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Optical Spectra of CsI, CsBr, ZnGeP₂, and SbSI

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ABSTRACT

We report here the study of the normal reflectivity spectra R and the corresponding derivative spectra $1/R \, dR/dE$ of SbSI between 2 and 6 eV. The spectra show very strong anisotropy. We have also tried to use the change in the wavelength modulation spectrum to monitor the change in the band structure of SbSI due to the phase transition at 292°C ($D_{2h}^{16} \rightarrow C_{2v}^9$). Careful examination of the spectra at various temperatures around T_c shows no observable change.

We report also the wavelength-modulated reflectivity spectra of the chalcopyrite crystal ZnGeP₂ at 5°K between 2 and 6 eV, for $E \parallel C$ and $E \perp C$. The experimental results

are compared with the theoretical band structure calculation by de Alvarez and Cohen.

We also present measurements on CsBr, CsI in vacuum uv (between 5 and 8 eV) at 1.8°K, showing noticeable difference with previous reflectivity measurements at 77°K.

CsBr-CsI

CsBr and CsI crystallize in the CsCl structure (simple cubic). The first band structure (for CsBr) was proposed by Phillips;¹ in his empirical model the upper valence band was formed by the Br-P electron and the conduction band by s and d electrons. More recently Onodera² and Rössler,³ using a Green's function method, have made new calculations; the main difference with the Phillips model is the overlapping of the s and d bands.

It has been shown by magnetoresistivity⁴ measurements on CsBr that the lowest conduction band has a Γ_6^+ symmetry; it is supposed to be also true for CsI. However, in the Onodera calculations² the levels M_7^+ , Γ_8^+ , and Γ_6^+ are very close.

Absorption^{5,6} at 10°K and reflectivity⁷ at 77°K have been previously reported.

We present here the reflectivity spectra (Fig. 1) at 1.8°K between 5.5 and 7.5 eV and the logarithmic derivative $1/R \, dR/dE$ (Figs. 2-3). The measurements were made with the same reflectometer (represented on Fig. 4) used before for KI.⁸ The intensity of the incident beam on the sample is kept constant during the wavelength scanning and the derivative is obtained by numerical differentiation of the reflectivity using a digital computer. The resolution is 1Å.

The first peak A corresponds to the $\Gamma_8^- \rightarrow \Gamma_6^+$ exciton with its spin-orbit partner, D. The values obtained for Δ are 1.106 eV for CsI and 0.546 eV for CsBr. In the case of CsBr a small shoulder appears on the high energy side of these peaks, with an energy separation of ~ 20 meV. This value is larger than this corresponding to the

emission of a optical phonon. This type of phonon sidebands has been observed for other alkali halides.^{8,9}

In the Onodera model,² the doublet B-C corresponds to the excitonic states of the $\Gamma_8^- \rightarrow \Gamma_8^+$ edge; the peak B is the triplet state, which becomes optically allowed owing to the fluting of the conduction band about Γ_8^+ . He also interprets the small structure at 6.22 and 6.31 eV (for CsI) as an n=2 Wannier states associates with $\Gamma_8^- \rightarrow \Gamma_6^+$ and $\Gamma_8^- \rightarrow \Gamma_8^+$, giving a band gap of 6.31 eV.

The main difference with the previous measurement is the fact that each peak A, B, C, is followed by a shoulder (indicated by an arrow on the reflectivity curve), clearly seen in the logarithmic derivative $1/R \, dR/dE$. These structures could be interpreted as the excitons corresponding to the $M_6^- \rightarrow M_7^+$ edge or $X_7^- \rightarrow X_7^-$ (parity forbidden). However, another possibility is to assign these shoulders to the n = 2 levels of the excitons. Indeed, Frölich and Stagninus have recently measured by two-photon spectroscopy the band gap of CsI and found $E_g = 6.07$ eV at $T = 20^\circ\text{K}$. By using this value and $m_c^* = 0.46 m_0$, the position of the n = 2 exciton is 5.87 eV; the experimental value is 5.89 eV. For CsBr no effective mass of the electron is available.

