.175 and 2.38 eV cannot be delineated. Our conclusions [that the spectra in the range 2–2.5 eV are due to overlapping of $M_1(\|)$, $M_1(\perp)$, and M_0 structures] are based on a consistent interpretation of all our data (different crystal faces, thin films, different applied fields), and they are also in good agreement with all previous experimental and theoretical results related to critical points around 2.0 eV.

As shown in Table II, the peaks at 2.12 and 2.32 eV are attributed to the Λ_3-Λ_1 transitions and those at 2.05 and 2.24 eV to the $L_{3'}$-L_1 transitions. The two values of each are due to spin-orbit splitting of the valence band.

We have carefully studied the region 1.6–2.0 eV for structures which would correspond to the structures

TABLE II. Peaks observed in electroreflectance spectra and the critical points to which they are related.

Transition	Type	Peak position in eV	Spin-orbit splitting in eV
$L_{3'}$-L_1	M_0	2.05, 2.24	0.19 at $L_{3'}$
Λ_3-Λ_1	$M_1(\|)$ and $M_1(\perp)$	2.12, 2.32	0.20 at Λ_3
$\Gamma_{25'}(\Gamma_8^+) \rightarrow \Gamma_{15}(\Gamma_6^-)$	M_0	2.8	0.13 at Γ_{15}
$\Gamma_{25'}(\Gamma_8^+) \rightarrow \Gamma_{15}(\Gamma_8^-)$	M_0	2.93	
$\Gamma_{25'}(\Gamma_7^+) \rightarrow \Gamma_{15}(\Gamma_6^-)$	M_0	3.09	0.29 at $\Gamma_{25'}$
$\Gamma_{25'}(\Gamma_7^+) \rightarrow \Gamma_{15}(\Gamma_8^-)$	M_0	3.22	
Δ_5-Δ_1	$M_1(\|)$	3.13	···
Σ_2-Σ_3	$M_2(\|)$	4.39	···
Σ_2-Σ_3	$M_2(\perp)$	4.39	···
(or X_4-X_1)	($M_1(\perp)$)	(4.17)	···
$L_{3'}$-L_3	$M_2(\|)$ and $M_2(\perp)$	5.35, 5.52	0.17 at $L_{3'}$
?	?	3.65	···
Δ_5-$\Delta_{2'}$	?	~5.00	···
?	?	5.85	···
?	?	6.2	···

observed by Potter at 1.74 and 1.94 eV.[15] Apart from the negative peak around 2 eV [attributed to the $M_1(\|)$ structure described above], which in thin films is around 1.97±0.02 eV, no other structures have been observed. The indication of a positive structure on the low-energy side of this peak in our earlier work[16] was found to result from scattered light.

The peak positions found in electroreflectance spectra vary with the applied voltage. The variation of intensity and position of the 2.12 and 2.32 eV peaks with ac voltage is shown in Fig. 7. We believe the positions of the peaks at low voltage are nearer to the critical points.

C. $\Gamma_{25'}$-Γ_{15} and Δ_5-Δ_1 Transitions

Around 3 eV $|\beta| > |\alpha|$ and the electroreflectance spectra are dominated by $\Delta\epsilon_2$. Careful study of structures around 3 eV indicates the existence of at least five overlapping structures as sketched in Fig. 8(a). Structures 1–4 are attributed to the $\Gamma_{25'}$-Γ_{15} transitions which occur at a type M_0 singularity. The fifth structure is attributed to the Δ_5-Δ_1 transition which occurs at a type M_1 singularity. According to Aspnes,[18,24] the M_0 structures should be isotropic while each of the M_1 and M_2 structures could be different, depending on the angle between the applied electric field and the symmetry axis defined by the reduced mass of odd sign. Although Aspnes does not consider explicitly the effects with polarized light, this electric field anisotropy can lead to differences in the electroreflectance spectra of differently polarized light in certain cases. To compute the effect of polarized light on the electroreflectance spectrum (at a given field) even qualitatively, for a given set of critical points, one needs to know the direction of the symmetry axis, the direction of the applied electric field, and also the polarizational selection rules for each equivalent

