Invited talk to be given at the
International Conference on Modulation
Spectroscopy. Tucson, Arizona
November 23-26, 1972

RECEIVED
LAWRENCE
RADIATION LABORATORY

LIBRARY AND
DOCUMENTS SECTION

LBL-1402
Preprint

OPTICAL WAVELENGTH-MODULATION SPECTROSCOPY

Y.R. Shen

November 1972

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LBL-1402

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Invited talk to be given at the
International Conference on Modulation
Spectroscopy, Tucson, Arizona
November 23-26, 1972

LBL-1402
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Berkeley Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

OPTICAL WAVELENGTH-MODULATION SPECTROSCOPY

Y. R. Shen

November 1972

Optical Wavelength - Modulation Spectroscopy

Y.R. Shen†

Department of Physics, University of California,
Berkeley, California 94720 and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory,
Berkeley, California 94720

ABSTRACT

Wavelength - modulation spectroscopy of solids is reviewed. The construction of a wavelength - modulation spectrometer is described and several examples on its applications to solids are given. It is shown that the results of pseudopotential calculations will agree with the experimental observations. The wavelength - modulation spectrometer can also be used to detect with high sensitivity small changes in a spectrum induced by an external perturbation.

I. INTRODUCTION

Optical spectroscopy of solids has long been a field of immense activity. More recently, out of mutual stimulation, both theoretical and experimental studies in the field have made a giant step forward. Theoretically, the calculations of the electronic band structures of solids have become so accurate that they can produce spectra with a resolution better than 0.1 eV and in special cases, better than 0.01 eV.[1] Experimentally, the recent advance of modulation spectroscopy has enabled us to obtain spectra with a resolution much better than 0.01 eV.[2]

It is well known that with the same instrument resolution, although theoretically the conventional spectroscopy should have the same resolution as the derivative or modulation spectroscopy in the zero noise limit, the latter always appears to have better resolution (or better detectability) in practice.[3] This fact has been fully recognized in NMR and EPR work,[4] where derivative spectra are usually recorded. Optical modulation spectroscopy of solids, however, did not receive much attention until very recently. Following the electroreflectance work of Seraphin,[5] various modulation techniques have been proposed.[2] The most common ones involve modulations by electric field, stress, temperature, light intensity, light polarization, and optical wavelenth.[2] All of them have succeeded in achieving better resolved spectra of solids. We would like to present here a brief review only on wavelength-modulation spectroscopy (WMS).

The WM technique differs from the other modulation techniques in

the following respect. With the other techniques, the sample must be under the influence of external perturbation. Therefore, the modulated spectrum depends critically on how the optical properties of the sample respond to the perturbation. The fact that such knowledge is often not available makes the analysis of the modulated spectrum rather difficult. If, however, the optical spectrum of the sample in the absence of perturbation is well understood, then the modulated spectrum can yield some information on the properties of the sample. In the WM scheme, the sample does not have to be perturbed. One simply obtains a plain derivative spectrum of the sample. With an external perturbation on the sample, we can then use the scheme to obtain additional information about the sample. Application of WMS is certainly not restricted only to solids. It is clearly more useful than the other modulation schemes in cases where application of external perturbation on a sample is difficult.

However, unlike the other modulation schemes, WMS has the inherent difficulty of eliminating a huge background in the output. This background is actually the derivative spectrum of the various dispersive optical components in the light path, and is often two to three orders of magnitude larger than the sample spectrum. The problem is most serious in the UV region where lamps with unavoidable narrow spectral lines are used as light sources. In order to eliminate such a huge background careful construction of the system with proper feedback loops is necessary. For this reason, WMS has not been as popular as the other modu-

lation schemes. Most of the WMS work has been limited to a narrow spectral range.

The history of WMS is a fairly long one. French and his coworkers[6] designed and built the first WM spectrometer and used it for absorption measurements on biological materials. Subsequently, several other derivative spectrometers came into being,[3,7] and various ways of achieving wavelength modulation were proposed.[6,8] The early applications of optical derivative spectroscopy were concentrated on the absorption measurements on chemical substances. Basler[9] was probably the first one to apply WMS to solids. He used the WM scheme in the absorption measurements to study the effect of uniaxial stress on the indirect gap of Si and Ge. Later on, several WM spectrometers were built for reflection measurements on solids.[10-12] More recently, the WM scheme has also been used in Raman spectroscopy.[13]

While most existing WM spectrometers are limited to a narrow spectral range due to background trouble, it is, however, possible to eliminate the trouble completely by a careful design.[11] In the following section, we give a brief description on how such a WM spectrometer should be constructed. We also comment on the design of some existing WM spectrometers. We then discuss in Sec. III the connection between the empirical pseudopotential calculations of band structures and derivative spectra of solids. In Sec. IV, we give a few examples of the applications of WMS on crystals, and in Sec. V, we show how the WM spectrometers can be modified to extend their application range.

II. CONSTRUCTION OF A WAVELENGTH-MODULATION SPECTROMETER

Consider a light beam with a spectral density $I(\lambda)$ passing through a monochromator. The slit function of the monochromator is $g(\lambda - \lambda_o)$ with $g(o) \equiv 1$ and $\int_{-\infty}^{\infty} g(\lambda)\, d\lambda \equiv W$. Then, when the beam falls on a photodetector with a spectral response $G(\lambda)$, the signal output at the photodetector is

$$S(\lambda) = \int_{-\infty}^{\infty} g(\lambda' - \lambda)\, T(\lambda')\, d\lambda' \qquad (1)$$

where $T(\lambda) \equiv I(\lambda)\, G(\lambda)$. If the wavelength of the beam is being modulated with $\lambda = \lambda_o + A \cos\omega t$, then $S(\lambda)$ can be expanded into a series of harmonics. For sufficiently small A and W, we can neglect the higher-order terms, and $S(\lambda)$ becomes

$$S(\lambda) = S^{DC}(\lambda_o) + S^{AC}(\lambda_o) \cos \omega t$$

where $S^{DC}(\lambda) = WT(\lambda)$ (2)

$$S^{AC}(\lambda) = WA(dT/d\lambda)\,.$$

Suppose there is a sample in the beam with a reflection or transmission spectrum $R(\lambda)$. We then have $T(\lambda) = R(\lambda)\, T_o(\lambda)$, where $T_o(\lambda)$ is the product of the spectra of all the optical components in the light path except the slits of the monochromator. Since we are only interested in $R(\lambda)$ and its derivative $dR/d\lambda$, it is important that we get rid of the effects of $T_o(\lambda)$ in the final output. In the presence of some highly dispersive optical components, such as the ore lamp, the background due to $T_o(\lambda)$ can be two to four orders of magnitude larger than the small structure in the derivative spectrum of the sample. To eliminate such a huge background is therefore not a trivial matter.

The most effective way to eliminate the background is to use a two-beam method. Let the beam be split into two which then go through equivalent paths, with the sample in only one of the paths. According to Eq. (2), the two beams lead to the following four outputs:

$$\begin{aligned} S_A^{DC}(\lambda) &= WT_o(\lambda) \\ S_A^{AC}(\lambda) &= WA(dT_o/d\lambda) \\ S_B^{DC}(\lambda) &= WR(\lambda)T_o(\lambda) \\ S_B^{AC}(\lambda) &= WA(dRT_o/d\lambda). \end{aligned} \tag{3}$$

Through feedback control, we can keep S_A^{DC} and S_B^{DC} constant, and then the difference signal $S_B^{AC} - S_A^{AC}$ becomes proportional to the logarithmic derivative $dR/Rd\lambda$.[10,12] However, this scheme has an obvious bad feature. With a large background, both S_A^{AC} and S_B^{AC} are much larger than the signal we want to detect. Since electronic subtraction may not be perfect, it is difficult to achieve a cancellation of the background to the level of a weak signal.

A much better scheme is to keep either S_A^{DC} or S_B^{DC} constant and either S_A^{AC} or S_B^{AC} null.[11] For example, suppose we let $S_A^{DC} = C$ (constant) and $S_B^{AC} = 0$. Then, from Eq. (3), we find immediately that $S_B^{DC} = CR$ and $S_A^{AC} = AC(dR/Rd\lambda)$. Note that here we can obtain simultaneously both R and $dR/Rd\lambda$. This is of course another big advantage of the present scheme. With the other combinations, we can also measure simultaneously R and $dR/d\lambda$, or 1/R and $dR/Rd\lambda$, or 1/R and $dR/R^2d\lambda$.

To keep S_A^{DC} (or S_B^{DC}) = C, the usual method is to use $S_A^{DC} - C$

(or S_B^{DC} - C) as an error signal to feedback control the gain of the photodetector. In order to make S_A^{AC} (or S_B^{AC}) vanish, we must modify the spectral profile of the light beam. As suggested by French,[6] this can be accomplished by a saw-tooth diaphragm cutting into the beam inside the monochromator; the diaphragm is being driven by S_A^{AC} (or S_B^{AC}) which acts as the error signal in this feedback loop.

The block diagram of such a WM spectrometer is shown in Fig. 1. The entrance slit of the monochrometer is here replaced by the slit E. The wavelength modulation is accomplished by the vibrating mirror M after E. The beam is split into two by the chopper C. In order to have the spectral range extended into the uv Al-coated mirrors are used to direct the beams. For more details on the construction of this spectrometer, the readers should consult Ref. 11. In Fig. 2, we use the reflection spectrum of GaAs as an example to show how well this spectrometer functions. Figure 2a gives the derivative spectrum $dR/d\lambda$. The arrows indicate the small structures which are residues of the strong spectral lines in the Xe-arc lamp. They have now been reduced to within the tolerable limit. Figures 2b and 2c show respectively the reflectivity spectrum $R(\lambda)$ obtained directly from measurement and $R(\lambda)$ obtained by numerical integration of Fig. 2a. The two curves agree very well as they should. Figure 2 also shows that while the weak structures in $R(\lambda)$ are not so obvious, they become clearly visible in the derivative spectrum $dR/d\lambda$.