At higher energy, in the case of CsI two new peaks surround D at 6.8 and 7.10 eV.

In conclusion a theoretical calculation of ϵ_2 would be very useful for the attribution of the different structures observed.

ZnGeP₂

ZnGeP₂ has the chalcopyrite structure (space group D_{2d}^{12}). This structure, corresponding to most of the II-IV-V₂ compounds has been recently extensively studied.¹¹ It is now well known that it is similar to the zinc blende with some differences, however:

- a) a distortion of the environment of the ions;
- b) a doubling of the unit cell along the c direction;
- c) a tetragonal compression.

The result is a complete lifting of the orbital degeneracy of the p-valence band maximum, giving additional peaks in the reflectivity.

The binary analog of ZnGeP₂ is GaP.

The only optical spectra reported about ZnGeP₂ concerns the band gap; values as different than 1.81,¹² 2.0,¹³ 2.25¹⁴ eV at room temperature have been presented.

We have studied the reflectivity and the wavelength modulation reflectivity spectra between 2 and 6 eV for $E \parallel C$ and $E \perp C$. The crystals used for these experiments were grown by North American Aviation; they were cut along the plane [100] polished and etched with "syton." The optical quality of the surface was very good, as can be seen by the high value of R in the uv (> 40%).

A transmission measurement at room temperature has given us a band gap of 2.1 eV; this means that at 5°K, $E_g \sim 2.23$ eV.

Figures 5 and 6 represent the results for $E \parallel C$ and $E \perp C$. It would be too long to discuss here all of the structures observed. Therefore, we have compared in Table II, our results with a pseudopotential calculation made by de Alvarez and Cohen;⁵ in this calcula-

tion no fit with the experiment has been attempted.

We have calculated the crystal field splitting of the valence band maximum using the equation¹¹

$$\Delta_C = \frac{3}{2} b \left(2 - \frac{c}{a} \right) \quad \text{where } b = -1.2$$

$$= 65 \text{ meV} \quad \frac{c}{a} = 1.961.$$

Using the spin orbit splitting of GaP, $\Delta_1 = 50 \text{ meV}$,¹⁶ we found

$$E_1(1) - E_1(2) = \sqrt{(\Delta_1)^2 + \left(\frac{\Delta_C}{3}\right)^2} = 63 \text{ meV}.$$

This small value explains why we have observed only one structure for $E_1(1) - E_1(2)$ and one for $E_1(3) - E_1(4)$. However, a very weak structure at 50 meV of $E_1(1)$ can be seen for $E \perp C$. Table II gives the experimental values of the structures above $E_1(1)$.

SbSI

The ferroelectric SbSI is a very interesting material because of its high anisotropic properties. Below the Curie point ($T_c \sim 292^\circ\text{K}$), its structure is orthorhombic C_{2v}^9 , above also orthorhombic but D_{2h}^{16} . The Sb and S atoms are displaced along the c axis of the crystal (0.2Å and 0.05Å for Sb and S atoms, respectively).

It was expected that this large change in the parameters would produce a change in the band structure. About 12 spectra at temperatures between 5 and 320°K have been performed. Careful examination of the spectra around the critical temperature does not show any observable difference. We have represented in Figs. 7 and 8 the logarithmic derivative of the reflectivity and the reflectivity at 5°K for $E \parallel C$ and $E \perp C$ to show the strong anisotropy of the crystal; a difference as large as a factor of 2 in the spectra is observed for the two polarizations.

The band structure of SbSI and the optical spectra will be published elsewhere.