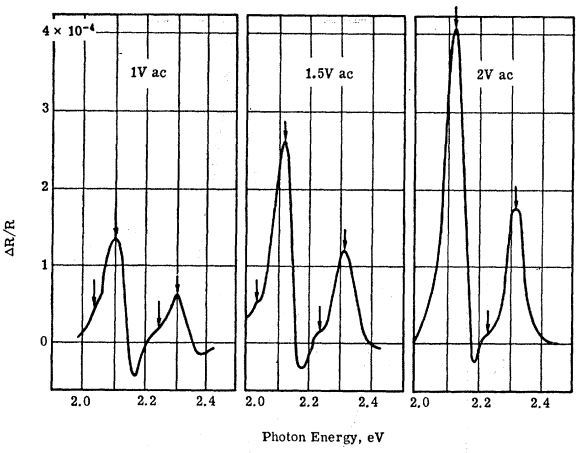

FIG. 6. Electroreflectance spectra around 2 eV at low ac voltages (dc 0.2 V). (111) crystal face.

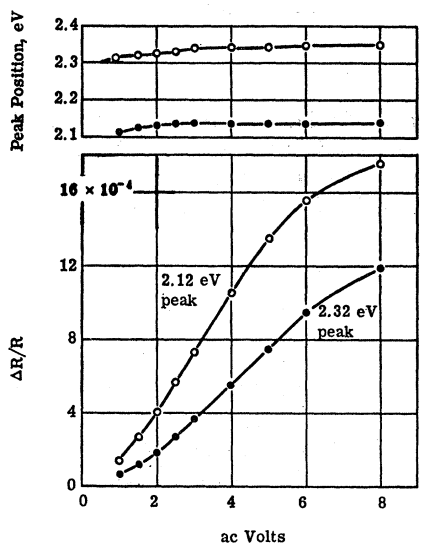

FIG. 7. Changes in intensity and position of the peaks around 2 eV with increasing ac voltage and constant dc voltage.

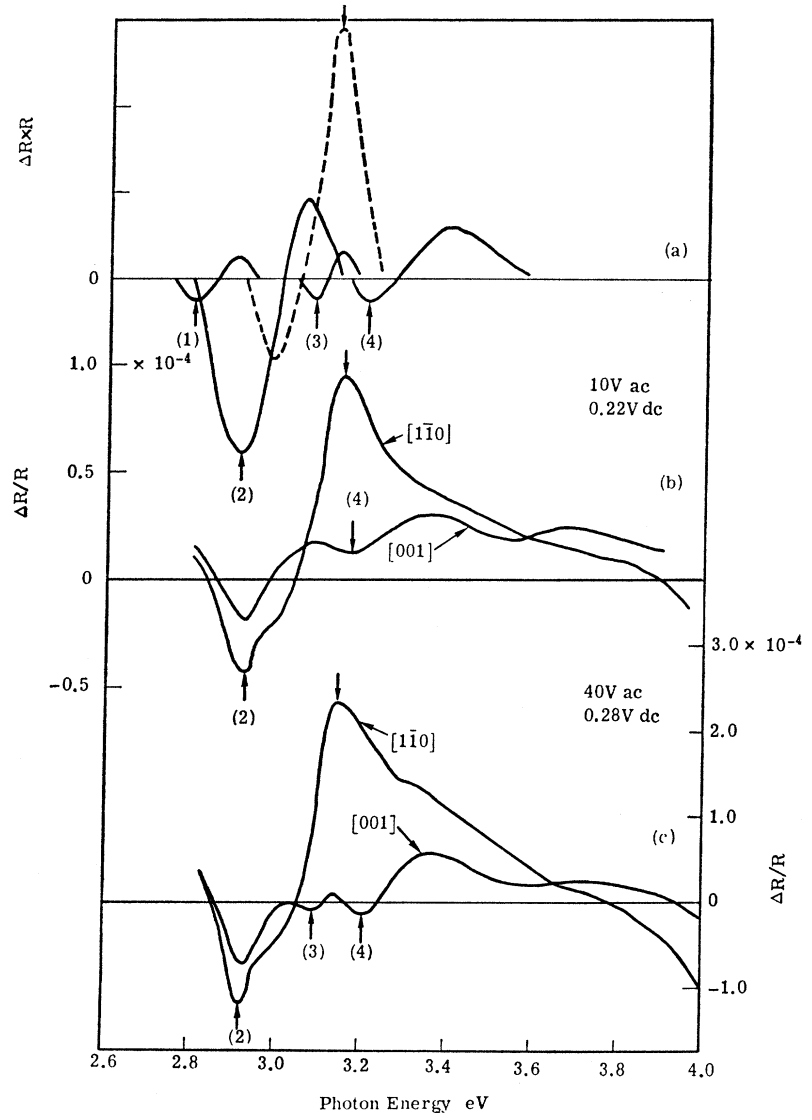

FIG. 8. (a) Sketch of the different structures believed to be present in the electroreflectance spectra of Ge around 3 eV. The relative intensities are not drawn to scale. Some of the peaks are located approximately at positions where one observes peaks in the electroreflectance spectra; (b) and (c) show the effect of polarized light on structures around 3 eV. Light polarized along [001] and [1$\bar{1}$0] directions, incident on a (110) crystal face.

