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# Fine structure of $E_1'$ peak in Ge and GaAs

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Parallels between electroreflectance and thermoreflectance data for the $E_1'$ peak near 5.6 eV in Ge are used to analyze thermoreflectance data for the $E_1'$ structure near 6.6 eV in GaAs.

## I. INTRODUCTION

The direct interband spectra[1] of tetrahedrally coordinated semiconductors with diamond and zinc-blende crystal structures have been studied exhaustively and analyzed in detail below 6 eV. With the aid of modulation techniques, especially low-field electroreflectance, it has become possible[2] to resolve fine structure associated with spin-orbit splittings as small as 0.08 eV at energies as high as 5 eV in GaAs. Such splittings, combined with information obtained from other optical experiments (especially photoemission), have made it feasible to assemble remarkably complete and detailed pictures of the electronic structure of many semiconductors.

The development of this knowledge is of interest for many reasons. For example, one of the general features of the electronic energy levels of semiconductors that have emerged from the low-field electroreflectance studies is the very small intrinsic decay widths $\Gamma$ associated with interband transitions taking place at rather high energies. If we assume that $\Gamma = \Gamma_e + \Gamma_h$, where $\Gamma_e$ and $\Gamma_h$ are the intrinsic decay widths of excited electron and hole states, then Aspnes and Studna have shown[2] that both $\Gamma_e$ and $\Gamma_h$ are smaller than 0.05 eV for electron and hole states as much as 3 eV away from the conduction- and valence-band edges, respectively. Thus the one-electron approximation is shown to have a much wider range of validity than one might have been led to expect, e.g., from the usually vague and inconclusive results of many-body theories.

There is a second, more quantitative, and more specific application of spectroscopic data that has been strikingly successful for semiconductors. Qualitatively speaking, the more ionic semiconductors show larger energy gaps than the less ionic ones, which reflects the larger energy required for charge-transfer in more ionic materials. Trends in structural and material properties of binary octet compounds (chemical formula $A^NB^{8-N}$) and their alloys can be correlated quantitatively with trends in spectroscopic energies.[3-6] The success of this correlation can be traced to the prominent emphasis placed in the analysis on averaging all the interband transitions (with appropriate spectroscopic weighting factors), thereby treating appropriately all the transitions of the bonding → antibonding type.

Empirical correlations of chemical trends with spectroscopic data are expected to be successful to the extent that they not only utilize the precision achievable spectroscopically but also are guided by close analogies with reliable quantum-mechanical calculations. Such empirical correlations become more than merely exercises in data pattern recognition when the atomic potentials used in the energy-band calculation contain parameters which are manifestly analogous to those contained in the spectrochemical theory.[3-6] It has been shown[7] in the case of Ge that such a parameterization is indeed possible, the atomic potential of Ge being represented by a local pseudopotential together with a nonlocal repulsive $d$ potential. The number of parameters needed to characterize this potential is four, three for the local potential and one for the nonlocal term.

In order for the parameters obtained in this way to have physical significance, and thereby to aid in understanding chemical trends from one material to another, it is essential to utilize all the spectroscopic data associated with bonding → antibonding transitions. In $A^NB^{8-N}$ diamond- and zinc-blende-type crystals, the important spectroscopic features have been given the conventional labels $E_0$, $E_0'$, $E_1$, $E_1'$, and $E_2$ by Cardona.[1] An important factor contributing to the success of the parameterization[7] of the pseudopotential of Ge was the analysis of the fine structure of the $E_1'$ peak in Ge by electroreflectance,[8] the fine structure of the $E_0$ and $E_1$ peaks at lower energy being well understood. Ordinary reflectivity measurements reveal only one feature, while the electroreflectance data exhibited three edges separated in a characteristic manner.

The fine structure of the $E_1'$ peak in Ge is found

below 6.2 eV, in a spectral range easily accessible to Schottky-barrier electroreflectance.[2] The fine structure of the $E_1'$ peak in GaAs falls between 6.3 and 7.0 eV, which is spectroscopically less convenient and has not been studied so far by electroreflectance. However, thermoreflectance data have been reported[9] for a number of semiconductors including Ge and GaAs, in the energy range 4–9 eV. In general, thermoreflectance data are less easily interpreted than low-field electroreflectance, but in this case the close similarity between the spectra of Ge and GaAs makes it possible to interpret thermoreflectance data in the latter by analogy with the former and with the former's electroreflectance edges.