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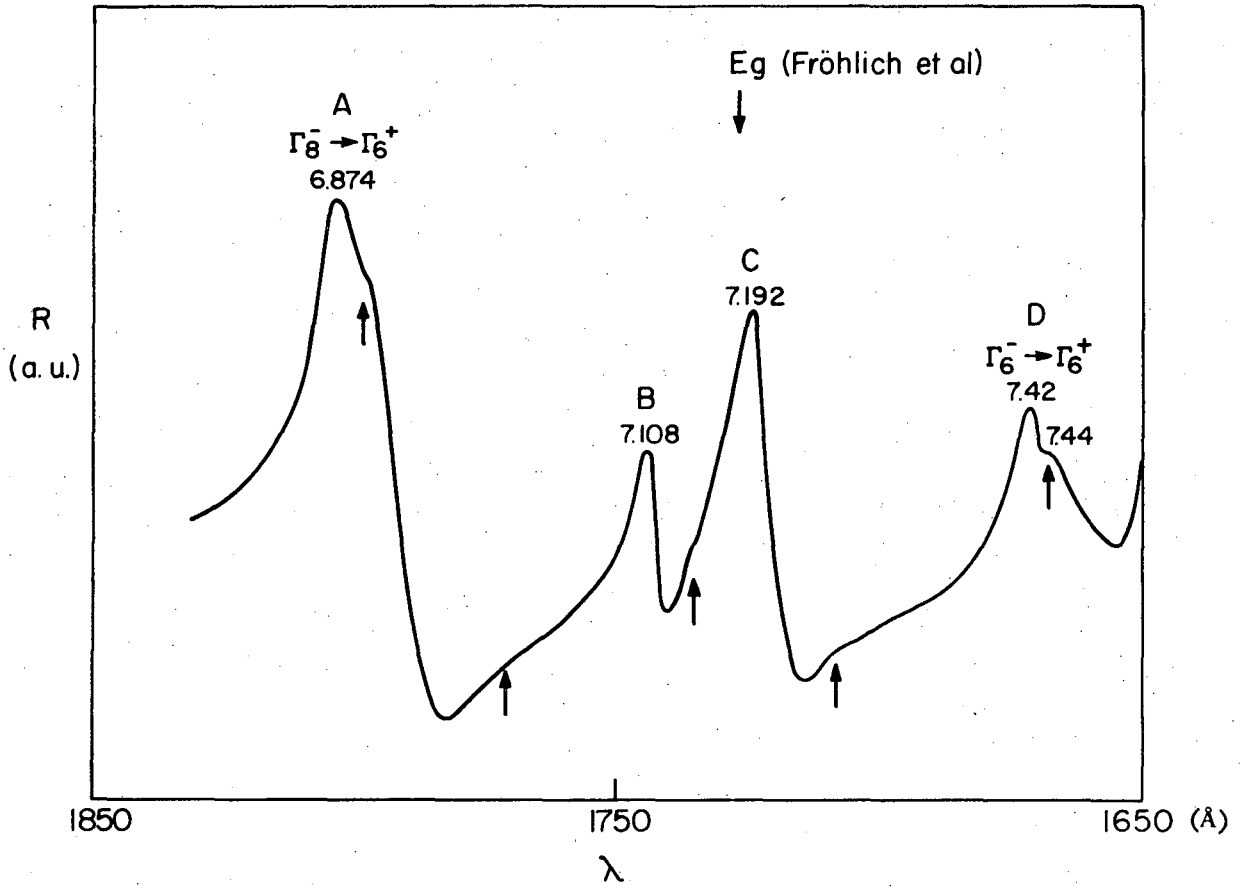
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Figure Captions

- Fig. 1. Reflectivity spectra of CsBr at $T = 1.8^\circ\text{K}$.
- Fig. 2. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of CsBr at $T = 1.8^\circ\text{K}$.
- Fig. 3. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of CsI at $T = 1.8^\circ\text{K}$.
- Fig. 4. Reflectometer used for low-temperature experiments in the vacuum-uv.
- Fig. 5. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of ZnGeP_2 at $T = 5^\circ\text{K}$ for $E \perp C$.
- Fig. 6. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of ZnGeP_2 at $T = 5^\circ\text{K}$ for $E \parallel C$.
- Fig. 7. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of SbSI at $T = 5^\circ\text{K}$ for $E \perp C$.
- Fig. 8. Reflectivity R and logarithmic derivative $1/R \, dR/dE$ of SbSI at $T = 5^\circ\text{K}$ for $E \parallel C$.