critical point. To demonstrate how structure dependent on the light polarization can come about let us assume, for example, that the symmetry axes of the reduced mass of odd sign for M_1 critical points along [100] are also along the [100] crystal axes, and that the electric field is perpendicular to the (110) face (Fig. 9). Then, according to our present discussions, the critical points along the [001] direction would give $M_1(\perp)$ type transitions, while those along the [100] and [010] directions would give either $M_1(\perp)$ or $M_1(\|)$ type transitions. This is because the applied electric field is perpendicular to the [001] direction but makes 45° angles with the [100] and [010] directions; thus both parallel and transverse components of the electric field are present for the later directions. If we now make a second assumption that the allowed optical transition is along the axis on which the critical point is located, then with [001] polarized light only $M_1(\perp)$ transitions (for the critical points along [001] direction) will be generated, while for [1$\bar{1}$0] polarized light either $M_1(\|)$ or $M_1(\perp)$ transitions (due to critical points along the

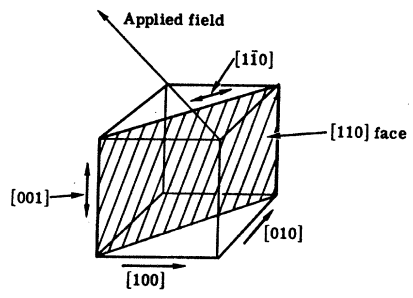

FIG. 9. Sketch of the crystal face, direction of applied field, and polarization directions of the incident light.

[100] and [010] axes) will be present. Under the conditions described, an $M_1(\|)$ structure can appear with $[1\bar{1}0]$ polarized light, but not with [001] polarized light.

Whether the conditions assumed above hold for the M_1 critical point at 3.13 eV is not known, but experimentally, we find that the $M_1(\|)$ transition appears only with $[1\bar{1}0]$ polarized light, as shown in Figs. 8(b) and 8(c). This $M_1(\|)$ structure, as already stated, is attributed to the Δ_5-Δ_1 transition. The valence band is possibly split at the Δ point, but since we observe only a single structure which could be attributed to the Δ_5–Δ_1 transition, we conclude that the splitting is negligibly small. Brust[3] predicts a peak at 3.17 eV due to a similar transition. In our earlier report,[16] a second Δ transition at 3.22 eV due to an M_2 type singularity was reported; but on the basis of the present work, we believe this same structure to be one of the $\Gamma_{25'}$-Γ_{15} transitions. Electroreflectance structures due to transitions at M_0 type singularities, if dominated by $\Delta\epsilon_2$, have their negative peak very close to the critical point.[23] In the present analysis the energy values quoted for these transitions are the positions of the negative peak.

Because of effects due to overlapping, it is difficult to prove experimentally that the structures attributed to the $\Gamma_{25'}$-Γ_{15} transitions are isotropic. The negative peak around 2.8 eV (Figs. 3 and 10) is part of one of the four M_0 type structures observed. The positive peak associated with it could not be resolved because of overlap with the strong negative peak at 2.93 eV. At first glance, the positive peak at 3.13 eV would seem to be associated with the 2.93 eV negative peak (Figs. 3 and 10). This was thought to be the case in our earlier work.[16] However, polarized light experiments as shown in Figs. 8(b) and 8(c) indicated that the negative peak associated with the positive peak at 3.13 eV is at 3.0 eV, and that the 2.93 eV negative peak is part of a separate structure whose associated positive peak is somewhere around 3.08 eV [Fig. 8(b)]. All of the polarization effects appearing in this region seem to be associated with the 3.0 eV peak, as described earlier. The 2.93-eV peak is independent of the direction of polarization; its apparent change with light polarization [Figs. 8(b) and 8(c)] is believed to be entirely due to its overlap with the 3.0 eV peak. Thus, the 2.93–3.08 eV structure is probably isotropic, and we believe it is the second structure of the M_0 quartet. The third M_0 transition has a negative peak around 3.09 eV and a positive peak around 3.15 eV [Fig. 8(c)]. The fourth M_0 structure as shown in Fig. 8(c) has a negative peak around 3.22 eV and a positive peak around 3.35 eV. Three of the four M_0 structures described above are more prominent with light polarized along [001] [Fig. 8(c)], because under this condition the $M_1(\|)$ structure attributed to the Δ transition is absent, and therefore does not mask these M_0 structures.