## II. ANALYSIS

For the reader's convenience our analysis is illustrated by a number of drawings based on experimental data taken by several different authors. The simple reflectance spectrum[10] of Ge is shown in Fig. 1. The minimum in the reflectivity, marked $A$, is at 5.55 eV, while the peak marked $B$ is at 5.95 eV. The situation in GaAs is shown[11] in Fig. 2. Again the dip $A$ and peak $B$ are seen in the reflectivity, this time at 6.27 and 6.62 eV, respectively.

Within the framework of the one-electron approximation,[1] edges in the direct interband optical spectra are found in $\epsilon_2$, and in the reflectance

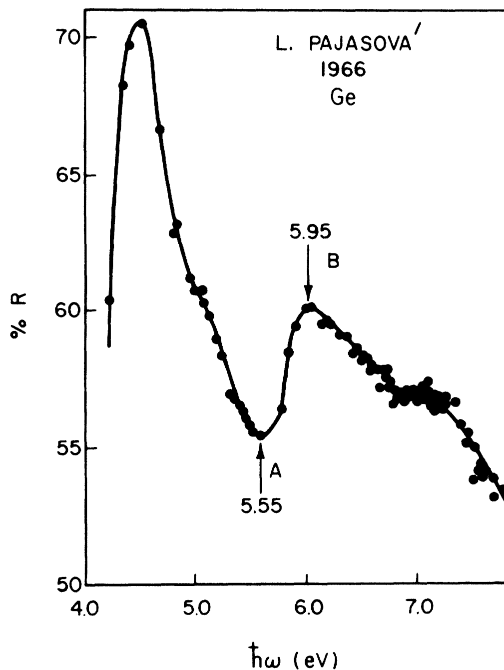


FIG. 1. Detail of the reflectivity of Ge near 6 eV, taken from Ref. 10.

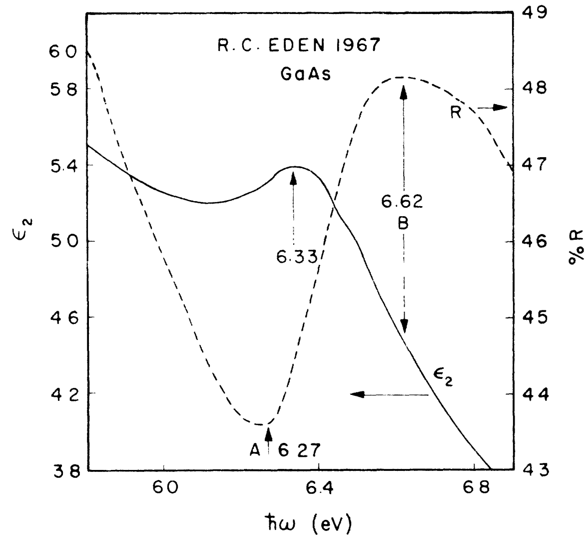


FIG. 2. Detail of $R$ and $\epsilon_2$ near 6.4 eV in GaAs, taken from Ref. 11.

$R$. In most cases structure in $R$ at a certain energy is echoed by structure in $\epsilon_2$ at a nearby energy. In Fig. 2 the peak in $R$ at 6.62 eV produces a peak in $\epsilon_2$ at 6.33 eV, which by accident nearly coincides with the minimum in $R$ at 6.27 eV.

We now consider modulated reflectivity (electroreflectance, thermoreflectance) data. For some time electroreflectance data were thought to be more difficult to interpret than, e.g., simple wavelength derivative spectra,[12] because of the distortion of line shapes caused by built-in surface barrier electric fields. These ambiguities can be removed in several ways, most elegantly through the use of the Schottky-barrier geometry.[2] On the other hand, the line shape of thermoreflectance oscillations can be calculated only when allowance is made for many electron-phonon interactions that occur over a large volume of momentum space, a task which has not so far been attempted over a broad set of energy bands. We therefore calibrate the thermoreflectance data relative to the electroreflectance data.

In Ge two strong electroflectance edges at 5.58 ($A$) and 5.84 eV ($B$) have been observed, followed by a weaker one at 6.06 eV ($C$). We have examined the thermoreflectance $\Delta R/R$ data[9] and have not found corresponding structure at similar energies. However, the Kramers-Kronig transforms[13] of the thermoreflectance data do show structure in $\Delta\epsilon_2$ which corresponds very accurately to the electroreflectance edges (within 0.02 eV, probably the limit of resolution of the thermoreflectance data). The corresponding energies $A$, $B$, and $C$ are marked in Fig. 3, and are 5.58, 5.82, and 6.07 eV, respectively.