This spectrometer has an operating spectral range from 8000 Å

to 2000 Å, but can easily be extended further into the uv and into the infrared. It has a sensitivity of $dR/Rd\lambda \simeq 10^{-5}/\text{Å}$, and a resolution limited by the modulation amplitude and the slit width. One often likes to have the spectrum on an energy scale, but the conversion of $dR/Rd\lambda$ to $dR/Rd\omega$ is straightforward.

There are two important points to be observed in the construction of any two-beam WM spectrometer. First, it is clear from Eq. (3) that the two beams in the system should go through equivalent paths. In particular, the two beams should fall on the same spot on the same photodetector since the response of the photocathode may vary across the surface. Otherwise, the background cancellation would not be perfect, as has happened with some WM spectrometers.[3,10] Second, the positions of the light spot on the sample and on the photodetector should remain stationary to avoid error induced by the motion of the light spot as a result of possible varying spectral response across an optical surface. This has also been the source of trouble in some WM spectrometers.[6,8]

III. THEORETICAL CONSIDERATION OF A DERIVATIVE SPECTRUM

It should be emphasized that a conventional spectrum $R(\lambda)$ should contain as much information as the corresponding derivative spectrum. In fact, numerical differentiation of $R(\lambda)$ with sophisticated iteration procedure can yield a derivative spectrum as good as the one obtained from a WM spectrometer.[14] Therefore, the derivative spectrum only has

the practical advantage of being able to improve the detectability of a spectrum. This is particularly true in the case of overlapping bands or small structure superimposed on big peaks.

Then, the better resolved spectrum is only meaningful if it can be interpreted or if it can yield useful information. In the early days, this was true for solids only in special cases.[9] The theoretical calculations on band structure can only be accurate to about 0.5 eV. More recently, high-speed computers and better calculation methods have greatly improved the accuracy. Weak structures in the spectrum are now theoretically identifiable. Consequently, derivative spectroscopy of solids becomes more meaningful.

Among the various methods of band-structure calculations, the empirical pseudopotential method (EPM)[1] seems to be most successful. The derivative spectrum obtained from the EPM agrees surprisingly well with the experimental derivative spectrum in many cases.[15-19] The EPM is based on the principle that for calculation of band structure, the periodic potential for electrons in a crystal can be replaced by a more slowly varying pseudopotential $V^P = \sum_{\ell,\alpha} V^P_\alpha (\vec{r} - \vec{R}_{\ell,\alpha})$ where $\vec{R}_{\ell,\alpha}$ denotes the position of the αth element in the ℓth unit cell of the crystal.[1] The pseudopotential V^P_α is mainly determined by the atomic properties of the αth element, with only small variation from solid to solid due to small changes in the Hartree-Fock interaction. The usual calculation procedure of the EPM is as follows:[1]

(1) Take the atomic pseudopotential V^P_α for each element determined

either from the atomic spectrum or from the band structure of a crystal which contains such an element.

(2) From the lattice structure of the crystal of interest, find the structure factors $S_\alpha(\vec{G}) = (1/N) \sum_\ell \exp(-i\vec{G}\cdot\vec{R}_{\ell,\alpha})$ and the form factors $V_\alpha^P(\vec{G}) = (1/\Omega) \int_\Omega V_\alpha^P(\vec{r}) \exp(-i\vec{G}\cdot\vec{r})\, d^3r$, where Ω is the volume of a unit cell.

(3) Compute the electronic band structure by diagonalizing the Hamiltonian with the pseudopotential $V^P(\vec{r})$. The nonvanishing matrix elements of $V^P(\vec{r})$ can be written as

$$V(\vec{G}) = \langle \vec{q} + \vec{G} \,|V^P(\vec{r})|\, \vec{q}\rangle = \sum_\alpha S_\alpha(\vec{G})\, V_\alpha^P(\vec{G}) . \qquad (4)$$

(4) Use the band structure and the corresponding pseudo-wavefunctions to calculate the complex dielectric constant $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$.

(5) From $\varepsilon(\omega)$, compute the reflectivity spectrum $R(\omega)$ and the derivative reflectivity $dR/Rd\omega$. Compare them with the experimental spectra. Then, make fine adjustments in the atomic pseudopotentials or $V_\alpha^P(\vec{G})$, and repeat the calculations to get better agreement.

What we learn about the crystal from such a calculation are: (1) an accurate band structure; (2) proper identification of the structure in the spectrum with certain optical transitions; and (3) the atomic pseudopotentials for the elements contained in the crystal. The pseudopotentials finally obtained from the calculation can of course be used as the starting pseudopotentials in the band structure calculations for new compounds containing these elements. They can also be used to calculate other physical properties of solids.[1] Clearly,

the derivative spectrum offers a much more stringent test on the theoretical calculation than the reflectivity; the calculation must reproduce not only the positions but also the shapes of the structure in $R(\omega)$.

It is sometimes physically more meaningful to consider the dielectric functions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ rather than $R(\omega)$, or $d\varepsilon_1/d\omega$ and $d\varepsilon_2/d\omega$ rather than $dR/Rd\omega$. As is well known, the dielectric functions can be obtained from the reflectivity spectrum through the relation of R and ε and the use of Kramers-Kronig transform.

In the derivative spectra of solids, the three-dimensional critical points should also appear with characteristic lineshape. Under the assumptions of a constant transition matrix element and a parabolic density of states, $d\varepsilon_1/d\omega$ and $d\varepsilon_2/d\omega$ around a critical point should have the functional forms listed in Table I,[20] where η is a damping factor, and $F(W = (\omega - \omega_o/\eta) = [(W^2 + 1)^{1/2} + W]^{1/2} [W^2 + 1]^{-1/2}$, as shown in Fig. 3. It has been a common practice to use the observed lineshapes to assist identification of structure in the spectra of solids.

IV. EXAMPLES OF WAVELENGTH-MODULATION SPECTROSCOPY

We shall now give a few examples of what has been done on WMS of solids. Let us consider first the WM work on GaAs. In Fig. 4 we reproduce the experimental spectra of $R(\omega)$ and $dR/Rd\omega$ of GaAs at 5°K obtained from a WM spectrometer and compare them with the theoretical spectra.[16] In this case, the form factor in Eq. (4) can be written as:

$$V(G) = V_S(G) \cos \vec{G} \cdot \vec{\tau} + V_A(G) \sin \vec{G} \cdot \vec{\tau}$$

$$V_S(G) = [V^P_{Ga}(G) + V^P_{AS}(G)]/2$$

$$V_A(G) = [V^P_{Ga}(G) - V^P_{As}(G)]/2$$

where $\vec{\tau} = (1.1.1)a/8$ and a is the lattice constant. Walter and Cohen[21] did their first empirical pseudopotential (PM) calculation on GaAs to fit only the reflectivity spectrum $R(\omega)$. They used the following values for the form factors: $V_S(G^2 = 3) = -0.245$, $V_S(8) = -0.005$, $V_S(11) = 0.075$, $V_A(3) = 0.062$, $V_A(4) = 0.035$, $V_A(11) = 0.003$ and $V_{S,A}(G^2 > 11) = 0$, all in Rydberg. Spin-orbit coupling was neglected in the calculation. The calculated $R(\omega)$, shown in Fig. 4a, seems to agree well with the experimental $R(\omega)$. However, in order to have the theoretical $dR/Rd\omega$ compare well with the experimental one, they had to make further adjustment on the form factors.[16] The $dR/Rd\omega$ spectrum calculated with $V_S(G^2 = 3) = -0.2460$, $V_S(8) = -0.0008$, $V_S(11) = 0.0737$, $V_A(3) = 0.0583$, $V_A(4) = 0.0509$, and $V_A(11) = 0.0011$ Ry, and with spin-orbit coupling included, is given in Fig. 4b.[15] It appears to have surprisingly good agreement with the experimental $dR/Rd\omega$. The peaks at 3.02 and 3.24 eV are much sharper in the experimental spectrum, but this is due to exciton effects[22] which have not been included in the calculation. At higher energies, the agreement between theory and experiment is worse. Such a discrepancy seems to be common in all the cases which have been investigated. The reason is yet unknown.

The good agreement between the theoretical and the experimental spectra suggests that the band structure of GaAs (Fig. 5) obtained from

the calculation is indeed valid to a good accuracy.[15] Furthermore, from the calculation, we can readily identify the structure in the spectrum with the various critical point transitions, as shown in Table II.[16] (Sometimes in other crystals, the structure can be due to transitions over a large volume in the Brillouin zone.[1])

It is interesting to compare the WM spectrum with the spectra obtained by other modulation techniques. In Fig. 6a, 6b, and 6c, we reproduce, respectively, the wavelength - modulation, the thermoreflectance,[23] and the electroreflectance spectra[24] of InAs. The WM spectrum is clearly better resolved than the thermoreflectance spectrum, especially in the high-energy region. The electroreflectance spectrum has structure as sharp as or sharper than the WM spectrum. Recently, Aspnes[25] has further improved the electroreflectance technique by his low-field, high-resolution method. However, in general, the electroreflectance spectrum over a wide range is still difficult to interpret. So far, no one has computed a theoretical electroreflectance spectrum in the band structure calculation.

