PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Inter-Conduction-Band Transitions in the Electroreflectance Spectrum of InSb

R. Glosser,* J. E. Fischer, and B. O. Seraphin
Michelson Laboratory, China Lake, California 93555

(Received 28 July 1969)

Band-population effects in the surface region of semiconductors facilitate identification of parts of their electroreflectance spectrum. Structure exhibiting a red, a blue, or no shift in response to an increase of the surface potential corresponds to transitions starting from, ending at, or bridging the Fermi level. Using this criterion in *n*-type InSb, structure at 3.1 and 3.5 eV, which shows a red-shift, is assigned to transitions from the populated lowest conduction band Γ_{6c} to the next-higher bands Γ_{7c} and Γ_{8c}. In addition, these observations, as well as the observation of complementary structure which we assign to valence-to-conduction-band transitions at or near the Γ point, give the separation between Γ_{8v} and Γ_{7c} as 3.4 eV.

ELECTROREFLECTANCE has considerably upgraded the experimental information that optical studies provide to band-structure analysis.[1] However, the unambiguous assignment of the observed spectra to features of the band structure is often difficult. In particular, the structure labeled E_0' in the reflectance spectrum of cubic semiconductors[2] presents problems. Customarily assigned to transitions at the center of the Brillouin zone terminating at higher conduction bands, this structure has its counterparts in multiple and diverse, but weak structure in the electroreflectance spectrum. Identification is complicated, because energetic position and spin-orbit splitting of these higher conduction bands are not sufficiently well known. We report here a new criterion of identification based on band population effects that is applicable for materials in which such effects influence their electroreflectance spectrum. On the basis of this criterion, we assign some of the structural features in the 3–4-eV region of the InSb spectrum to transitions starting from the populated conduction band at the Γ point.

Band-population effects such as the Burstein-Moss shift[3] have long been known to affect the fundamental absorption edge of semiconductors with a small effective mass of the conduction band. They have also been postulated in the interpretation of electroreflectance spectra.[4] We have recently established band-population effects as an additional modulation mechanism in InSb through systematic variation of the potential barrier in the reflecting surface.[5] In response to this variation, changes in the conduction-band population within the space-charge region—the only part of the sample active in the generation of the electroreflectance signal—are then produced by bending of the bands with respect to the Fermi level. This in turn affects the spectral position of interband transitions ending at or starting from the Fermi level. In good agreement with measurements of the Burstein shift and of the field effect of the surface conductance, we observed a blue shift of the peak associated with transitions from the lower spin-orbit split valence band Γ_{7v} (in double group notation) to the conduction band Γ_{6c}, when, by applying bias, the edge of this band was moved down with respect to the Fermi level, filling final states previously open for the transition. The change in surface potential caused other structure to shift into the opposite direction by a similar amount, and some structure was virtually unaffected in its spectral position. Accordingly, we suggested the classification of structure into three categories; red, blue, or no shift correlates to transitions starting from, ending at, or bridging the Fermi level.

On the basis of this criterion, a doublet near 3.2 and 3.5 eV which shifts to the red must be assigned to transitions from the bottom of the populated conduction band Γ_{6c} to the higher conduction bands Γ_{7c} and Γ_{8c}, respectively. This assignment accurately determines energetic position and relative separation of Γ_{7c} and Γ_{8c} and hence contributes information in an area in which calculated band models give controversial interpretations.[6–8]

Results were obtained in the (metal-oxide-semiconductor) MOS[9] and the electrolytic[10] configuration. The samples were spark-cut, polished to 1 μ, etched in CP 4A and rinsed in deionized water containing 10^{-6} molar Na_2S.[11] The MOS configuration was then obtained by subsequently coating the surface with 200 Å Al_2O_3 and a

---

* Present address: Department of Physics, University of California, Santa Barbara, Calif. 93106.

[1] J. C. Phillips, in *Proceedings of the International School of Physics "Enrico Fermi," Course XXXIV*, edited by J. Tauc (Academic Press Inc., New York, 1966), p. 316.

[2] M. Cardona, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 181.

[3] E. Burstein, Phys. Rev. **93**, 632 (1954); T. S. Moss, Proc. Phys. Soc. (London) **B76**, 775 (1954).