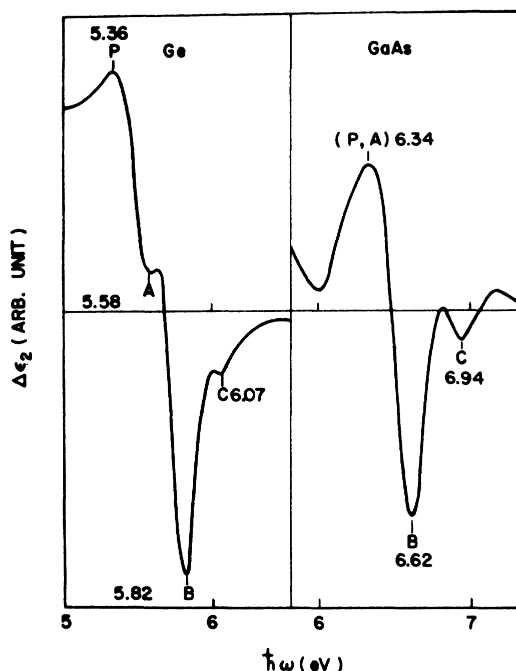


FIG. 3. Comparison of Kramers-Kronig transformed thermoreflectance of Ge and GaAs. Data from Refs. 9 and 13.

We make no claim of fundamental significance for this coincidence, which is probably accidental and is a consequence of several factors combining to compensate for the difference in $\Delta R$ (electro, Ge) compared to $\Delta\epsilon_2$ (thermo, Ge). However, it appears that the agreement of the energy differences is significant, as is the relative order of strength of the oscillations ($B$, $A$, $C$ in both cases).

The Ge spectrum shown in Fig. 3 contains an additional oscillation $P$ which may be associated with the $M_3$ critical point, marking the end of transitions between bands four and five. It is of little concern to us here, except that in GaAs $P$ and $A$ are not resolved separately, so that the energy of $A$ becomes less certain in GaAs than it was in Ge.

When we turn to the spectrum for $\Delta\epsilon_2$ in GaAs, also shown in Fig. 3, we find a series of oscillations very similar to those in Ge, in strength and spacing, the spacing being about 0.30 eV, compared to 0.25 eV in Ge. If the spacing reflected only the spin-orbit splitting[2] $\Delta_1 = \lambda$ of the $L_{3v}$ valence band states, it would be about 0.20 eV in Ge and 0.23 eV in GaAs. The fact that the observed splitting is somewhat larger than $\lambda$ suggests that not all of the critical points giving rise to these oscillations are at $\vec{k} = L$. On the other hand, the splitting is not much greater than $\lambda$, and the oscillations observed in GaAs are very similar to those observed in Ge in $\Delta\epsilon_2$ (thermo). This suggests that the critical points that are involved are not far from $L$ and have similar locations in both crystals.

In the thermoreflectance data the oscillations that are observed are broad and overlap appreciably. In the low-field electroreflectance data for Ge the oscillations are well-resolved, with $A$ strong, $B$ very strong, and $C$ weak. This suggests that $A$ and $B$ may originate from states near the same initial state (the upper $L_{3v}$ state, or more properly speaking, $L_{3'}$ in Ge, and $L_{3v}$ in GaAs), while $C$ originates from a state near the lower $L_{3v}$ state and ends at a state near the upper $L_{3c}$ state. A fourth transition $D$ from the lower $L_{3v}$ state to the lower $L_{3c}$ state, may also contribute to $B$ and this may explain why $B$ appears to be stronger than $A$ in the low-field electroreflectance data for Ge. This picture is consistent with a previous discussion[14] of $L_{3'v} \to L_{3c}$ transitions in Si; that discussion found three critical points near $L$ and showed that the energies involved were those of $L_{3c} - L_{3'v}$ to within a few hundredths of an eV.

The data analyzed here suggest that the center of gravity of the spin-orbit split transitions near $L_{3v} \to L_{3c}$ in GaAs is $6.62 \pm 0.02$ eV in the reflectivity $R$, and $6.33 \pm 0.05$ eV in $\epsilon_2$. The Kramers-Kronig (K-K) transformed value (the $\epsilon_2$ value) may be misleading, however. In the region of the $E_2$ peak one finds[11] a peak in $\epsilon_2$ near 4.5 eV, whereas the correct value for $E_2$, as determined from electroreflectance,[2] is 5.0 eV. (Apparently the K-K transform has shifted the peak in $\epsilon_2$ from $E_2$ to $E_0'$.) Thus, in analogy with this behavior, we believe that the apparent reflectance value, based on modulation data, is more nearly correct. This is the value that is used[15] in constructing a nonlocal pseudopotential for GaAs.

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