Most of the WM work on solids has been done on semiconductors.[9,15-18,22,26-28] A few more examples are given as separate papers in this proceeding.[29] The only WM work on metals is on Cu, Ag, and Au.[19, 30]. In Fig. 7 we show the good agreement between the experimental WM spectrum of Cu and the theoretical derivative spectrum obtained by EPM. In the calculations, four local and four non-local pseudopotential form factors were used. In addition, the pseudo-wavefunctions were modified to include the core-state contribution so that

they were orthogonal to the core states. Without this core contribution the negative portion between 2.2 and 4.2 eV in the derivative spectrum cannot be explained. We notice in Fig. 7 that the theoretical spectrum actually reproduces even the very weak structure in the experimental spectrum. These structures would of course be difficult to detect in the ordinary reflectivity spectrum.

Besides being able to resolve fine structure in a spectrum, WMS can also improve the accuracy of detecting changes in a spectrum. In fact, the first WM work on solids by Baslev[9] was to measure the change of the indirect gap of Si induced by a uniaxial stress. This type of measurement is often localized to a narrow spectral region, and hence the background trouble one may encounter in WMS (see Sec. II) is much less serious here. Figure 8 gives an example of such a measurement.[15] It shows how the E_1 (due to $\Lambda(3-4)$ and $\Lambda(3-5)$ transitions) and the E_2 (due to $\Sigma(4-5)$ transitions) peaks of GaAs vary with temperature. The advantages of the derivative spectroscopy are clearly demonstrated here. The shifts of the peaks with temperature can be measured very accurately by the shifts of the zeroes in the spectrum. Sharpening of the peaks with lowering temperature is now very obvious. The EP calculation incorporating the thermal effects suggests that the temperature shifts of the peaks are mainly due to the Debye-Waller effect, with only a small fraction caused by thermal expansion.[15] Sharpening of the E_1 peaks at lower temperatures is, however, mainly due to exciton contribution.[22]

WMS has been used in several cases in conjunction with a uniaxial stress on a sample.[9,22,27] The results not only help one identify the peaks with critical point transitions through symmetry argument, but also yield numerical values for the deformation potentials around the critical points. WMS can, of course, also be used to study the effects of other external perturbations, but work has not yet been reported. It is also possible to use WMS to probe spectral changes induced by impurities, by alloying,[26] and by phase transitions.[28] Little work has been done in all these cases.

V. DISCUSSION

In some cases (for example, in deducing deformation potentials from measurements with uniaxial stress) we would like to know accurately the net spectral change induced by the external perturbation. Then, in the derivative spectrum $dR(x)/R(x)d\lambda$ where x is the parameter corresponding to the external perturbation, the unperturbed spectrum $dR(o)/R(o)d\lambda$ actually plays the role of a background. In order to measure the net change accurately, we must get rid of this background. This is particularly true when the net change is small.

A review of Sec. II will show that a two-beam WM spectrometer can in fact be used for such measurements. If we have two samples, one with and one without perturbation, in the two beams separately, then Eq. (3) becomes

$$S_A^{DC} = W\ T_o R(0)$$
$$S_B^{DC} = W\ T_o R(x)$$
$$S_A^{AC} = W\ A\ [dT_o R(0)/d\lambda] \qquad (5)$$
$$S_B^{AC} = W\ A\ [dT_o R(x)/d\lambda]\ .$$

Either of the two schemes described in Section II can be used to obtain the difference signal $dR(x)/R(x)d\lambda - dR(0)/R(0)d\lambda$. Here, we shall consider only the one which does not require electronic subtraction. Let $S_A^{DC} = C$ (constant and $S_B^{AC} = 0$. We then have

$$S_B^{DC} = CR(x)/R(0) = \text{constant} + C[R(x) - R(0)]/R(0)$$
$$S_A^{AC} = CA[dR(x)/R(x)d\lambda - dR(0)/R(0)d\lambda]. \qquad (6)$$

The two output signals give us simultaneously the net changes of the reflectivity and its logarithmic derivative induced by the external perturbation. We recognize that $[R(x) - R(0)]/R(0)$ is just the spectrum one would obtain by using x as the modulated parameter. Our method should have a sensitivity at least as good as the other modulation techniques.

In fact, we can even greatly simplify the construction of the WM spectrometer. Instead of having two beams, we can now use only one beam, but switch the perturbation on and off alternatively. The electronic part of the system remains unchanged. The results are expected to be better than one can obtain from a two-beam system, since the trouble of matching the two beams is now completely eliminated.

So far, no wide-range WM spectrometer operating the infrared (> 8000 Å) or in the uv (< 2000 Å) has been reported. It is relatively simple to extend the operating range further into the infrared. The signal-to-noise ratio will be worse since the infrared photodetector is less sensitive, but it would not be intolerable in many circumstances. Extension to the far uv is more difficult because of the lack of light source with continuous spectrum. However, we expect no difficulty to extend the uv operating limit to about 1400 Å. Work along this line is presently in progress.

ACKNOWLEDGEMENTS

I would like to thank R. R. L. Zucca, Y. Petroff, S. Kohn, and J. Stokes for discussions on the experiment part, and M. L. Cohen and C.Y. Fong for discussions on the theoretical part. I would also like to express my gratitude to the Vincent-Hayes Foundation for a senior research fellowship at Harvard University.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

References

† Guggenheim Fellow, on leave at Harvard University.

1. See, for example, M. L. Cohen and V. Heine, Solid State Physics 24, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, Inc., N.Y. 1970) p. 37.
2. See, for example, M. Cardona, "Modulation Spectroscopy" Solid State Physics, Supplement 11 (Academic Press, N.Y., 1969).
3. G. Bonfiglioli and P. Brovetto, Physics Letters 5, 248 (1963); Appl. Optics 3, 1417 (1964).
4. See, for example, G. E. Pake, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., N.Y., 1956), Vol. 2, p. 1.
5. B. O. Seraphin and R. B. Hess, Phys. Rev. Letters 14, 138 (1965); B. O. Seraphin and N. Bottka, Phys. Rev. 145, 628 (1966).
6. C. S. French and A. B. Church, Carnegie Inst. of Washington Year Book 54, 162 (1954); 56, 281 (1956); A. T. Giese and C. S. French, Appl. Spectroscopy 9, 78 (1955); C. S. French, Proc. Inst. Soc. Am. 8, 83 (1957).
7. A. Collier and C. Singleton, J. Appl. Chem. 6, 495 (1956); E. C. Olson and C. D. Alway, Anal. Chem. 32, 370 (1960).
8. K. G. McWilliam, J. Sci. Instr. 36, 51 (1959); A. Gilgore, P. J. Stoller, and A. Fowler, Rev. Sci. Instr. 38, 1535 (1967); G. Bonfiglioli, P. Brovetto, G. Busca, S. Levialdi, G. Palmieri, and E. Wanke, Appl. Optics 6, 447 (1967); A. Perregaux and G. Ascarelli, Appl. Optics 7, 2031 (1968).
9. I. Baslev, Sol. State Comm. 3, 213 (1965); Phys. Rev. 143, 636 (1966).

10. K. L. Shaklee and J. E. Rowe, Appl. Optics 9, 627 (1970); K. L. Shaklee, J. E. Rowe, and M. Cardona, Phys. Rev. 174, 828 (1968).

11. R. R. L. Zucca and Y. R. Shen, Phys. Rev. B1, 2668 (1970); R. R. L. Zucca, Ph.D. Thesis (University of California, Berkeley, 1971) (unpublished).

12. M. Welkowsky and R. Braunstein, Rev. Sci. Instr. 43, 399 (1972); D. M. Korn and R. Braunstein, Phys. Rev. B5, 4837 (1972).

13. Y. Yacoby, I. Wagner, J. Bodenheimer, and W. Low, Phys. Rev. Letters 27, 248 (1971).

14. D. D. Sell and E. O. Kane, Phys. Rev. B5, 419 (1972); S. E. Stokowski and D. D. Sell, Phys. Rev. B5, 1636 (1972).

15. J. P. Walter, R. R. L. Zucca, M. L. Cohen, and Y. R. Shen, Phys. Rev. Letters 24, 102 (1970).

16. R. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, Solid State Comm. 8, 627 (1970).

17. R. N. Cahn and M. L. Cohen, Phys. Rev. B1, 2569 (1970); C. Varea de Alvarez, J. P. Walter, M. L. Cohen, J. Stokes, and Y. R. Shen, Phys. Rev. B6, 1412 (1972).

18. K. Kohn, Y. Petroff, P. Y. Yu, and Y. R. Shen, "Proceedings of the Conference on Physics of IV-VI Compounds and Alloys", Philadelphia, Penn. (1972) (to be published).

19. C. Y. Fong, M. L. Cohen, R. R. L. Zucca, J. Stokes, and Y. R. Shen, Phys. Rev. Letters 25, 1486 (1970); J. Stokes, Y. R. Shen, Y. W. Tsang, M. L. Cohen, and C.Y. Fong, Phys. Letters 38A, 347 (1972).

20. B. Batz, Ph.D. Thesis, Univ. Libre de Bruxelles (1967).

21. J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969).

22. K. L. Shaklee, J. E. Rowe, and M. Cardona, Phys. Rev. 174, 828 (1968); J. E. Rowe, F. H. Pollak, and M. Cardona, Phys. Rev. Letters 22, 933 (1969).

