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UCRL-19119

Wavelength Modulation Spectra of GaAs and Silicon*

by

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ABSTRACT

Wavelength modulation spectra of GaAs and Si are presented at 5°K in the range 2.8 to 6.0 eV. The empirical pseudopotential method (including spin-orbit contributions for GaAs) is used to calculate the electronic band structure and the logarithmic derivative of the reflectivity $R'(\omega)/R(\omega)$. A comparison shows good agreement between experiment and theory. The electronic transitions causing the reflectivity peaks are identified.

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Among the many different schemes for differential spectroscopy,[1] the wavelength modulation method is the most attractive. The fact that the wavelength modulation spectrum is simply the derivative of the normal spectrum leaves no ambiguity in its interpretation. We have constructed a wavelength modulation spectrometer which covers a spectral range from the near infrared to 6.0 eV. In this paper we present the derivative reflectivity spectra $R'(\omega)/R(\omega)$ for GaAs and Si in the range 2.8 to 6.0 eV at $5^{o}K$. In order to identify the optical structure, we have used the empirical pseudopotential method[2,3] to calculate the electronic band structure and $R'(\omega)/R(\omega)$.

In our experiments wavelength modulation is achieved through vibration of a mirror in the optical path inside the spectrometer. A double-beam method is used to eliminate the background noise.[4] The dc and ac outputs of the two beams are I_o, I_oR, and $\Delta I_o/\Delta\lambda$, $\Delta(I_oR)/\Delta\lambda$, respectively, where I_o is the beam intensity in the absence of the sample. Two feedback loops are used to make $\Delta I_o/\Delta\lambda = 0$ and I_oR = constant. Consequently, the other two outputs yield the spectra $R'(\lambda)/R(\lambda)$ and $1/R(\lambda)$. The derivative spectrum is then converted to the functional form $R'(\omega)/R(\omega)$. The samples are polished and etched wafers of single crystals with (1,1,1) orientation. The GaAs sample is n-type with a carrier concentration of 10^{16} cm^{-3} , and the Si sample is p-type with a carrier concentration of 10^{13} cm^{-3} .

The electronic band structure is calculated using the empirical pseudopotential method.[2,3] This method consists of adjusting pseudopotential form factors to achieve agreement with experimental results for the principal

optical transitions. Spin-orbit effects[5] are included in the band structure calculation for GaAs, but they are not included for Si because of its negligibly small spin-orbit splitting, e.g., about 0.04 eV at $\Gamma_{25'}$. The pseudopotential form factors used for GaAs are $V^S(G^2=3) = -0.2460$, $V^S(8) = -0.0008$, $V^S(11) = 0.0737$, $V^A(3) = 0.0583$, $V^A(4) = 0.0509$, and $V^A(11) = 0.0011$ Ry. The lattice constant is 5.64Å, and the spin-orbit parameter is adjusted so that the spin-orbit splitting at Γ_{15} is 0.35 eV. The pseudopotential form factors used for Si are $V^S(3) = -0.21$, $V^S(8) = 0.04$, $V^S(11) = 0.08$, with the antisymmetric form factors equal to zero. The lattice constant is 5.43Å and the spin-orbit splitting at $\Gamma_{25'}$ is taken to be zero. For both crystals the form factors for $G^2 > 11$ are constrained equal to zero.

The imaginary part of the dielectric function $\epsilon_2(\omega)$, the reflectivity $R(\omega)$, and the derivative of the reflectivity $R'(\omega)/R(\omega)$ are all calculated as described in Ref. 3. For GaAs we have tried a cubic interpolation (instead of the usual linear interpolation) of the energies and the matrix elements within each cube; the result is that the critical point transitions are accentuated slightly in $\epsilon_2(\omega)$.