Figure 10 shows the effects of increasing ac voltage on the spectral region around 3 eV. We believe these

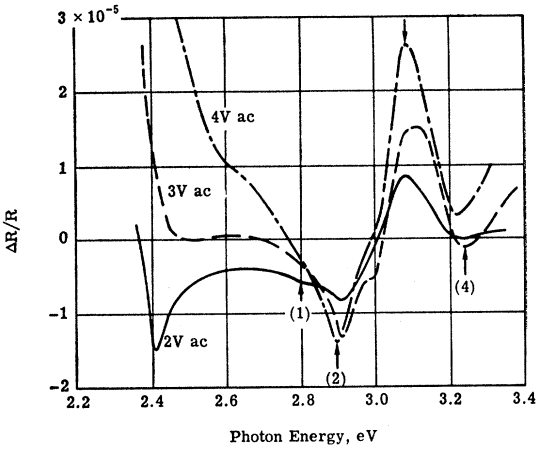

FIG. 10. Changes in the structures around 3 eV at low ac voltage. (111) crystal face.

changes to be due to differences in the rates of growth of the different structures with applied ac voltage. Peaks (1), (2), and (4) of the M_0 quartet and the $M_1(\|)$ structure attributed to Δ transitions are all evident in the spectra. The negative peak around 2.4 eV at low ac voltage is part of the Λ transition described earlier. At higher ac voltages, there is an indication of a shoulder around 2.6 eV.

As shown in Table II, the four structures with negative peaks at 2.8, 2.93, 3.09, and 3.22 eV are attributed to the $\Gamma_{25'}$-Γ_{15} transitions. Both the $\Gamma_{25'}$ and Γ_{15} levels are assumed to be split due to spin-orbit interactions. The origin of the structure having a positive peak at about 3.65 is not known.

D. X_4-X_1 and Σ_2-Σ_3 Transitions

Between 4 and 4.5 eV one observes a negative peak at about 4.20 eV, followed by a positive peak at 4.40 eV, and a second negative peak at about 4.50 eV. The position and intensity of these peaks depend on the applied voltage. At low ac voltages, one observes only the positive peak followed by a negative peak as in Fig. 3, while at higher ac voltages one observes the negative peak followed by a positive peak as in Fig. 2. At intermediate voltages, one observes a composite structure as shown in Fig. 11. The change in intensity and position of the peaks with ac voltage is shown in Fig. 12. The 4.5-eV negative peak (after a small initial increase) decreases in intensity with increasing ac voltage while the other peak intensities increase. Experiments with polarized light have yielded additional information on the nature of these structures. Figure 13 shows the spectra for differently polarized light incident on the (110) crystal face. The structure, which consists of a positive peak at about 4.4 eV and a negative peak at about 4.5 eV is stronger with light polarized along the [001] direction, while the structure with a negative peak around 4.2 eV and a positive peak around 4.4 eV is stronger with light polarized along the $[1\bar{1}0]$ direction.

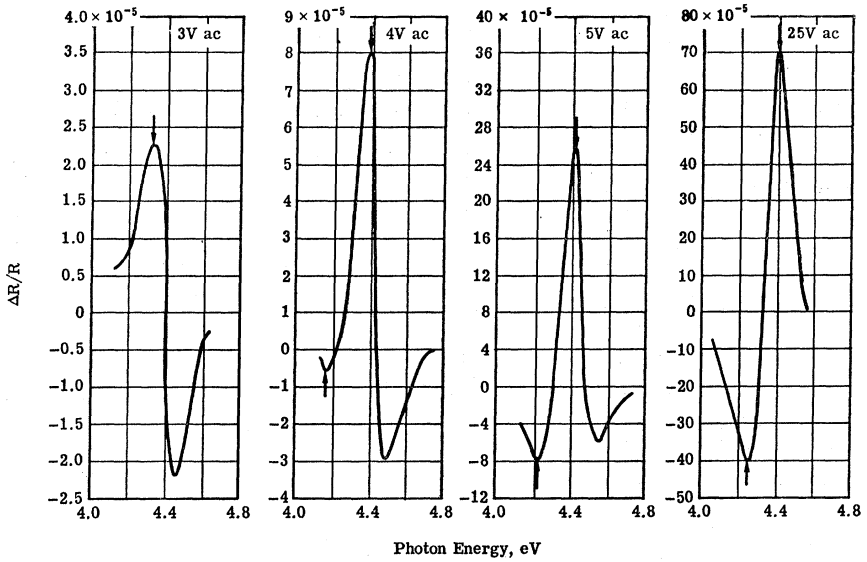

FIG. 11. Variation of the shape of the 4.4 eV structures with ac voltages. (111) crystal face.