23. M. Matatagui, A. G. Thompson, and M. Cardona, Phys. Rev. 176, 950 (1968).

24. M. Cardona, K. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

25. D. E. Aspnes, Phys. Rev. Letters 28, 168 (1972); 28, 913 (1972).

26. D. M. Korn, M. Welkowsky, and R. Braunstein, Solid State Comm. 9, 2001 (1971); R. Braunstein and M. Welkowsky, Phys. Rev. B5, 497 (1972); D. M. Korn and R. Braunstein, Phys. Rev. B5, 4837 (1972).

27. F. H. Pollak and G. W. Rubloff, Phys. Rev. Letters 29, 789 (1972); J. Koo, Y. R. Shen, and R. R. L. Zucca, Solid State Comm. 9, 2229 (1971).

28. K. W. Blazey, Phys. Rev. Letters 27, 146 (1971); The spectral change with temperature reported in this paper has been shown to have no connection with phase transition by D. Redfield and W. J. Burke, Phys. Rev. Letters 28, 435 (1972).

29. Y. Petroff, S. Kohn, and Y. R. Shen, in this proceedings.

30. M. Welkowsky and R. Braunstein, Solid State Comm. 9, 2139 (1972).

Figure Captions

Fig. 1. Block diagram of the wavelength-modulation spectrometer in Ref. 11. E: external slit; M: vibrating mirror; D: saw-tooth diaphragm; C: beam chopper; S_1, S_2, S_3, S_3', S_4: spherical mirrors.

Fig. 2. Reflectivity spectra of GaAs at 5°K. (a) $dR/d\lambda$ vs λ; (b) R vs λ; (c) R vs λ obtained by numerical integration of $dR/d\lambda$ in (a).

Fig. 3. F(W) as a function of W (see the text) (reproduced from Ref. 20).

Fig. 4. A comparison of theoretical and experimental spectra for GaAs. (a) Reflectivity $R(\omega)$; (b) Derivative reflectivity $dR/Rd\omega$.

Fig. 5. Electronic band structure for GaAs along the principal symmetry directions.

Fig. 6. A comparison of the modulated reflectivity spectra of InAs obtained by different techniques. (a) Wavelength-modulated reflectivity spectrum at 80°K; (b) Thermoreflectance spectrum at 77°K (reproduced from Ref. 23); (c) Electroreflectance spectrum at room temperature (reproduced from Ref. 24).

Fig. 7. A comparison of the theoretical and experimental $dR/Rd\omega$ for Cu.

Fig. 8. Plots of $R'(\omega)/R(\omega)$ in the regions of the E_1 doublet peak and the E_2 major peak. Plots 1 through 5 refer to temperatures of 5, 80, 150, 225, and 300°K, respectively.

Table Captions

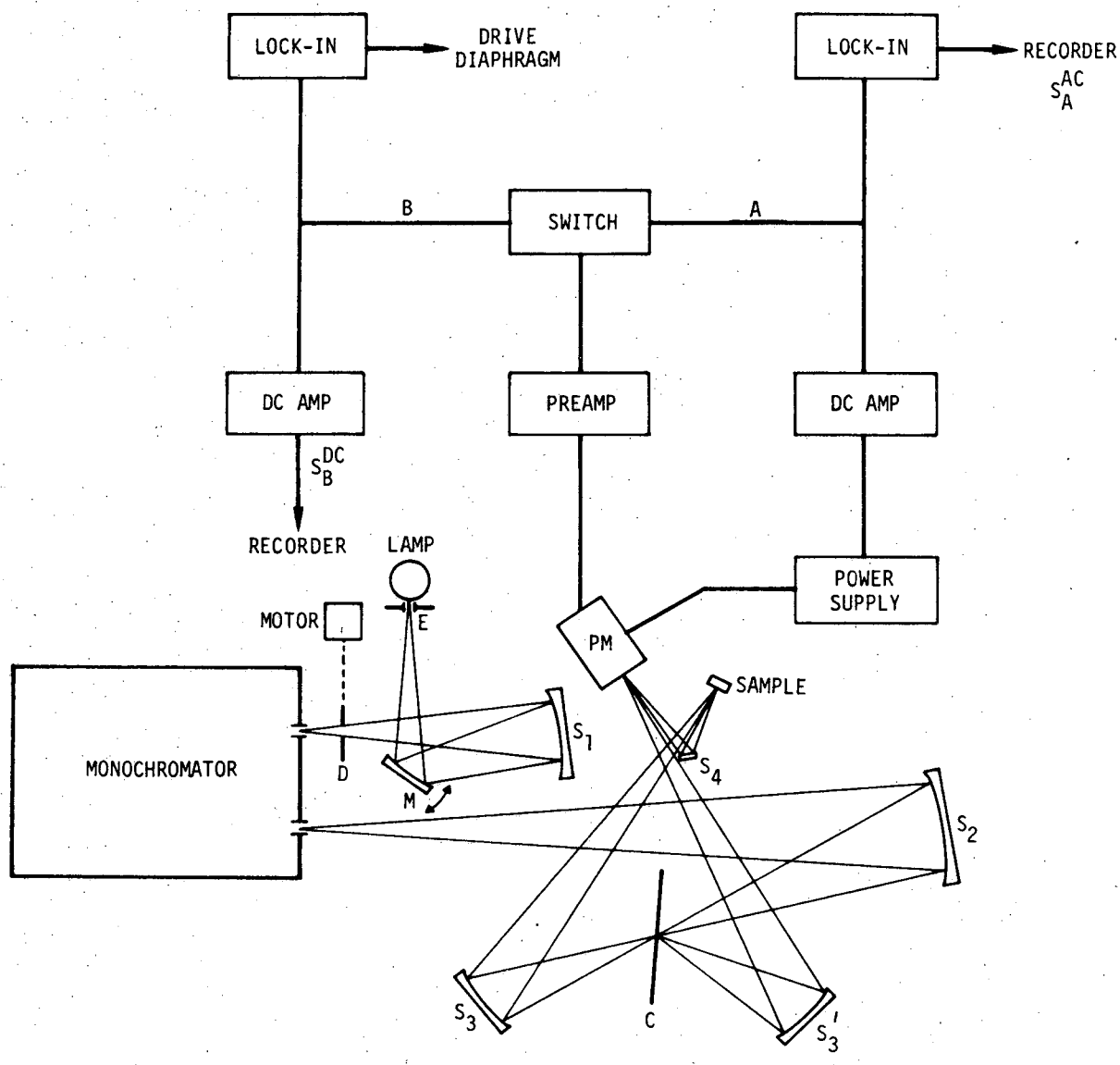
Table I. Derivatives $d\varepsilon_1/d\omega$ and $d\varepsilon_2/d\omega$ for the four types of three dimensional critical points (allowed transitions) in terms of the function F(W) of Fig. 4 (from Ref. 20).

Type of Critical Points	$2\eta^{1/2}d\varepsilon_1/d\omega$	$2\eta^{1/2}d\varepsilon_2/d\omega$
M_o	F(-W)	F(+W)
M_1	-F(+W)	F(-W)
M_2	-F(-W)	-F(+W)
M_3	F(+W)	-F(-W)

Table II. Theoretical and experimental reflectivity structure at 5°K and their identifications, including the location in the Brillouin zone, energy, and symmetry of the calculated critical points for GaAs.