GaAs

The calculated band structure of GaAs appears in Figure 1, and identifications of the important reflectivity structure are tabulated in Table I. A comparison of the theoretical and experimental derivative spectra appears in Figure 2. The positions of the important reflectivity peaks are given by those zeroes of $R'(\omega)/R(\omega)$ at which the slope is negative. The other structure appearing in the derivative spectrum is much finer; some of these details are practically imperceptible when seen in the reflectivity spectrum.

The fundamental gap occurs at Γ at 1.52 eV in both theory and experiment.[6] The major structure in the 2.8 to 3.3 eV region is a double reflectivity peak caused by the spin-orbit split Λ transitions. The first peak at 3.02 eV is caused by $\Lambda(4-5)$ transitions and the second peak at 3.24 eV is caused by $\Lambda(3-5)$ transitions. The theoretical peaks occur at 3.05 and 3.25 eV, giving excellent agreement with the experiment. Although no such structure is apparent in the experimental spectrum,[7] a fine structure caused by $L(4-5)$ transitions does appear in the theoretical spectrum at 2.90 eV. The next major reflectivity structure occurs at 5.11 eV in the experimental measurements and at 4.94 eV in the theoretical calculations. It is caused by a combination of $\Sigma(4-5)$, $\Delta(3-5)$, and $\Delta(4-5)$ transitions, all with large matrix elements. The fine structure in this region (4.2 to 5.1 eV) consists of three peaks in the experimental derivative spectrum. The structure in the 4.2 to 4.7 eV region appears in the reflectivity spectrum only as two small bulges on the low-energy side of a much larger peak. These are located at 4.44 and 4.60 eV and are caused by $\Delta(4-5)$ and $\Delta(3-5)$ transitions. The major peak at 5.11 eV in the experimental spectrum is caused by $\Sigma(4-5)$ transitions but does not show the fine structure present in the theoretical spectrum. Both epxeriment and theory show a broad ($\sim \frac{1}{2}$ eV) structure immediately above the $\Sigma(4-5)$ peak. This is caused by $\Delta(4-6)$ and $\Delta(3-6)$ transitions.

Si

The band structure for Si is identical to the one appearing in Ref. 1. A comparison of the theoretical and experimental derivative spectra appears in Figure 3. Identifications of the important reflectivity structures are tabulated in Table II.

No structure corresponding to the fundamental gap of 3.13 eV at L appears either in the theoretical or the experimental spectrum, however, the agreement between experiment and theory in this region is good enough to suggest that the first direct gap is at L. The first major peak in the reflectivity appears at 3.45 eV in the experimental spectrum and at 3.46 eV in the theoretical spectrum and is caused mainly by $\Lambda(4-5)$ transitions and by $\Delta(4-5)$ transitions. A small dip occurs in the spectra at 3.40 eV for the experiment and at 3.35 eV for the theory. This structure is attributed to (4-5) transitions in a volume centered at (0.3, 0.3, 0.2) (units of $2\pi/a$) and to $\Delta(4-5)$ transitions close to Γ. A small peak caused by $\Lambda(3-5)$ transitions appears in the theoretical reflectivity at 3.68 eV, but it does not appear in the experimental spectrum. The major reflectivity peak occurs at 4.57 eV in the experimental measurements and at 4.51 eV in the theoretical calculations. It is caused almost entirely by $\Sigma(4-5)$ transitions near (0.4, 0.4, 0.). The small experimental structure at 4.32 eV is attributed to (3-5) transitions near (0.3, 0.2, 0.1) and to (4-5) transitions in the vicinity of X. The next reflectivity peak occurs at 5.48 eV for the experiment and at 5.38 eV for the theory and is caused by (4-6) transitions in a volume centered at (0.6, 0.4, 0.3) (near Λ).

The location in the zone of transitions responsible for a particular reflectivity structure is somewhat speculative for Si. The reason for this is that there are many critical points in the joint density of states and it is difficult to distinguish which of these are the more important for a particular structure. Other authors[8] have made similar comments as to the great density of critical points in the Si band structure.