In an earlier paper,[16] it was suggested that the negative peak followed by a positive peak around 4.4 eV was due to an M_1 type singularity and hence, related to the X_4-X_1 transition, while the positive peak followed by a negative peak was due to an M_2 type singularity and hence, related to the Σ_2-Σ_3 transitions. The following description of the present more detailed investigation throws more light on the nature of these transitions.

Recently Aspnes[18,24] has shown that the structures associated with M_1 and M_2 type singularities are different for parallel and transverse applied fields. Around 4.4 eV in Ge, $|\alpha| > |\beta|$ and α is negative. The main contribution to the electroreflectance around 4.4 eV comes from $\Delta\epsilon_1$, but the sign of $\Delta R/R$ is opposite to that of $\Delta\epsilon_1$. Accordingly, for $M_1(\|)$ the spectrum should appear as a positive peak followed by a negative peak, the critical point being coincident with the negative peak. A similar structure should appear for $M_2(\|)$ but in this case the positive peak coincides with the critical point. For $M_1(\perp)$ and $M_2(\perp)$ the structure should be a negative peak followed by a positive peak, the critical point coinciding with the negative peak in the first case and with the positive peak in the second case. The general character of the observed structures is similar to that computed by Seraphin and Bottka[23] for a Lorentzian broadening parameter $\delta = 0.035$ eV and fields of 45 kV/cm.

Based on the above analysis of structure shapes, the structure with a negative peak followed by a positive peak (the A structure) must be due to either $M_1(\perp)$ or $M_2(\perp)$, while the structure with positive peak followed by a negative peak (the B structure) must be due to either $M_1(\|)$ or $M_2(\|)$.

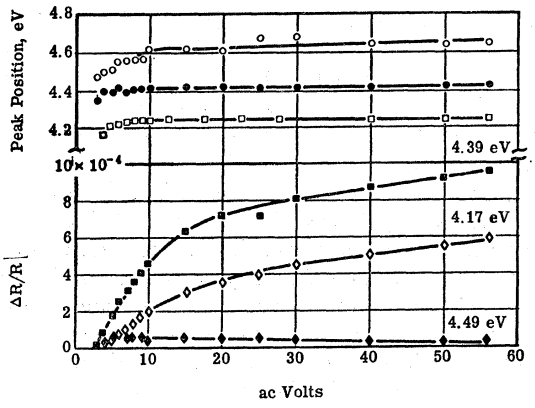

FIG. 12. Changes in the position and intensity of the different peaks around 4.4 eV with ac voltage.

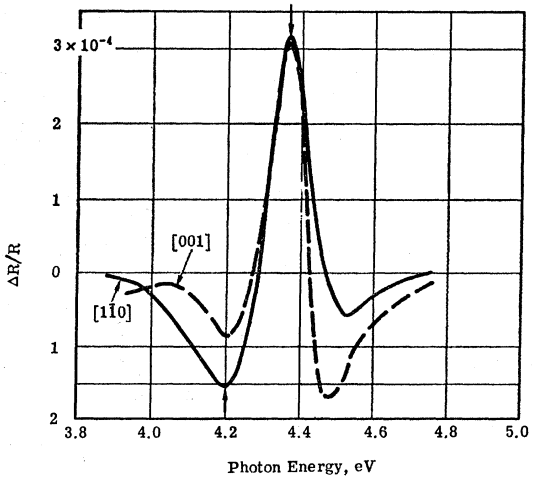

FIG. 13. Effect of polarized light on structures around 4.4 eV. Light polarized along [1$\bar{1}$0] and [001] directions, incident on (110) crystal face.