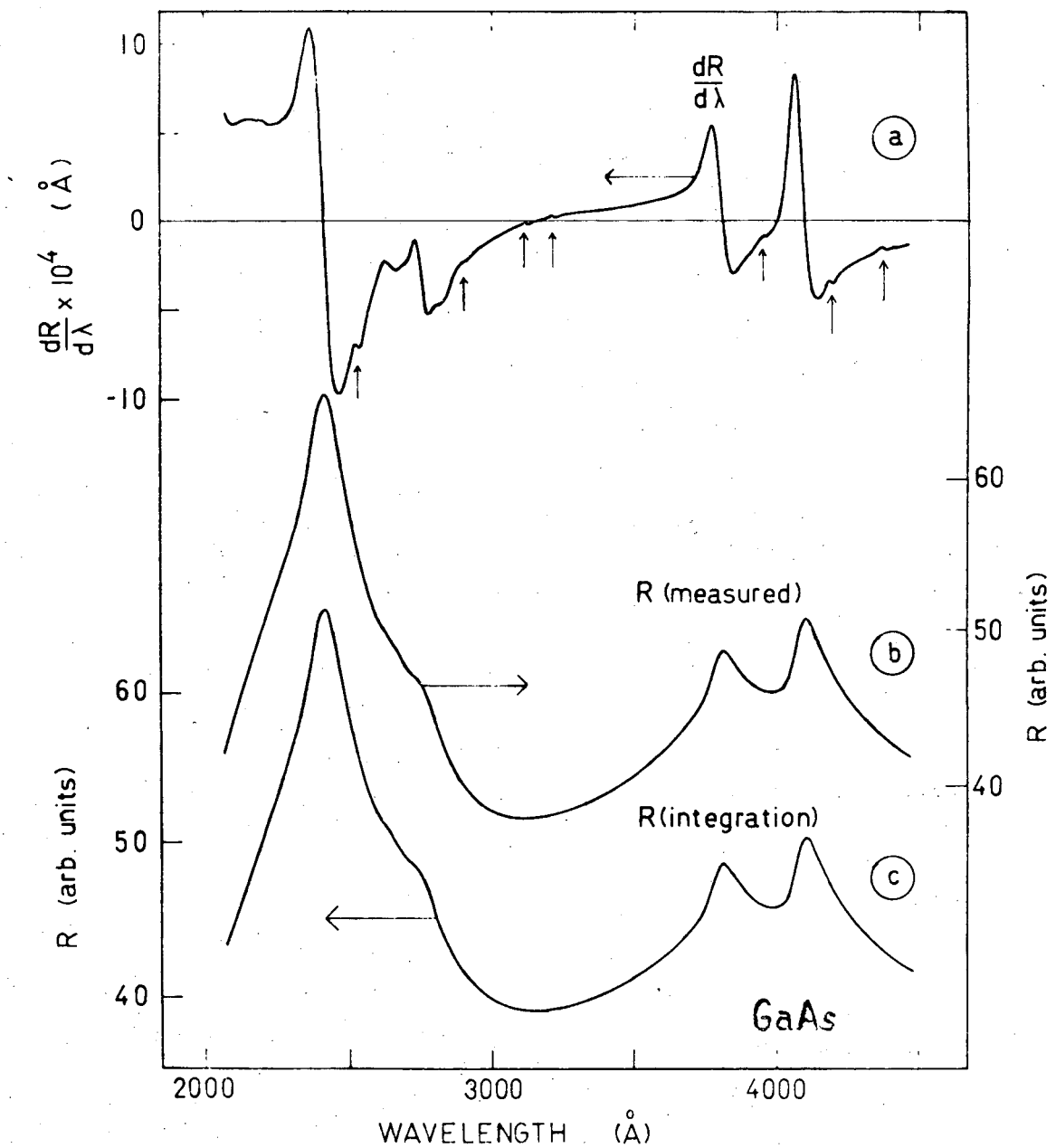
Reflectivity structure (eV)		Associated critical points		
Theory	Experiment	Location in zone	Symmetry	CP Energy (eV)
1.52	1.52*	$\Gamma_8-\Gamma_6$ (0., 0., 0)	M_0	1.52
2.90	---	L (4–5) (0.5, 0.5, 0.5)	M_0	2.82
3.05	3.02	Λ (4–5) (0.2, 0.2, 0.2)	M_1	3.02
3.25	3.24	Λ (3–5) (0.2, 0.2, 0.2)	M_1	3.25
4.35	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

* STURGE M.D., *Phys. Rev.* **127**, 768 (1962).