For both GaAs and Si, the $\Lambda(4\text{-}5)$ peaks are much sharper in the experimental spectra than in the theoretical spectra. The theoretical structure in this region more closely resembles the room temperature spectrum than the low temperature spectrum. This same low-temperature sharpening of the Λ peaks consistently occurs in other III-V cubic semiconductors,[4] and it is thought to be caused by exciton effects. Furthermore, electroreflectance line shapes also indicate exciton effects are present.[9] Thus, the sharpening of the Λ peaks can be explained in terms of the reduction of lifetime broadening of the hyperbolic excitons associated with Λ.

Our low-temperature derivative spectra for GaAs and Si show clear improvement in spectral resolution over other techniques. Furthermore, the results are in excellent agreement with spectra computed from the pseudopotential band structures. The extent of this agreement gives us confidence that our identifications of the important optical transitions are substantially correct.

ACKNOWLEDGEMENTS

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Table Captions

Table I - Theoretical and experimental reflectivity structure at $5^{o}K$ and their identifications, including the location in the Brillouin zone, energy, and symmetry of the calculated critical points for GaAs.

Table II - Theoretical and experimental reflectivity structure at $5^{o}K$ and their identifications, including the location in the Brillouin zone, energy, and symmetry of the calculated critical points for Si.

Figure Captions

Figure 1 - Electronic band structure for GaAs along the principal symmetry directions.

Figure 2 - A comparison of theoretical and experimental modulated reflectivity for GaAs. The transitions which cause the major reflectivity peaks are identified.

Figure 3 - A comparison of theoretical and experimental modulated reflectivity for Si. The transitions which cause the major reflectivity peaks are identified.

Table I

GaAs

Reflectivity Structure (eV)		Associated Critical Points		
Theory	Experiment	Location in Zone	Symmetry	CP Energy (eV)
1.52	1.52[a]	Γ_8-Γ_6 (0., 0., 0)	M_0	1.52
2.90	----	L(4-5) (0.5, 0.5, 0.5)	M_0	2.82
3.05	3.02	Λ(4-5) (0.2, 0.2, 0.2)	M_1	3.02
3.25	3.24	Λ(3-5) (0.2, 0.2, 0.2)	M_1	3.25
4.35	4.44	Δ(4-5) (0.6, 0., 0.)	M_0	4.23
4.50	4.60	Δ(3-5) (0.6, 0., 0.)	M_0	4.36
4.60		Δ(4-5) (0.2, 0., 0.)	M_1	4.38
4.78		Δ(3-5) (0.2, 0., 0.)	M_1	4.55
4.94	5.11	Σ(4-5) (0.6, 0.6, 0.)	M_2	4.88
5.85	5.91	Δ(4-6) (0.5, 0., 0.)	M_1	5.67
		Δ(3-6) (0.5, 0., 0.)	M_1	5.81

[a] M. D. Sturge, Phys. Rev. 127, 768 (1962).