[4] D. E. Aspnes and M. Cardona, Bull. Am. Phys. Soc. **13**, 27 (1968). Comments were made in the presentation; B. O. Seraphin, J. Phys. (Paris) **29**, C4 (1968).

[5] R. Glosser and B. O. Seraphin, Phys. Rev. **187**, 1021 (1969).

[6] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967).

[7] S. Bloom and T. K. Bergstresser, Solid State Commun. **6**, 465 (1968).

[8] F. Herman, R. L. Kortum, C. D. Kuglin, and J. P. Van Dyke, in *Methods in Computational Physics*, edited by B. Adler, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1968).

[9] C. R. Pidgeon, S. H. Groves, and J. Feinleib, Solid State Commun. **5**, 677 (1967); R. Ludeke and W. Paul, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 123.

[10] K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters **15**, 883 (1965).

[11] J. L. Davis, in *Solid Surfaces*, edited by H. C. Gatos (North-Holland Publishing Co., Amsterdam, 1964), p. 33.

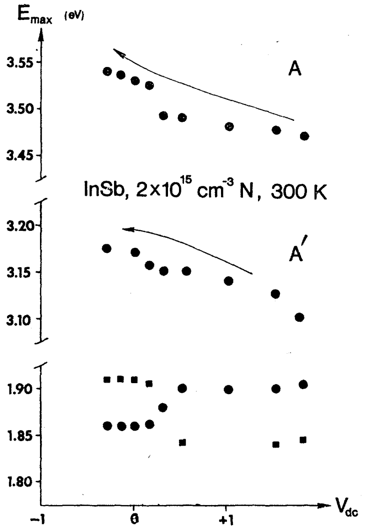

FIG. 1. Spectral shift with bias of structure associated with transitions starting from a populated conduction band (upper two plots), as compared to reference structure associated with a transiting bridging the Fermi level (lower plot). The crossover point at 0.25 V represents the flat-band position. Circles represent positive and squares negative extrema of the response. Arrows point in the direction of increasing peak magnitude. All data are taken by the electrolyte technique.

semitransparent Ni field electrode.[12] In the electrolyte version, the etched sample was placed opposite a platinum electrode in a Beckman Buffer pH 7.00 electrolyte. In Fig. 1, we compare the spectral position of this doublet with the $(\Lambda_4+\Lambda_5)-(\Lambda_6)$ calibration structure near 1.90 eV which bridges the Fermi level and hence permits monitoring the surface conditions as set by the dc bias.[13] The data were taken at room temperature with the electrolyte method. The calibration structure near 1.9 eV indicates in the typical crossover pattern[13] that the flat-band condition is being passed near +0.25 V bias. The total shift of this calibration structure over the bias range is 20 meV. This is in marked contrast to the red shift of 80 meV of the higher doublet (labeled A and A'), as the dc bias sweeps through the identical range towards positive values. Each member of the doublet exhibits only one peak at 300°K. No other structure was seen in the 3- to 4-eV energy range.

A spectrum taken at liquid-nitrogen temperature in the MOS configuration is shown in Fig. 2. The A-A' doublet is seen near 3.2 and 3.5 eV, complemented by weaker structure (B-B') near 3.4 and 3.8 eV.

In the MOS structure, determination of the field and temperature shifts are complicated by internal photoemission filling trapping states in the surface oxide.[14] The trapped electrons act as a screening electrode which tends to keep the surface p type. The photon energy threshold for this process is about 2.3 eV in this MOS configuration. Thus the determination of the flat-band condition at 1.9 eV is not applicable to the structure in the 3- to 4-eV region. Since the spectral position of the A-A' structure depends on the surface potential, a direct determination of the temperature shift cannot simply be obtained. The B-B' structure when observable at room temperature is too small and broad for comparison with the structure at low temperature.

We conclude from our results that A-A' on the one, and B-B' on the other hand are mated pairs in the sense of the components of a spin-orbit split doublet. We further conclude that A and A' correlate to transitions starting from the Fermi level and ending in higher conduction bands. B and B' probably end in the same set of conduction bands, but start from the top of the valence band.