To further delineate these structures we have analyzed the results of polarized light experiments, assuming an M_1 type singularity along the [100] directions (the X points) and an M_2 type singularity along the [110] directions (the Σ points). Earlier, we discussed the Δ transition which also occur at an M_1 type critical point along the [100] directions. It was found experimentally in that case that light polarized along [001] and incident on a (110) crystal face did not generate structure due to $M_1(\|)$. If we assume that the transition selection rules and the direction of the symmetry axes are the same for X points as for Δ points, then the X point should behave similarly, and we would not expect to generate structure due to $M_1(\|)$ with light polarized along [001]. Since the B structure becomes more prominent under these conditions (Fig. 13), we conclude that the B structure is due to $M_2(\|)$, and thus represents the Σ_2-Σ_3 transition. The transition energy is about 4.4 eV.

The possible choices for the A structure are $M_1(\perp)$ and $M_2(\perp)$. If the structure is due to $M_1(\perp)$, it represents the X_4-X_1 transition, and the critical point should be roughly coincident with the negative peak at about 4.2 eV. On the other hand, if the structure is due to $M_2(\perp)$ (the Σ_2-Σ_3 transition), the critical point would be roughly coincident with the positive peak at 4.39 eV. We have no firm basis for making a choice at this time. However, if we extend the analogy between the X point and the Δ point, we must slightly favor the later choice, because no $M_1(\perp)$ structure was observed for the Δ transitions under similar experimental conditions. No clear explanation of the changes in relative intensities of the two overlapping structures with differently polarized light can be given at this time because not enough information is available to us to allow us to compute the expected peak intensities when many different components contribute.

E. $L_{3'}$-L_3 Transitions

The negative peak around 5.5 eV in Fig. 2 is found to be composed of two peaks at 5.34 and 5.52 eV at low ac voltages (Figs. 3 and 4). We attribute these peaks to the $L_{3'}$-L_3 transitions. These transitions have M_2 type singularity.[3] Around 5.5 eV $|\alpha| > |\beta|$ and is negative.[22,23] The spectra for $M_2(\|)$ under such conditions should be a positive peak followed by a negative peak, with the critical point being nearer to the positive peak. The $M_2(\perp)$ spectra under these same conditions should be a negative peak followed by a positive peak, with the critical point being nearer to the positive peak.[24] Based on the recorded spectra it is difficult to decide whether the observed structures are due to $M_2(\|)$ or $M_2(\perp)$. The $L_{3'}$-L_3 transitions occur at critical points along the (111) directions, and for any given direction of the applied field it is possible to observe both parallel and transverse components. Since the positive peaks associated with the structures around 5.5 eV are difficult to locate, we have associated the transition energies with the positions of the negative peaks. We believe the error in doing this should not be more than ± 0.1 eV.

The spin-orbit splitting of the $L_{3'}$-L_3 transition is about the same as that of the $L_{3'}$-L_1 transition (0.19 eV). Therefore, the splitting can be associated entirely with the valence band at $L_{3'}$. The splitting of the L_3 level, if there is any, must be very small. A small spin-orbit splitting at L_3 has been justified by Phillips and Liu.[21]

F. Other Transitions

There are a few unassigned peaks in the electroreflectance spectra of Ge. We have already mentioned the one at 3.65 eV. At low ac voltages there is a broad structure with a negative peak roughly around 5 eV (Fig. 3) which could be associated with the Δ_5-$\Delta_{2'}$ transition.[7] Two other structures are observed at 5.85 and 6.12 eV as shown in Fig. 2. With low ac voltage (Fig. 3) only the 5.85 eV peak is seen; the 6.12 eV peak could not be resolved because of the noise level.

Normal reflectivity measurements do not show any structure above the $L_{3'}$-L_3 transition energy. However, photoelectric emission studies of Ge by Allen and Gobeli[26] show some structures at 5.8 eV which they suggest may correspond to transitions from the upper valence band to the second or fourth upper conduction bands, which have critical points in the Σ region. The peak in electroreflectance at 5.85 eV may be associated with such a transition. There is also a possibility that the 5.85 eV peak is part of the 5.5-eV structure. A second structure seen at 6.18 eV in photoelectric emission could correspond to the 6.2-eV peak seen in electroreflectance.

5. SUMMARY

The present work indicates that by the proper choice of applied field and crystal orientation, and the use of polarized light, it is possible to delineate some overlapping structures in the electroreflectance spectra. The electroreflectance peaks and the critical points to which they are related are summarized in Table II.

ACKNOWLEDGMENTS

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[26] F. G. Allen and F. W. Gobeli, Phys. Rev. 144, A558 (1966).