Title
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Publication Date
1972-11-01

Presented at the First
International Conference on Modulation
Spectroscopy, Tucson, Arizona,
November 23-26, 1972

LBL-1407
Preprint

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

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Paper to be given at the First International Conference on Modulation Spectroscopy to be held in Tucson, Arizona November ~~28-December 1,~~ 23-26 1972

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Berkeley, California

AEC Contract No. W-7405-eng-48

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NOVEMBER 1972

Wavelength Modulation Spectra of GaSe, GaS, and Alloys

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ABSTRACT

Recently electroreflectance (at 300°K) and thermoreflectance (at 77°K) of the layer compound GaSe have been reported. For comparison we have measured the wavelength modulation spectra 1/R dR/dE of GaSe, GaS, $GaSe_{0.2}$ $S_{0.8}$, and $GaSe_{0.8}$ $S_{0.2}$ at 5°, 77°, and 300°K between 2 and 6 eV. A large number of new structures are reported.

I. INTRODUCTION

The interest in the properties of layer materials has grown considerably in the last few years. In particular the optical properties of GaSe have been widely investigated.

The first reflectivity spectra were reported by Bassani et al.[1] and Gasanova et al.[2] Somewhat later, two band structures calculations, using the tight binding approach were published by Bassani et al.[3] and Kamimura et al.[4]. More recently electroreflectance,[5] electroabsorption,[6] and thermoreflectance[7] measurements have been reported. There is some disagreement about the position of the electronic transitions and also their assignment.

To help a new pseudopotential band structure calculation of GaSe, we have measured the wave-modulation spectra in the energy range 2 - 6 eV at 300°K, 77°K, and 5°K, of GaSe, GaS, $GaSe_{0.8}S_{0.2}$, and $GaSe_{0.2}S_{0.8}$. A large number of new structures has been observed.

II. EXPERIMENTAL

The experimental setup used for the wavelength-modulation measurements has been described in detail elsewhere.[8] The samples were maintained in liquid or gaseous helium to avoid any possible pollution of the surface, allowing us to keep the crystal at low temperature for a few days.

All samples were cleaved. The reflectivity measurements were made with unpolarized light with an incidence of 7°. We have also tried unsuccessfully to measure the reflectivity with $E \parallel C$ by polishing and etching the side of the samples but the results were non reproducible,

probably due to the destruction of the layer structure.

The magnitude of the reflectivity is the absolute value, except for GaS where some of the light was lost because of the small size of the sample used.

III. RESULTS AND DISCUSSION

β-GaSe and GaS crystals have the space group symmetry D'_{3h}, with eight atoms in the unit cell. The Ga and Se have 3 and 6 valence electrons, occupying the 4S, $4P_x 4P_y$ (σ) orbitals in the layer and the $4P_z$ (π) orbitals, perpendicular to the layer. In the approach of Kamimura et al.[4] the σ bands are fully occupied and are energetically below the π bands. That means that the bottom of the conduction band and the top of the valence band consists of π bands. In the Bassani et al.[3] model there is a mixing of the S and P_z orbitals.

The reflectivity and wavelength modulation spectra of GaSe, $GaSe_{0.8}S_{0.2}$, $GaSe_{0.2}S_{0.8}$, and GaS are represented in Figs. 1-4. Tables I and II give the energy position of the structures observed, with the results obtained by other methods. To simplify we have represented only the results above 3 eV; the only structure observed below corresponds to the excitonic band gap.

In the case of GaSe, the first structure occurs at 3.38 eV. It has been extensively studied by several workers, but interpreted quite differently. Subashiev et al. attributed this one to a hyperbolic exciton associated with a M_1 critical point.[9] This interpretation was challenged by Balzarotti et al.[5] who associated their structures observed at 3.23 and 3.53 eV at room temperature to the spin orbit

splitting of the valence band, the value of $\Delta = 0.30$ eV being a little smaller than that of atomic Se. On the other hand, Grandolfo et al.[7] have analyzed their thermoreflectance data and found that only a theory taking account for an excitonic effect can explain their structure at 3.658 eV (at 77°K).