We support these assignments by the following arguments:

(a) The spectral shift of A and A' with surface potential correlates it with a transition starting from the Fermi level, in quantitative agreement with the complementary and well identified spectral shift of the Γ_{7v}-Γ_{6c} transition ending there.[5]

(b) Interpretation of modulated spectra in terms of calculated band models must keep in mind that the exact location of an interband edge inside the width of structure is uncertain. This limits the read-out to approximately ±50 meV. In contrast, splittings can be read out to within ±5 meV from the separation of alike structure.

Bloom and Bergstresser calculate the splitting of Γ_{7c} and Γ_{8c} to 0.38 eV, varying little inside the neighborhood of $k=0$.[7] This value is in excellent agreement with the splitting of the A-A' doublet, which we believe stems from transitions terminating in these levels (Fig. 2).

The separation of A and B on the one, and A' and B' on the other hand is 0.21 eV. This is very close to the fundamental gap of InSb at liquid-nitrogen temperature, as required by our assignment.

Instead of originating at the top of the valence band, however, B-B' could start from a point off $k=0$ in the Δ direction, where Bloom and Bergstresser predict a splitting of the Γ_{8v} band by 0.42 eV. Since this is sufficiently close to the observed value of 0.38 eV, this possibility must be considered too. Further experiments will be needed to resolve this question.

The value we determine from our experiments for the position of Γ_{7c} does not depend upon the exact origin of B-B'. We find for the separation of Γ_{7c} from the top of the valence band a value of 3.4 eV, as compared to the calculated value of 3.6 eV.[7]

(c) Comparing our results and the electroreflectance

---

[12] J. E. Fischer, N. Bottka, and B. O. Seraphin (to be published).

[13] B. O. Seraphin, Surface Sci. **8**, 399 (1967); **13**, 136 (1969).

[14] R. K. Mueller and R. L. Jacobson, J. Appl. Phys. **35**, 1524 (1964); R. Glosser and B. O. Seraphin, Z. Naturforsch. **24a**, 1320 (1969).