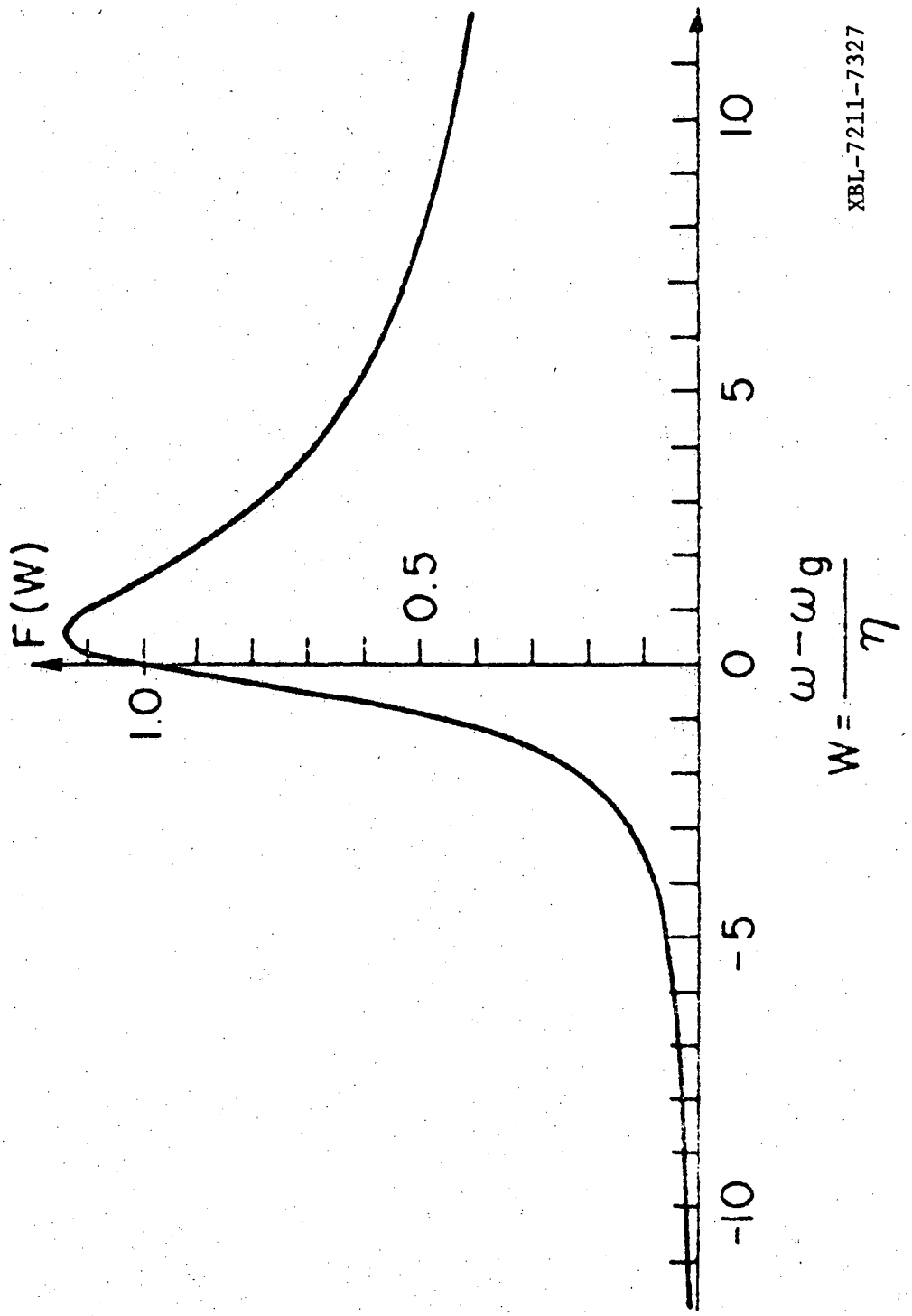
XBL-7211-7326

Fig. 1



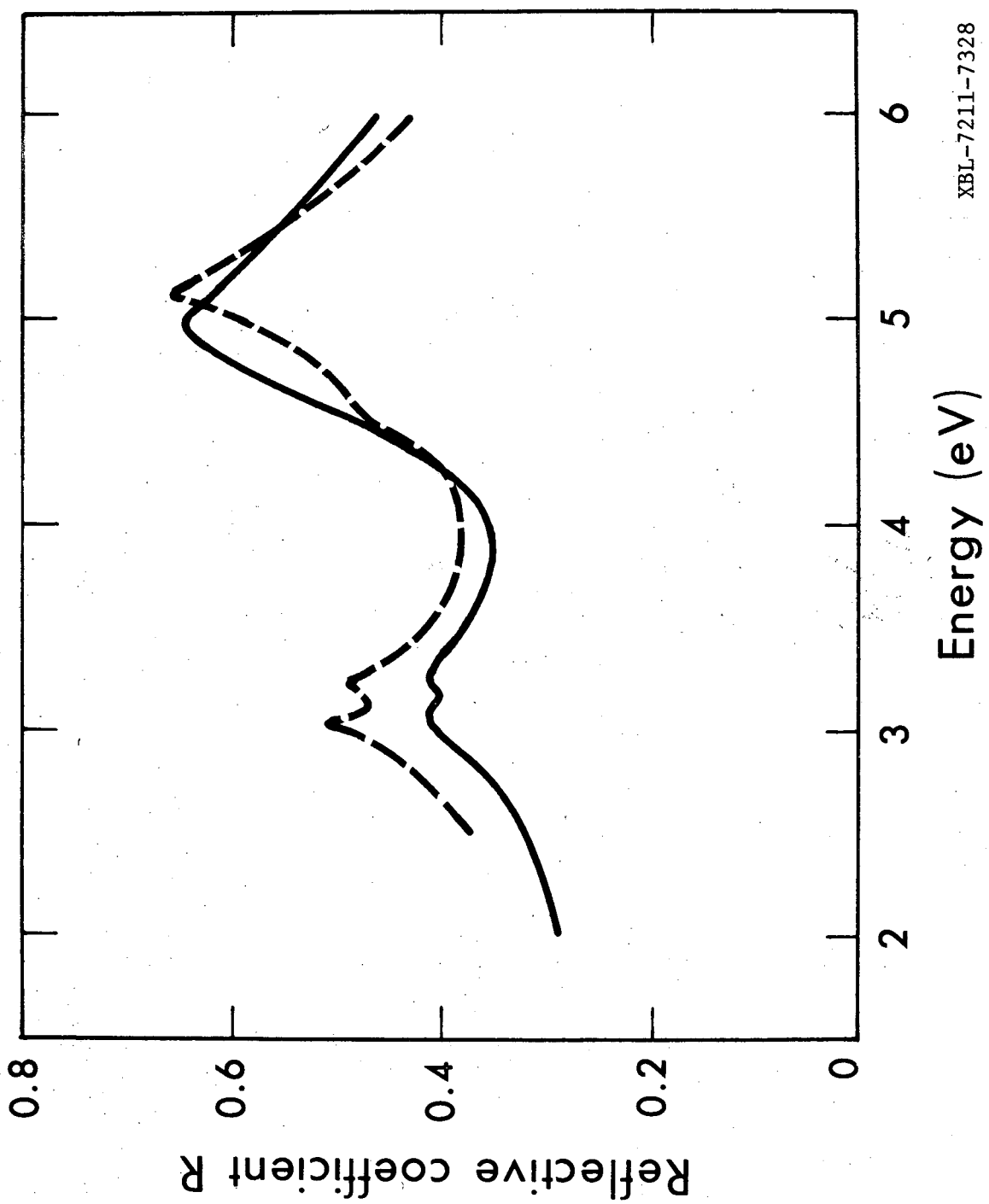
XBL 7011-6898

Fig. 2



XBL-7211-7327

Fig. 3