Table Captions

- Table I. Position (in eV) of the different peaks observed in reflectivity at $T = 1.8^\circ\text{K}$ for CsBr and CsI.
- Table II. Theoretical and experimental values for the structures in the reflectivity curve for ZnGeP_2 .



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Fig. 1

Cs Br
T = 1.8 °K

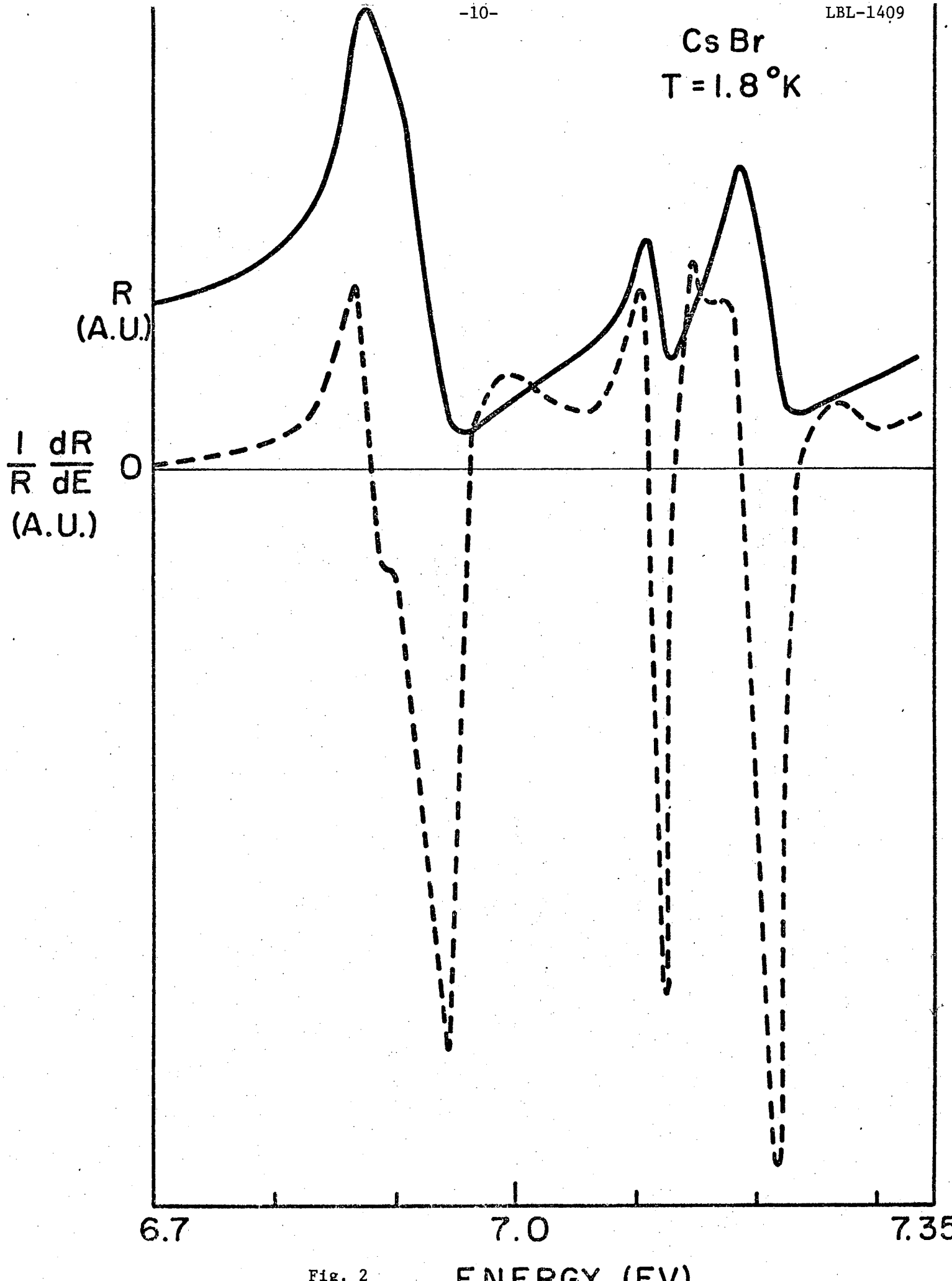
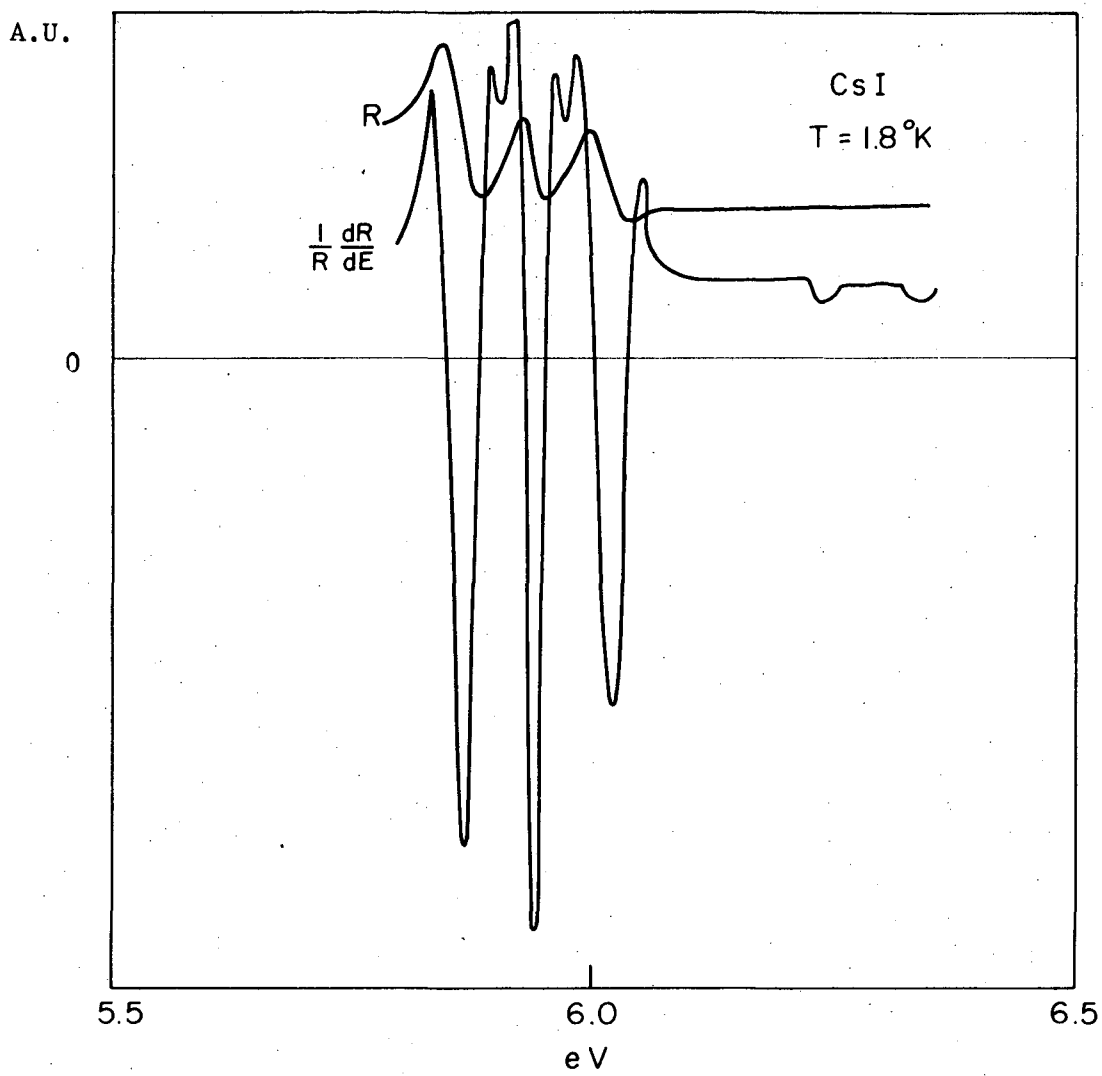