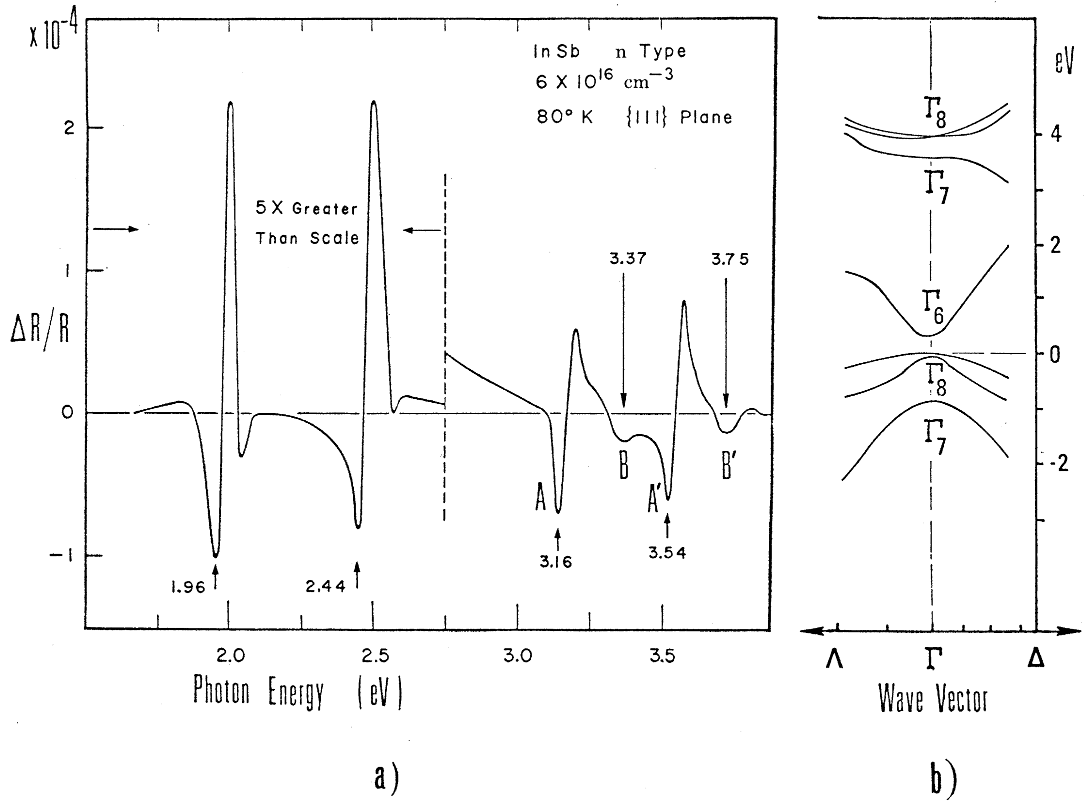

FIG. 2. (a) Electroreflectance spectrum of an InSb MOS-sample at liquid-nitrogen temperature. The doublets *A*-*A*′ and *B*-*B*′ are discussed in the text. (b) Band structure of InSb near the center of the Brillouin zone (after Bloom and Bergstresser, Ref. 7).

spectra of Shaklee *et al.*[15] and Cardona and co-workers[6] with the InSb thermoreflectance spectra reported by Matatagui and co-workers,[16] we obtain further support for our assignment of the *A*-*A*′ structure. Electroreflectance spectra for *n*-type InSb always display the *A*-*A*′ structure, and weak or no structure at *B*-*B*′. Thermoreflectance spectra, in contrast, show no structure at *A*-*A*′, but response at *B*-*B*′. The remainder of the two types of spectra are entirely comparable, in particular structural features near 2 and 4 eV. This is in line with our assignment of the *A*-*A*′ structure to transitions starting from the lowest conduction band. Thermal modulation should only weakly affect a transition that starts above the band minimum at the Fermi level, in contrast to electric field modulation operating at such a transition through band population effects.

(d) The *A*-*A*′ structure gradually disappears as the conduction band is being depopulated. In a 7×10^{17}-cm^{-3} *p*-type sample[17] carrying a *p*-type surface, *A*-*A*′ is absent except for some very weak residual effect probably caused by excitation of electrons through the probing light and/or the surface field. The structure can be turned on even in *p*-type material by biasing the surface towards the flat-band condition, thereby increasingly populating the conduction band. This further supports our assignment.

Our assignment of *A*-*A*′ is in disagreement with that given in Refs. 6 and 15. They assign this pair to transitions from the split valence band in the Δ direction to the second lowest conduction band. Their assignment in InSb is consistent with the corresponding assignment in other III-V compounds. Our new assignment of *A*-*A*′ does not necessarily affect the over-all trends they observed in the III-V compounds. We would simply argue that the *B*-*B*′ pair which lies 0.2 eV higher than *A*-*A*′ should be compared with the structure they label E_0' and $E_0'+\Delta_0'$ in the other III-V compounds although we do not necessarily agree with their assignment of the origin of this structure.

In summary, we have identified a doublet in the electroreflectance spectrum of InSb as correlated to transitions between the populated conduction band Γ_{6c} as the initial and the spin-orbit split higher conduction bands Γ_{7c} and Γ_{8c} as the final states. This

---

[15] K. L. Shaklee, M. Cardona, and F. H. Pollak, Phys. Rev. Letters **16**, 48 (1966).

[16] E. Matatagui, A. G. Thompson, and M. Cardona, Phys. Rev. **176**, 950 (1968).

[17] We wish to thank Dr. C. R. Pidgeon for providing this sample.

identification places Γ_{7c} and Γ_{8c} at 3.4 and 3.8 eV, respectively, above the top of the valence band. A second doublet, separated from the first by the energy of the fundamental gap, most likely correlates to transitions from the top of the valence band into the same spin-orbit split set of final states.

This interpretation of some of the multiple and weak structure in the E_0' region on the basis of band population effects will facilitate identification. Our interpretation provides accurate values for energetic position and splitting of higher conduction bands in materials in which band population effects are of importance, such as GaSb and InAs which are under study in this laboratory. Such data provide semiempirical band models with experimental input in a spectral region for which such input is particularly needed.

PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Effect of Internal Strains on the Paraelectric Resonance of Li^+ in KCl†

R. W. Timme, B. Dischler,* and T. L. Estle
Department of Physics, Rice University, Houston, Texas 77001

(Received 10 September 1969)

Paraelectric-resonance data for KCl:Li^+ with a number of crystal orientations at 29.2 GHz are presented. The spectra are in serious disagreement with the predictions of the simple eight-⟨111⟩-dipole model in that two lines appear for certain orientations where only one is expected, and one line appears for other orientations where two are expected. However, these spectra can be explained if internal strains are incorporated into the description.

I. INTRODUCTION

PARAELECTRIC resonance[1,2] may be defined as the process of stimulating electric dipole transitions between energy levels of a paraelectric defect. A paraelectric defect is a crystal imperfection having a permanent electric dipole moment which can exist in one of several equivalent but geometrically different orientations. The particular paraelectric defect produced by the replacement of a K ion in KCl with a Li ion has been studied by several investigators. The theoretical calculations of Quigley and Das[3] and Dienes, Hatcher, Smoluchowski, and Wilson[4] and the experimental findings of Byer and Sack[5] show that the Li ion exists off center of the K-ion vacancy in potential minima with the Li along the ⟨111⟩ crystallographic directions. There is one potential minimum for each of the eight ⟨111⟩ directions, thus, eight different directions along which the electric dipole of the defect may align. This is the basis of the eight-⟨111⟩-dipole model of the KCl:Li^+ system as presented by Bowen, Gomez, and Krumhansl.[6]

Recently, several studies have been made on the paraelectric resonance of KCl:Li^+. Höcherl and Wolf[7] have published spectra obtained at 35 GHz with field parallel to ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions in the crystal. Herendeen and Silsbee[8] have reported paraelectric resonance at 9, 24, and 63 GHz in KCl:Li^+. Their data were for ⟨100⟩ and ⟨110⟩ orientations. In retrospect, it appears that the paraelectric resonance thought to be OH^- in KCl [9] is in fact caused[2,7,10,11] by Li^+, at least for the data obtained above 10 GHz.

The purpose of this paper is to present the paraelectric-resonance spectra obtained for a number of crystal orientations of KCl:Li^+ and to compare the data with the predictions with strains. The angular dependence of the paraelectric resonance in KCl:Li^+ has been little studied. The effect of internal strains on the paraelectric resonance of KCl:Li^+ has been briefly presented by the authors previously[12] and has been discussed in a perturbation sense by Herendeen and Silsbee.[8] The major discrepancies of the simple eight-

---

† Work supported by National Aeronautics and Space Administration. This paper is based in part on a thesis submitted by R. W. Timme to Rice University in partial fulfillment of the requirements for the M. A. degree.

* Present address: Institut für Elektrowerkstoffe, Freiburg/Br., Germany.

[1] H. B. Shore, Phys. Rev. **151**, 570 (1966); G. Pfister, Helv. Phys. Acta **39**, 602 (1966).

[2] T. L. Estle, Phys. Rev. **176**, 1056 (1968).

[3] R. Quigley and T. Das, Phys. Rev. **164**, 1185 (1967); Solid State Commun. **5**, 487 (1967).

[4] G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. Wilson, Phys. Rev. Letters **16**, 25 (1966); Phys. Rev. **161**, 888 (1967).

[5] N. E. Byer and H. S. Sack, Phys. Rev. Letters **17**, 72 (1966); J. Phys. Chem. Solids **29**, 677 (1968).

[6] S. P. Bowen, M. Gomez, and J. A. Krumhansl, Phys. Rev. Letters **16**, 1105 (1966); Phys. Rev. **153**, 1009 (1967).

[7] G. Höcherl and H. C. Wolf, Phys. Letters **27A**, 133 (1968).

[8] R. A. Herendeen, Bull. Am. Phys. Soc. **13**, 660 (1968); R. A. Herendeen and R. H. Silsbee (unpublished).

[9] L. D. Schearer and T. L. Estle, Solid State Commun. **4**, 639 (1966); G. Feher, J. W. Shepherd, and H. B. Shore, Phys. Rev. Letters **16**, 500 (1966).

[10] G. Höcherl, D. Blumenstock, and H. C. Wolf, Phys. Letters **24A**, 511 (1967).

[11] J. G. Carnes (private communication).

[12] T. L. Estle, B. Dischler, and R. W. Timme, Bull. Am. Phys. Soc. **14**, 346 (1969).