In our experiment the two peaks are located at 3.38 and 3.80 eV at T = 5°K (3.22 and 3.68 eV at 300°K). The increase of the magnitude of 1/R dR/dE of the two structures is exactly the same when the temperature is decreased from 300°K to 5°K. Also the shape of 1/R dR/dE and $d\varepsilon_2/dE$ seem to suggest a exciton associated with an M_1 singularity, like in the case of E_1 peaks in the II-VI[10,11] and III-V compounds.[12]

At higher energy the spectrum is dominated by four peaks located at 4.88, 5.15, 5.56, and 5.80 eV. In the Kamimura et al.[4] band structure calculation they can be related to the transitions

$$M_1^+ \rightarrow M_1^+ \quad (\pi_2 \rightarrow \pi_4)$$

$$K_1^+, K_1^- \rightarrow K_1^+ \quad (\pi_2 \rightarrow \pi_4)$$

$$M_2^- \rightarrow M_1^+ \quad (\pi_1 \rightarrow \pi_4).$$

The joint density of states, calculated by Bassani et al.[3,5] shows two main structures at 3.4 and 4.2 eV. As can be seen from our curves this latter value is too low by 1 eV.

In the case of the alloys (Figs. 2 and 3) this structure is very broad.

GaS presents a structure very similar to GaSe. However, the corresponding peak to the 3.38 eV transition in GaSe is not observed here; this can be explained if it is an excitonic transition because in GaS the exciton at the band gap is very weak.[1] Also, two small, very sharp and strongly temperature dependent peaks are observed at 4.57 and 4.64 eV.

IV. CONCLUSIONS

In conclusion, the wavelength modulation spectra of GaSe, and GaS show a large number of new structures. The assignments of these structures will be published elsewhere, with a pseudopotential band structure calculation.

ACKNOWLEDGEMENTS

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

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FIGURE CAPTIONS

Fig. 1. Reflectivity R (dashed line) and 1/R dR/dE (full line) for GaSe at 5°K.

Fig. 2. Reflectivity R (dashed line) and 1/R dR/dE (full line) for $GaSe_{0.8}S_{0.2}$ at 5°K.

Fig. 3. Reflectivity R (dashed line) and 1/R dR/dE (full line) for $GaSe_{0.2}S_{0.8}$ at 5°K.

Fig. 4. Reflectivity R (dashed line) and 1/R dR/dE (full line) for GaS at 5°K.

TABLE CAPTIONS

Table I. Structures on GaSe spectra observed by various methods.

Table II. Structures on GaS spectra observed by various methods.

Table I

GaSe

Reflectivity[a] (T=300°K)				3.63	4.1			4.9			5.9
Reflectivity[b] (T=300°K)				3.69	4.1			5.1			
Thermoreflectivity[c] (T=77°K)	3.255			3.658	~4.1		4.577				
Electroreflectance[d] (T=300°K)	3.23	3.53			3.88		4.7	4.97			
Electro-Absorption[e] (T=77°K)	3.378										
Wavelength Modulation (T=5°K)	3.38	3.43,3.60,3.70		3.80	4.07	4.26,4.43,4.64	4.88	5.15	5.56	5.80	6.1
Wavelength Modulation (T=300°K)	3.22			3.68			4.78	5.07	5.48	5.75	6.05

a) From Ref. 1.