Fig. 2

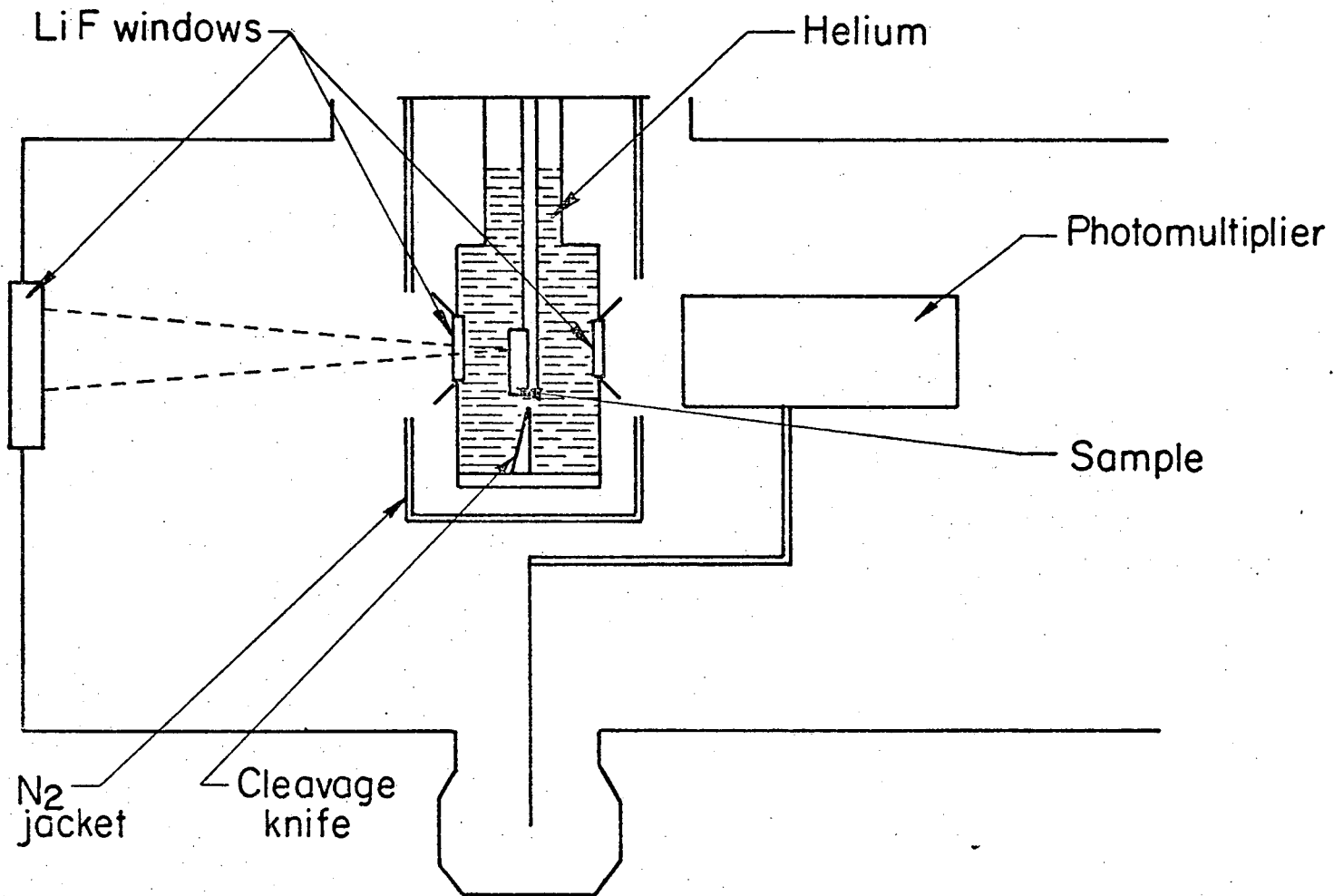
ENERGY (eV)