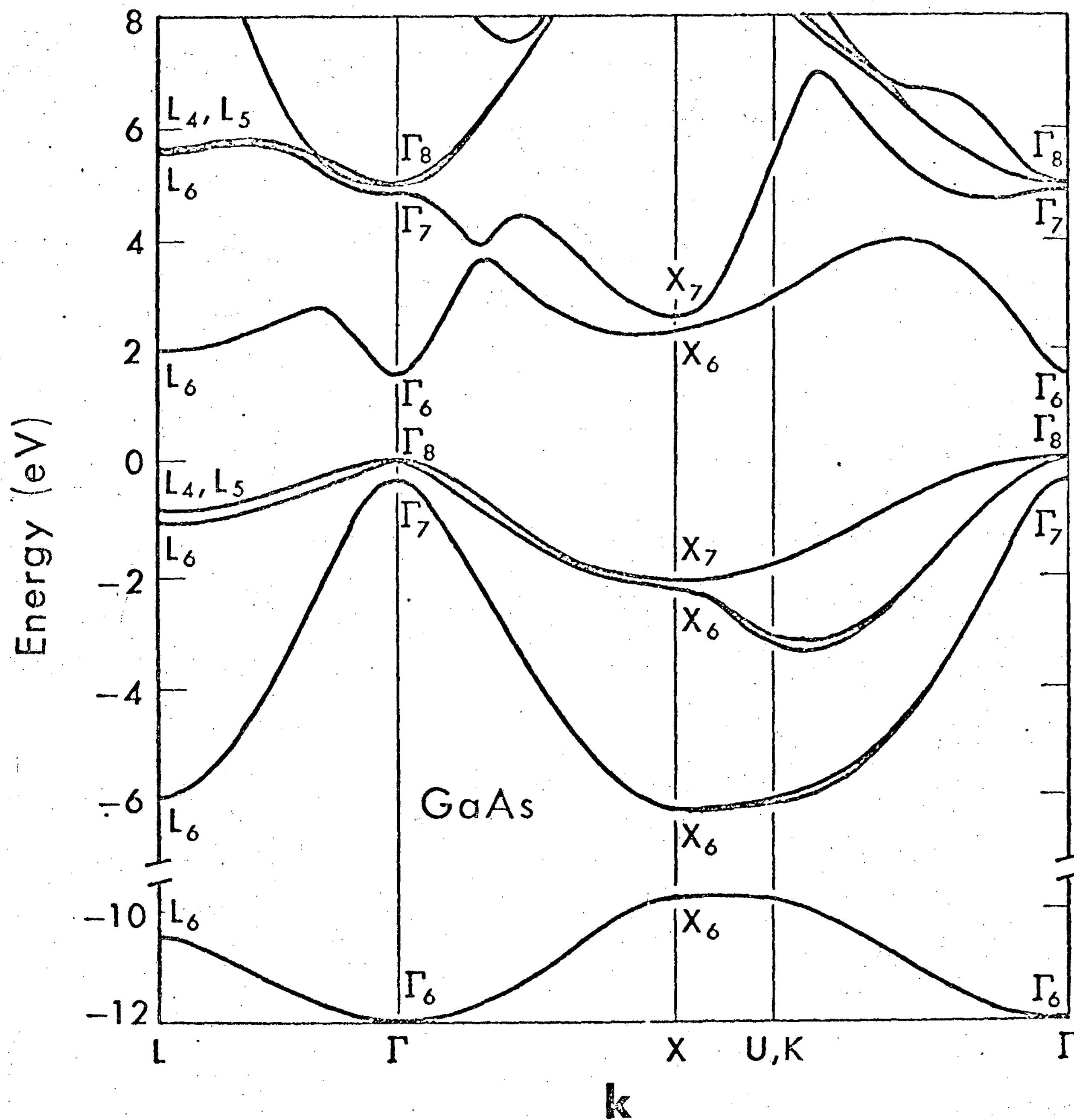

Fig. 1

Table II

Si

Reflectivity Structure (eV)		Associated Critical Points		
Theory	Experiment	Location in Zone	Symmetry	CP Energy (eV)
3.13	---	L(4-5) (0.5, 0.5, 0.5)	M_0	3.13
3.35	3.40	(4-5) transitions near (0.3, 0.3, 0.2)	--	3.26
		Δ(4-5) (0.1, 0., 0.)	--	3.42
3.46	3.45	Λ(4-5) (0.1, 0.1, 0.1)	M_1	3.46
3.68	3.66	(3-5) transitions near (0.2, 0.1, 0.1)	M_2	3.77
4.11		(4-5) transitions near (1.0, 0., 0.)	M_1	3.97
4.22	4.30	(3-5) transitions near (0.3, 0.2, 0.1)	--	4.10
4.51	4.57	Σ(4-5) (0.4, 0.4, 0.)	M_2	4.41
5.38	5.48	(4-6) transitions near (0.6, 0.4, 0.3)	--	5.29