b) From Ref. 2

c) From Ref. 7

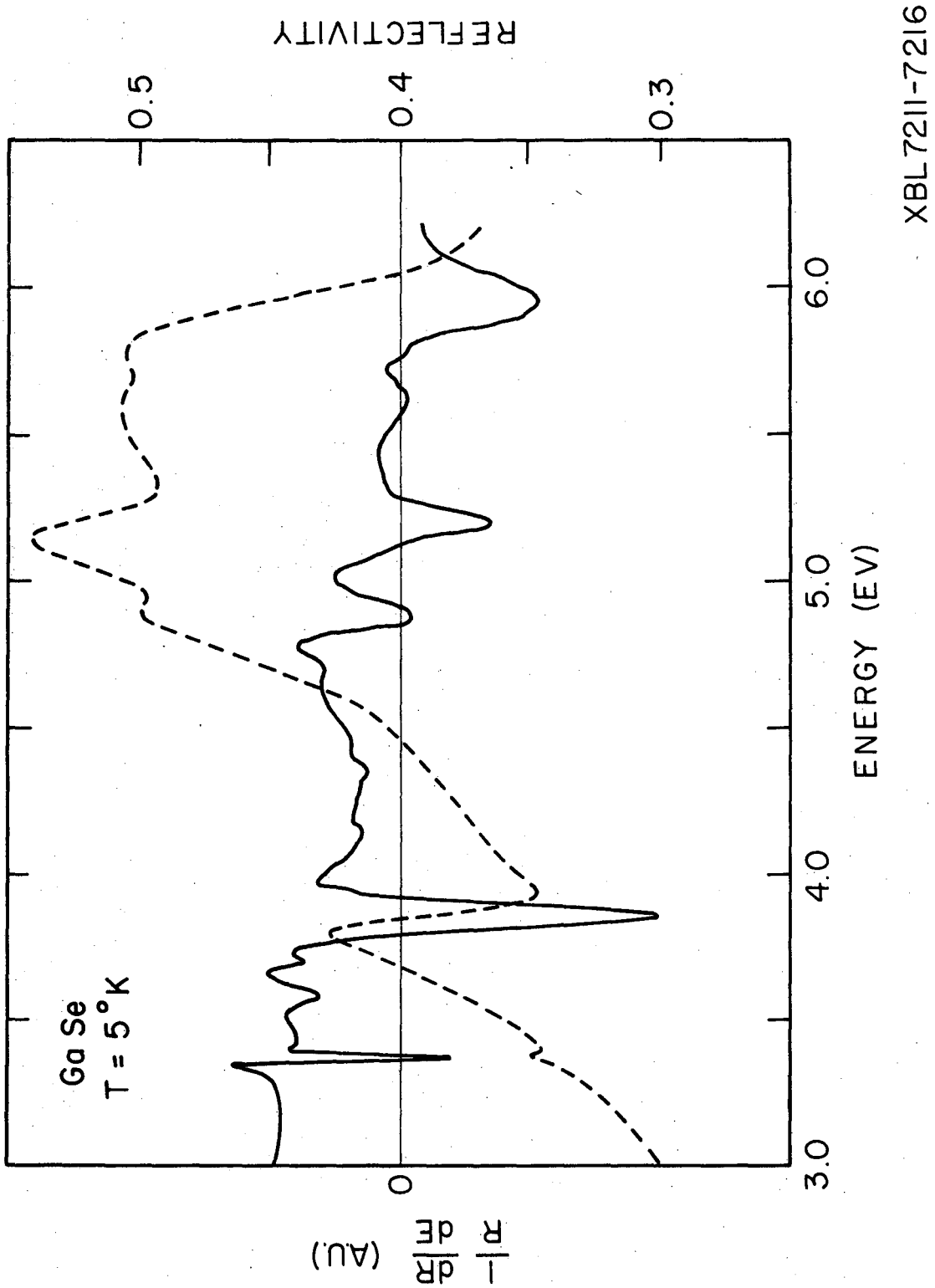
d) From Ref. 5

e) From Ref. 6

Table II

GaS

Reflectivity[a] (T=300°K)	3.9		4.75		5.4	5.7	6.1
Reflectivity[b] (T=300°K)	3.85		4.63		5.48		
Thermoreflectance (T=77°K)	3.993			5.26			
Wavelength Modulation (T=5°K)	4.04	4.20,4.57,4.64	4.85	5.26	5.61	5.79	6.23
Wavelength Modulation (T=300°K)	3.93	4.45	4.75		5.55	5.74	6.2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0.4