XBL-7211-7328

Fig. 4a

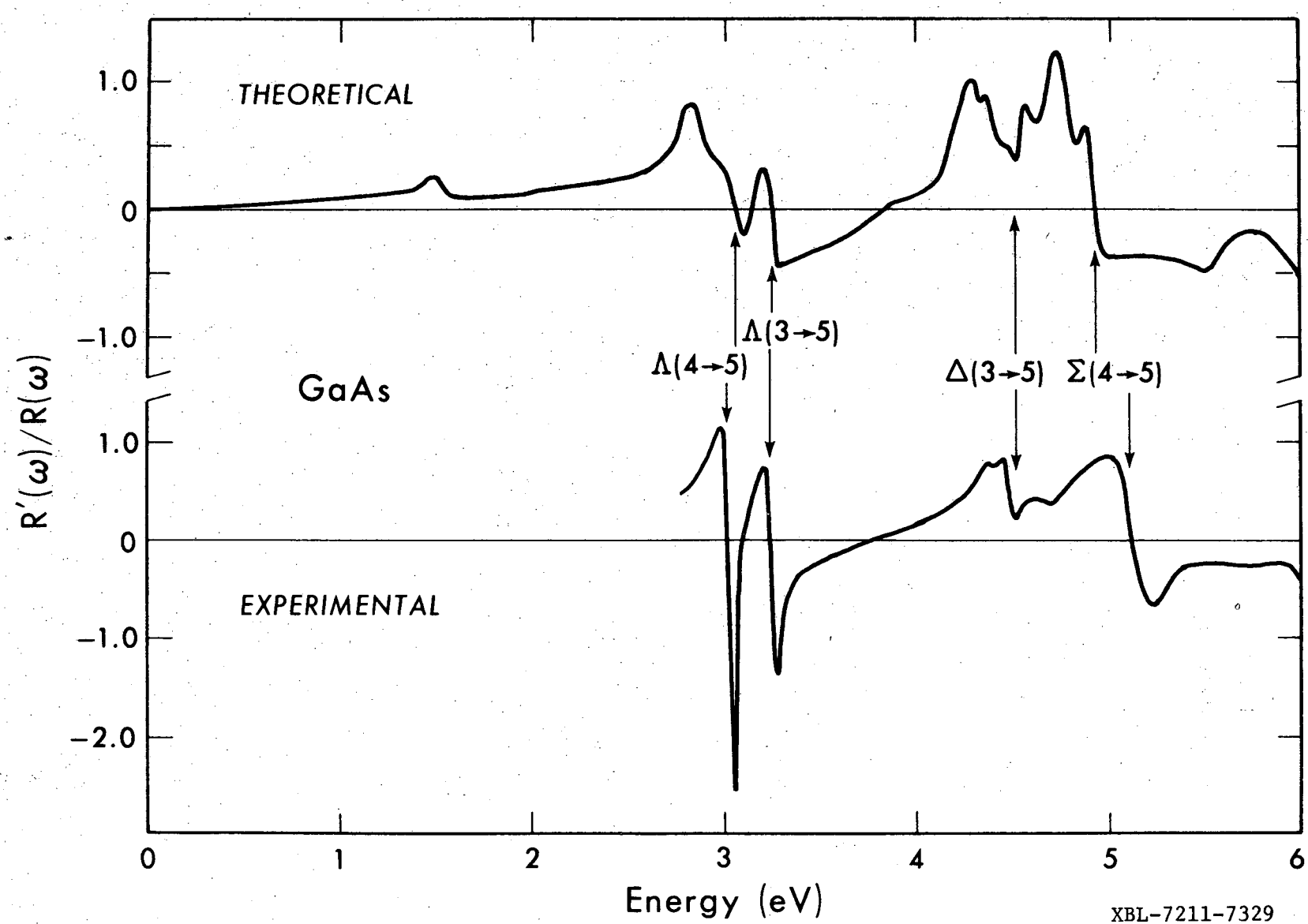
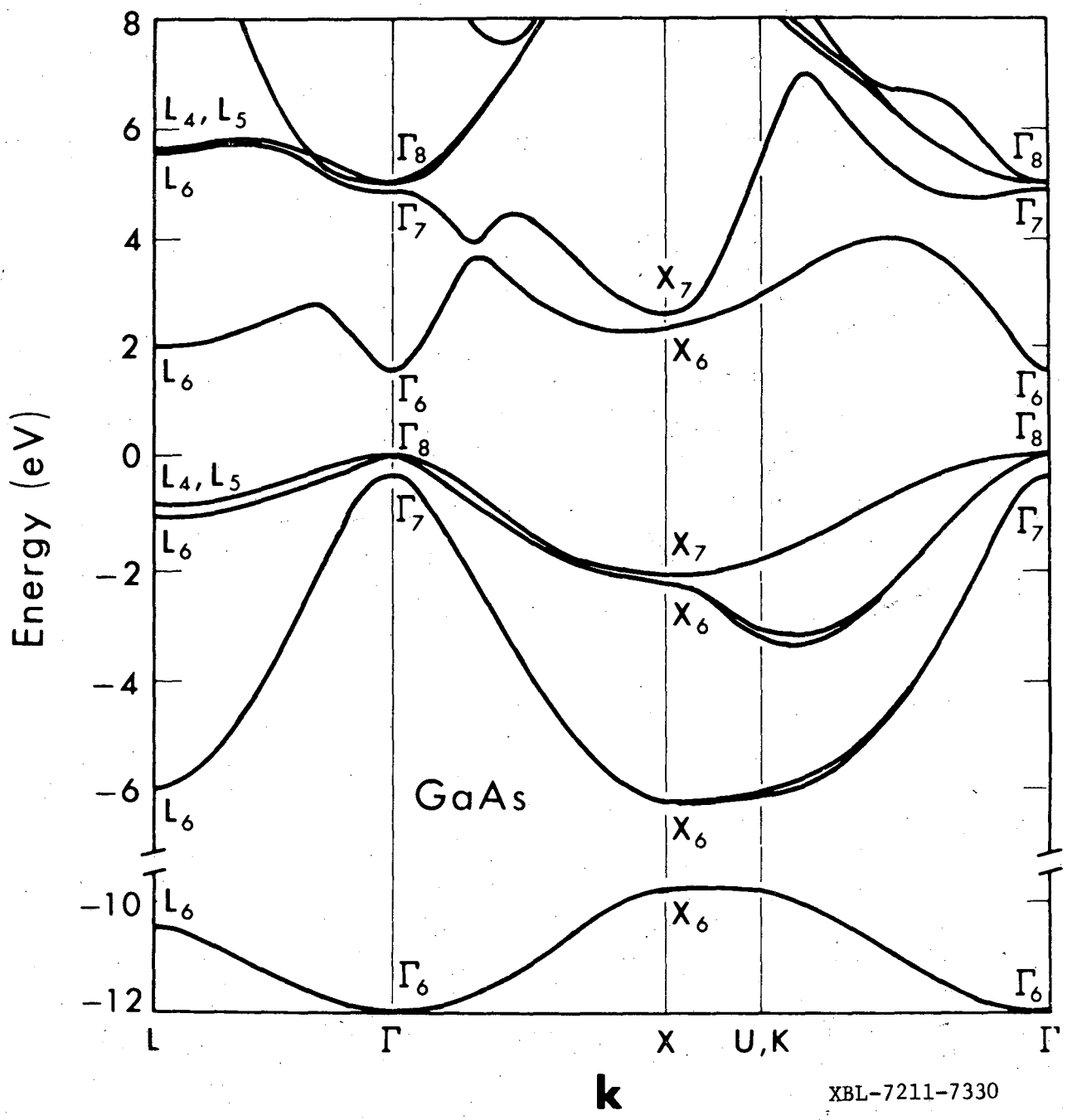
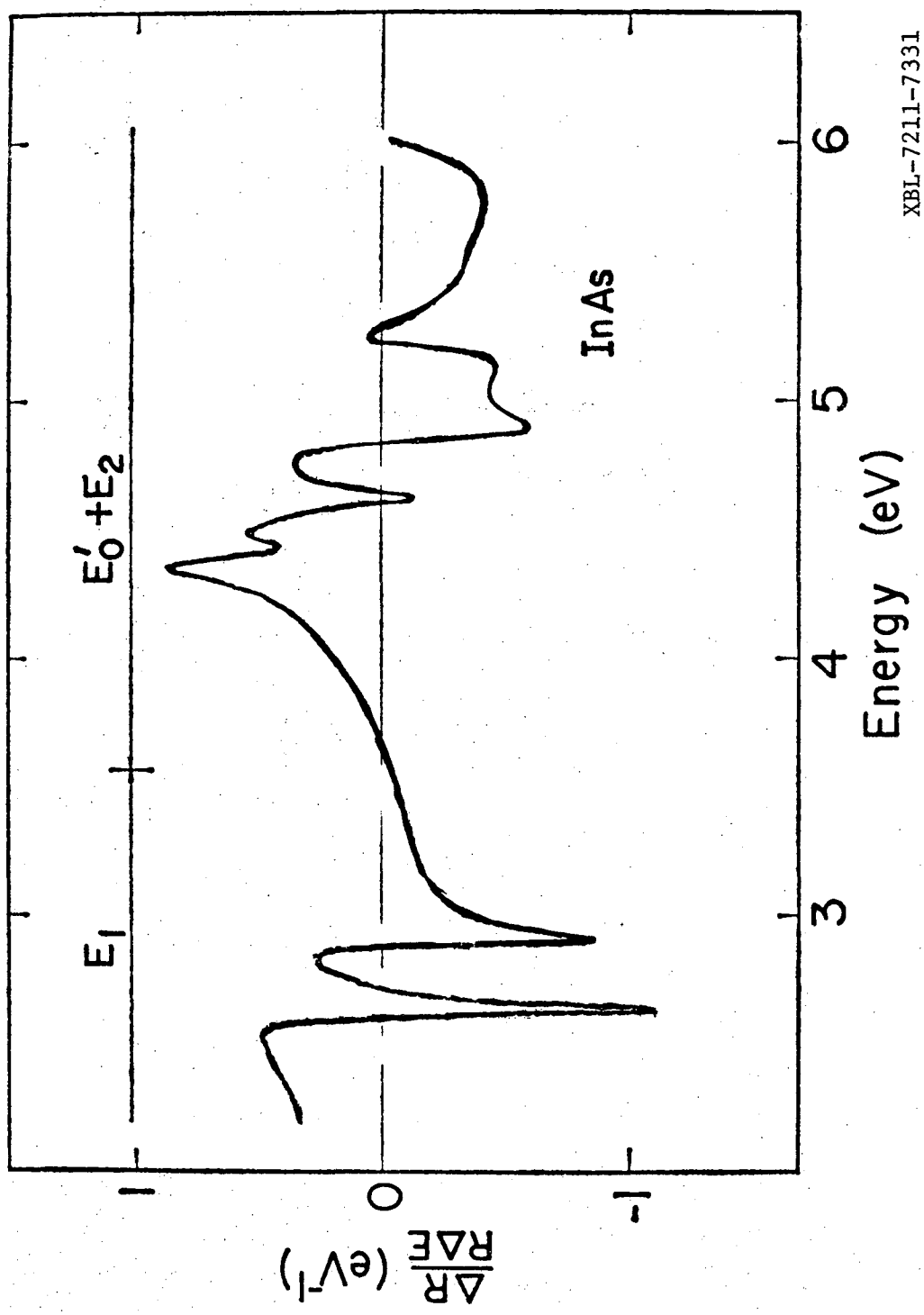