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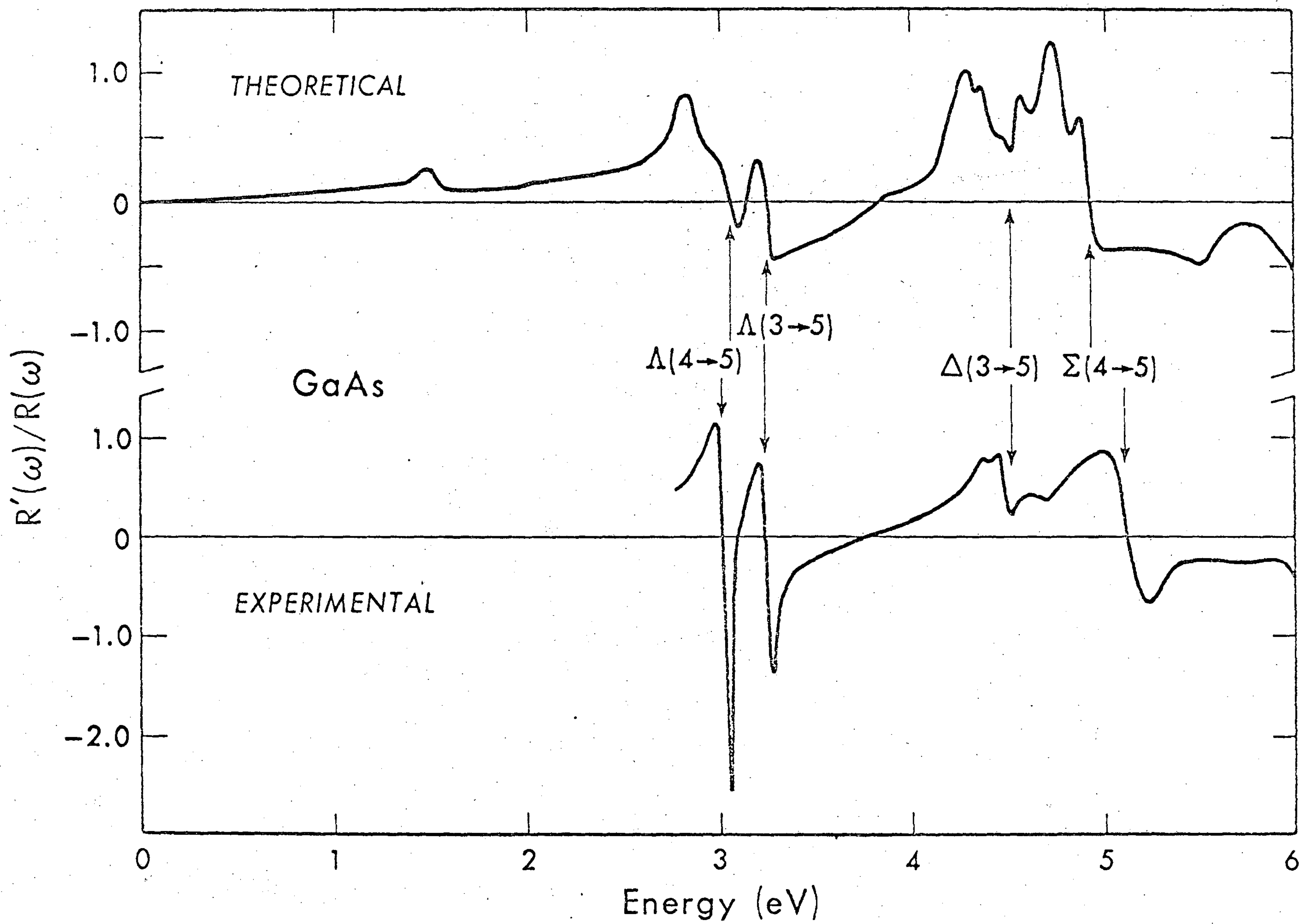