0.3
6.0
5.0
4.0
3.0
ENERGY (EV)
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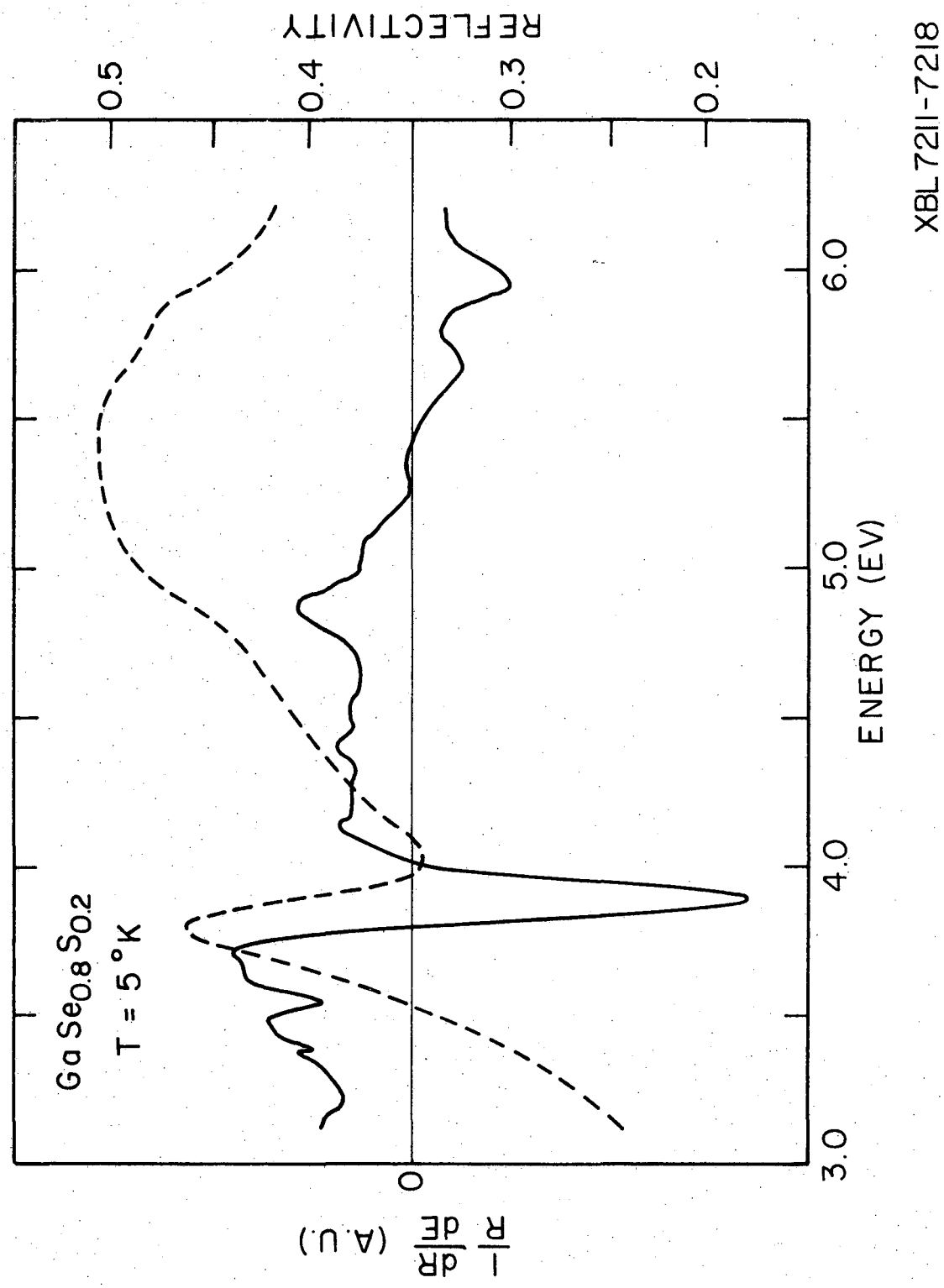
$\frac{1}{R}\frac{dR}{dE}$ (A.U.)
Ga Se
T = 5°K

Fig. 1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0.4
0.3
0.2
XBL 7211-7218
6.0
5.0
4.0
3.0
ENERGY (EV)
O
$\frac{1}{R}\frac{dR}{dE}$ (A.U.)
$GaSe_{0.8}S_{0.2}$
T = 5 °K