THEORETICAL
GaAs
EXPERIMENTAL
Λ(4→5)
Λ(3→5)
Δ(3→5)
Σ(4→5)
R′(ω)/R(ω)
1.0
0
−1.0
1.0
0
−1.0
−2.0
0
1
2
3
4
5
6
Energy (eV)
XBL-7211-7329

Fig. 4b



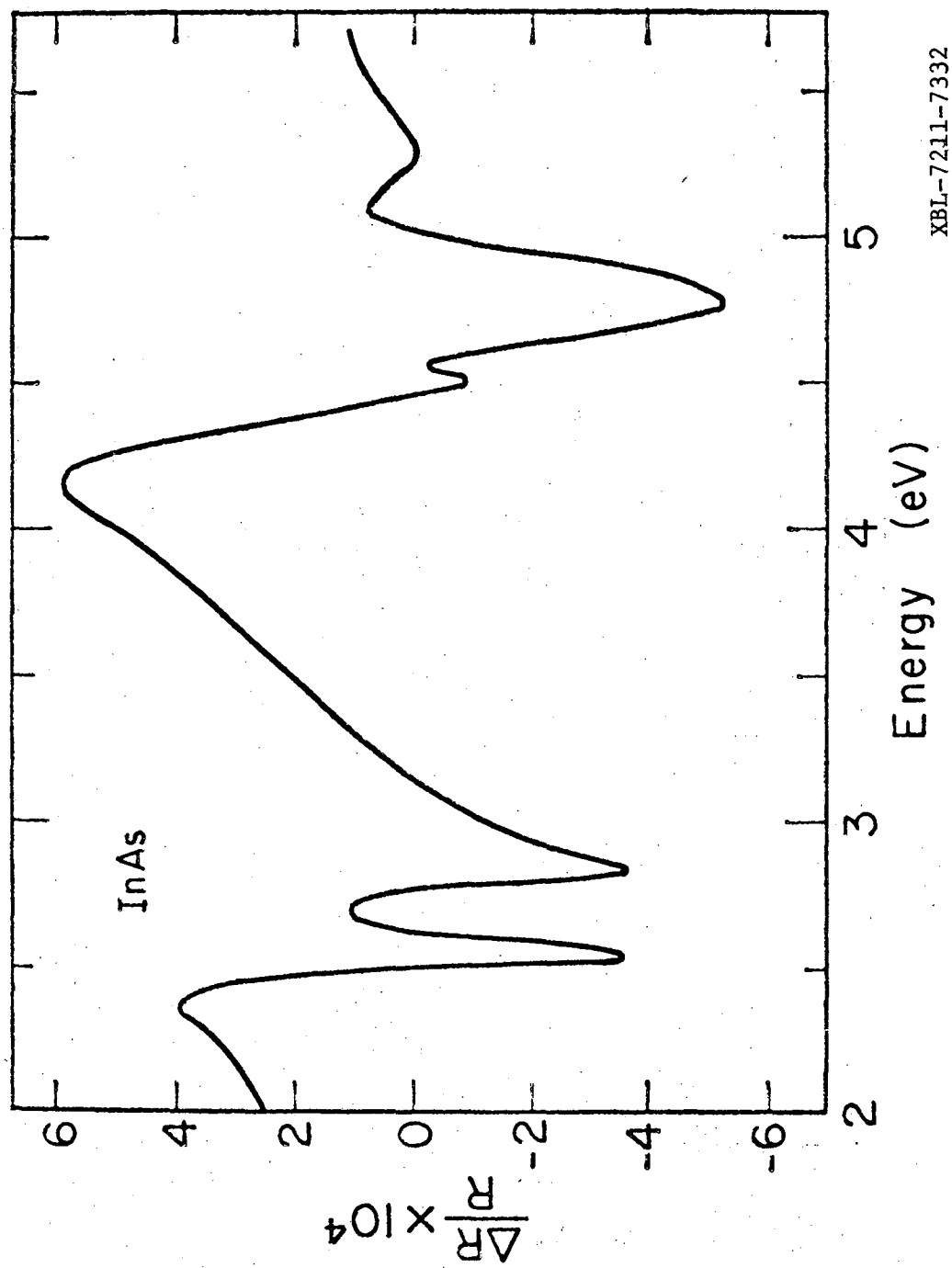
XBL-7211-7330

Fig. 5



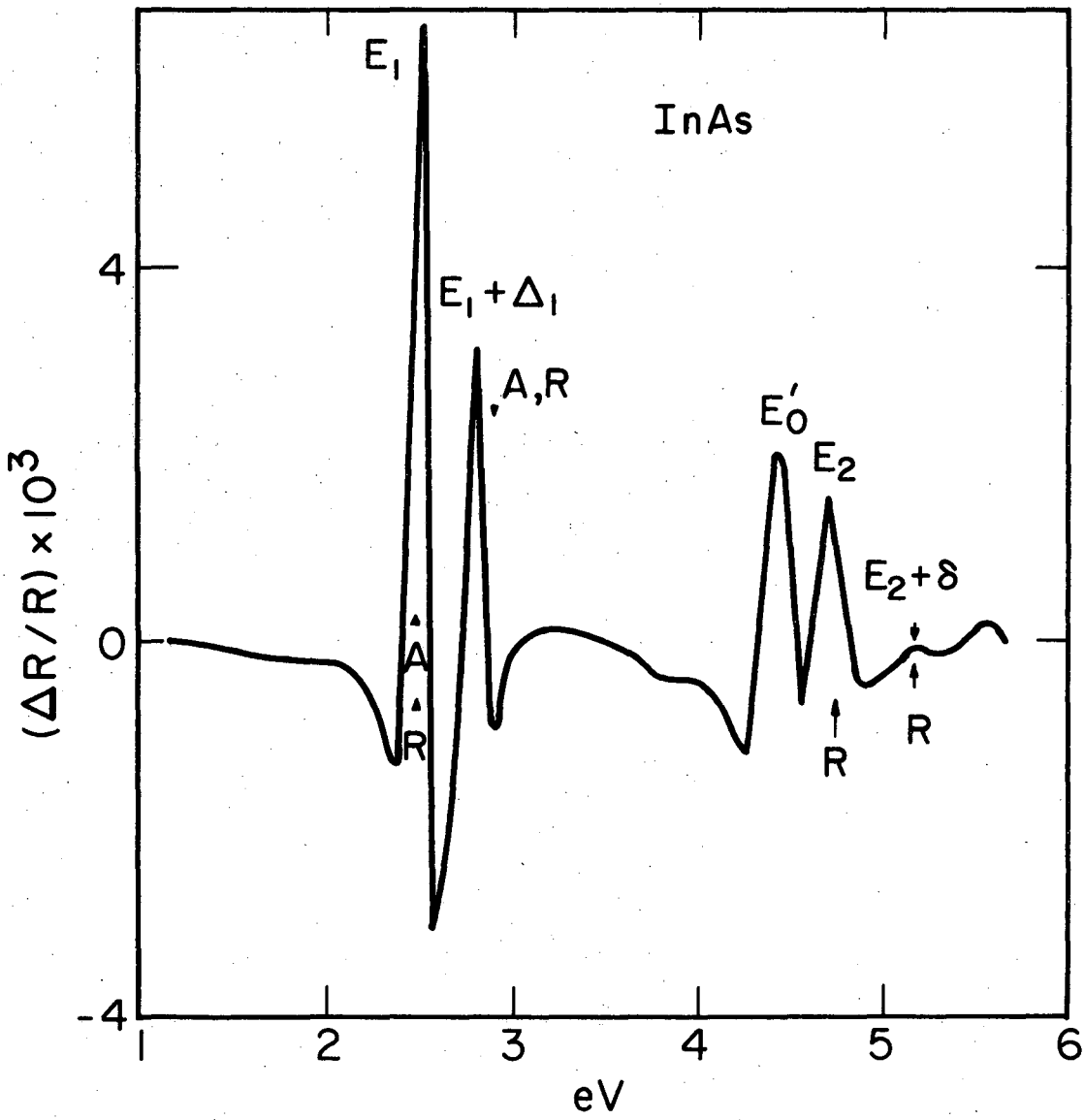
XBL-7211-7331

Fig. 6a



XBL-7211-7332

Fig. 6b



XBL699-3863

Fig. 6c

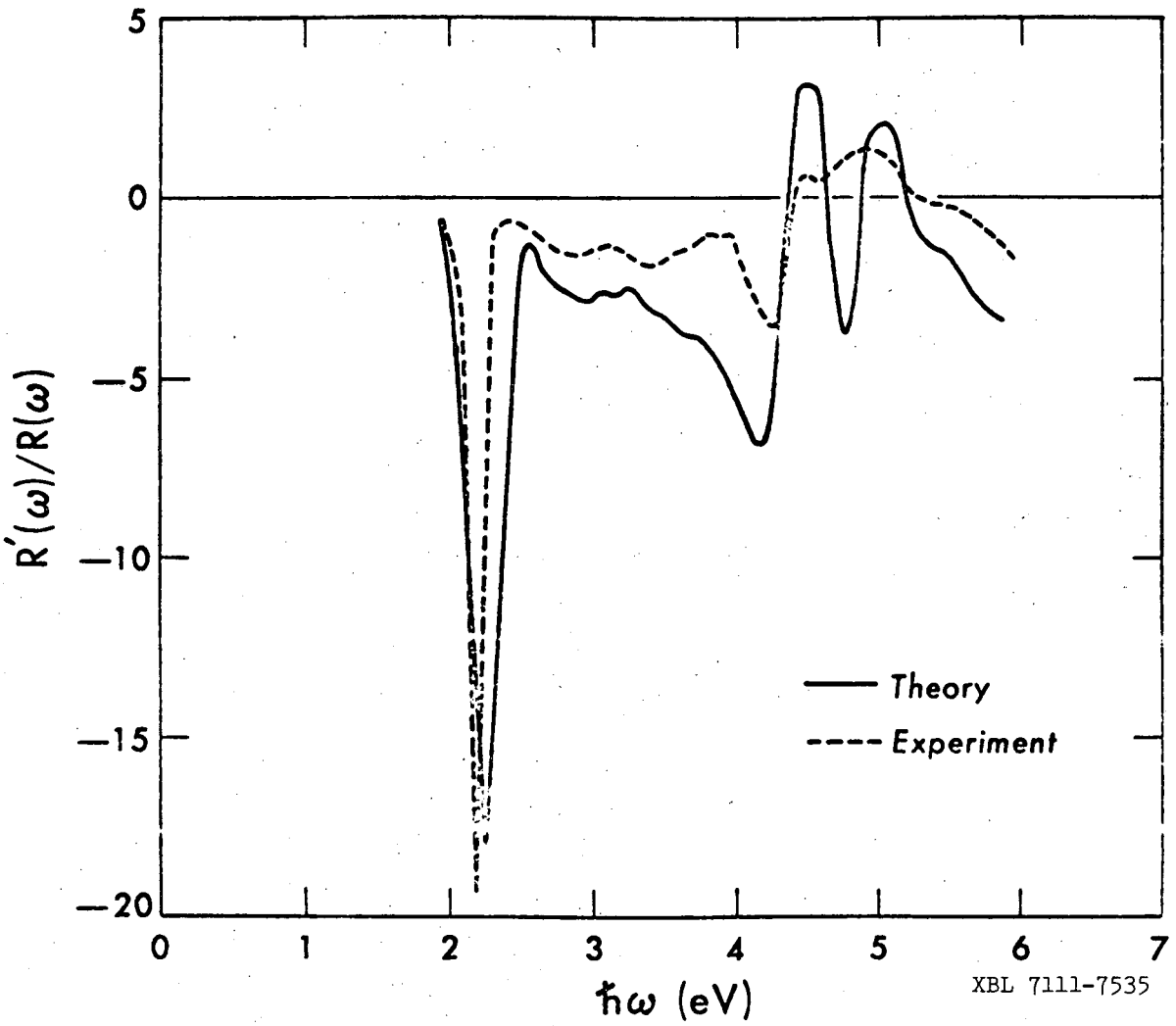
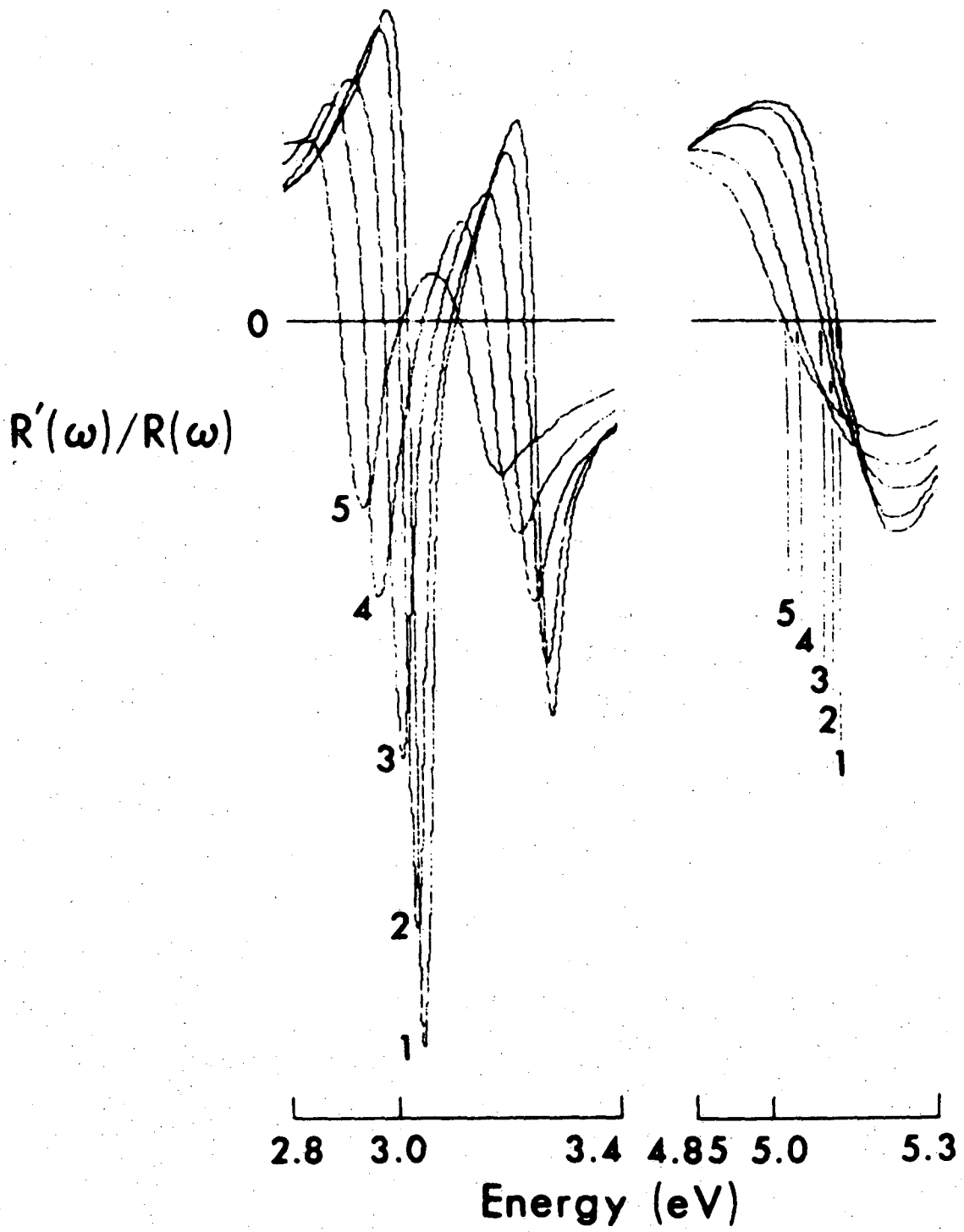

5
0
−5
−10
−15
−20
R′(ω)/R(ω)
0
1
2
3
4
5
6
7
ħω (eV)
Theory
Experiment
XBL 7111-7535

Fig. 7



-- XBL 7211-7419 --

Fig. 8

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720