Fig. 2

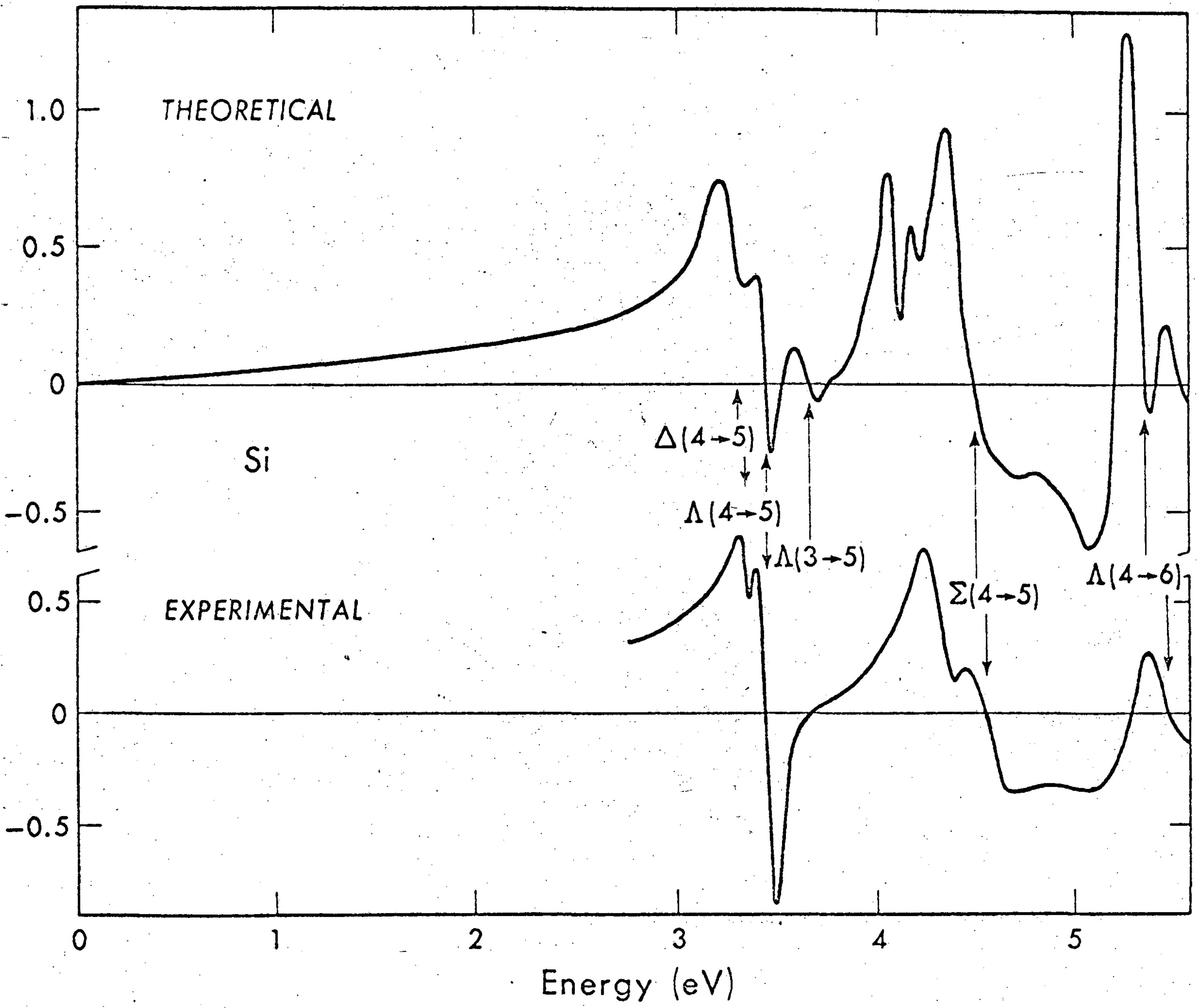

Fig. 3

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