Fig. 2

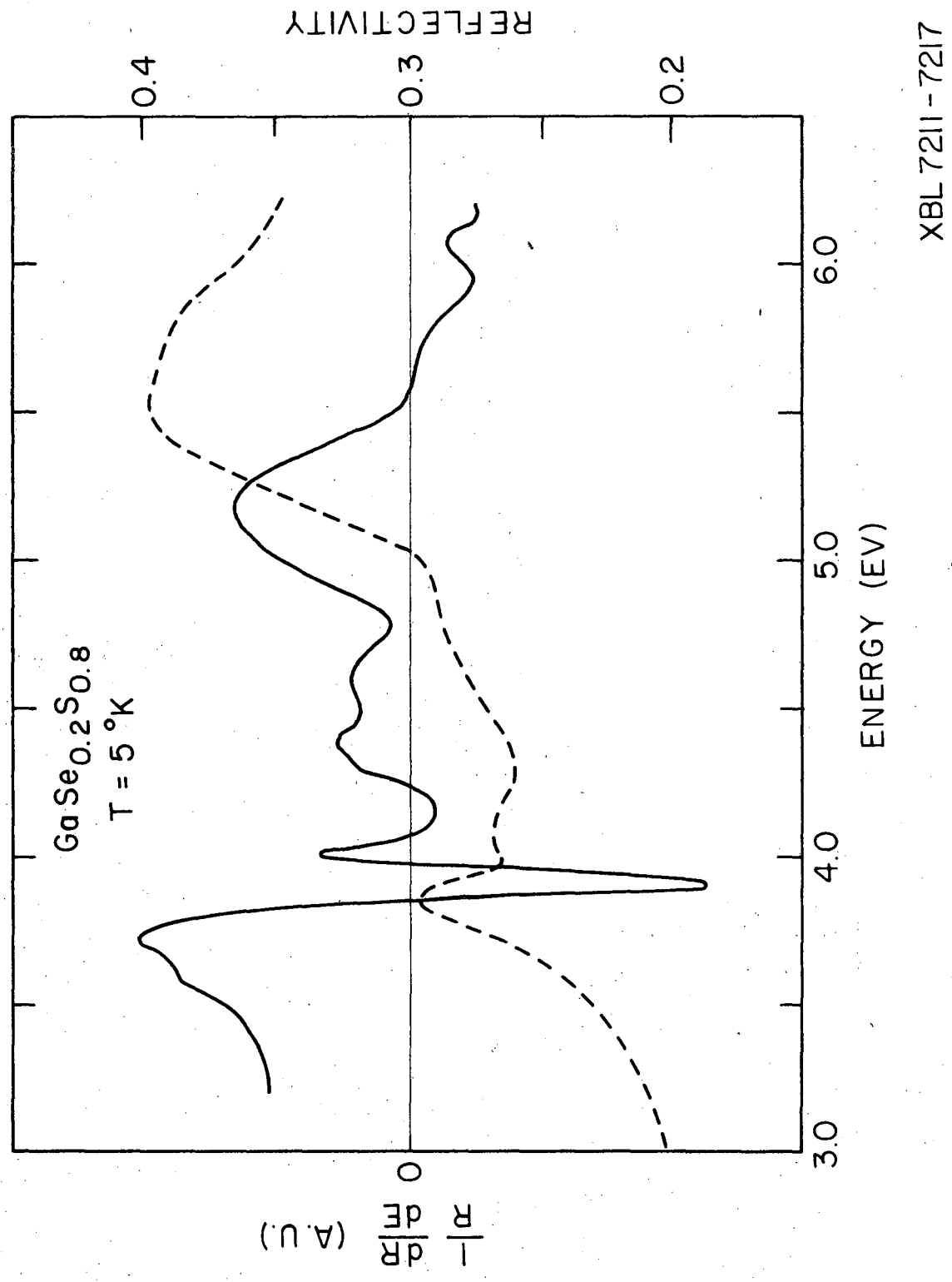
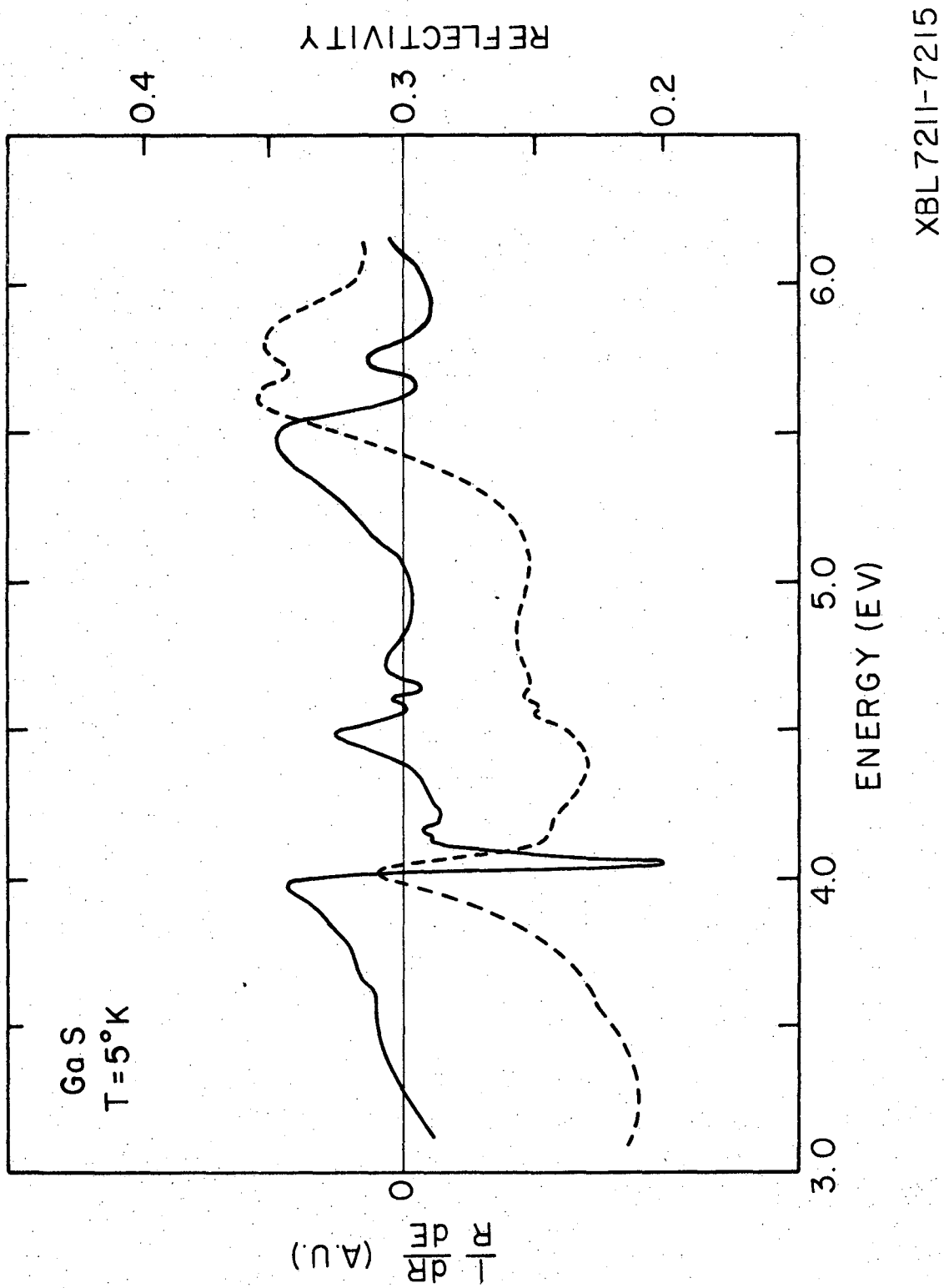

REFLECTIVITY
0.4
0.3
0.2
$GaSe_{0.2}S_{0.8}$
T = 5 °K
6.0
5.0
4.0
3.0
ENERGY (EV)
XBL 7211-7217
$\frac{1}{R}\frac{dR}{dE}$ (A.U.)
0

Fig. 3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0.3
0.2
GaS
T=5°K
3.0
4.0
5.0
6.0
ENERGY (EV)
0
$\frac{1}{R}\frac{dR}{dE}$ (A.U.)

Fig. 4

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