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Fig. 3

FIG. 4

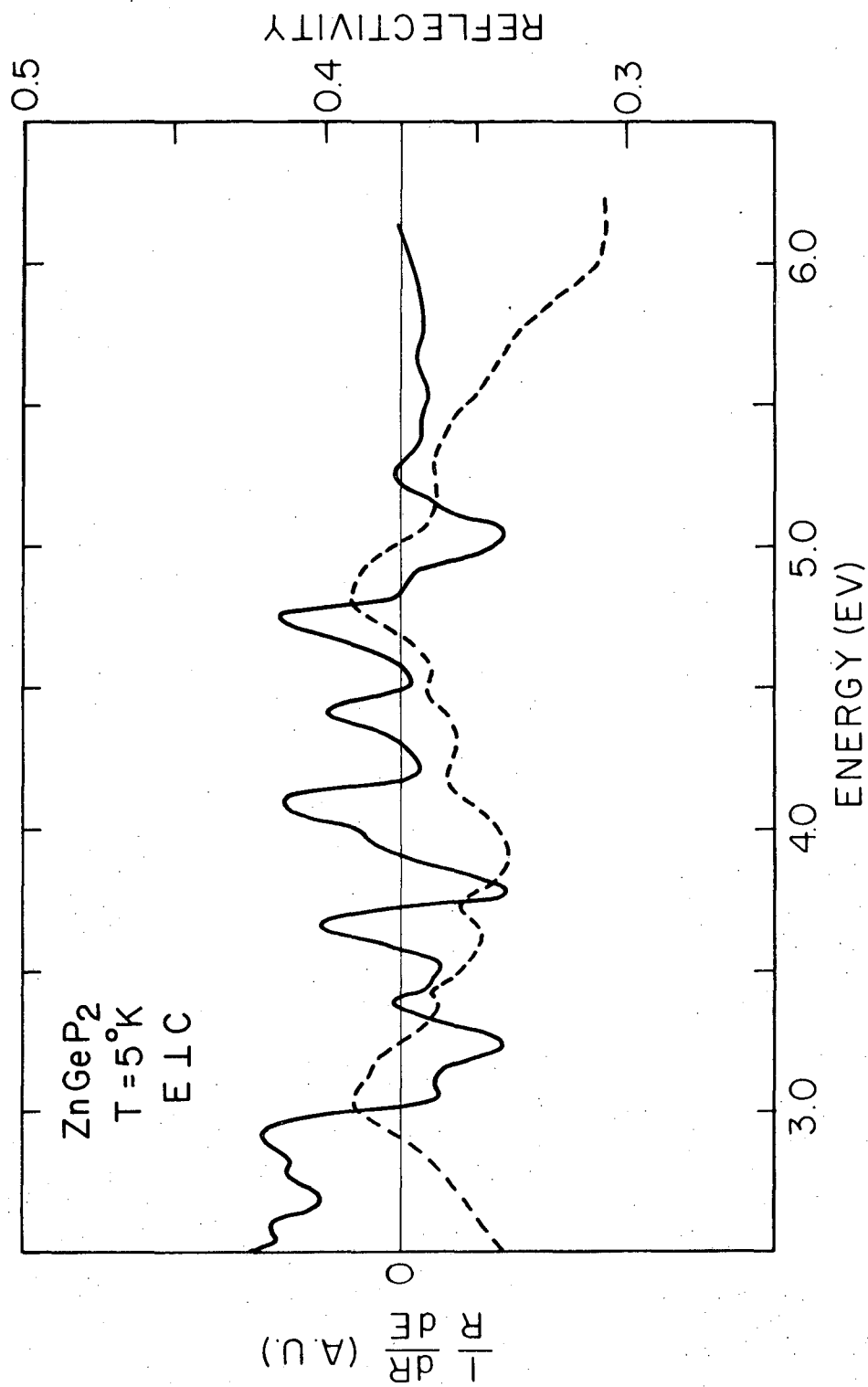


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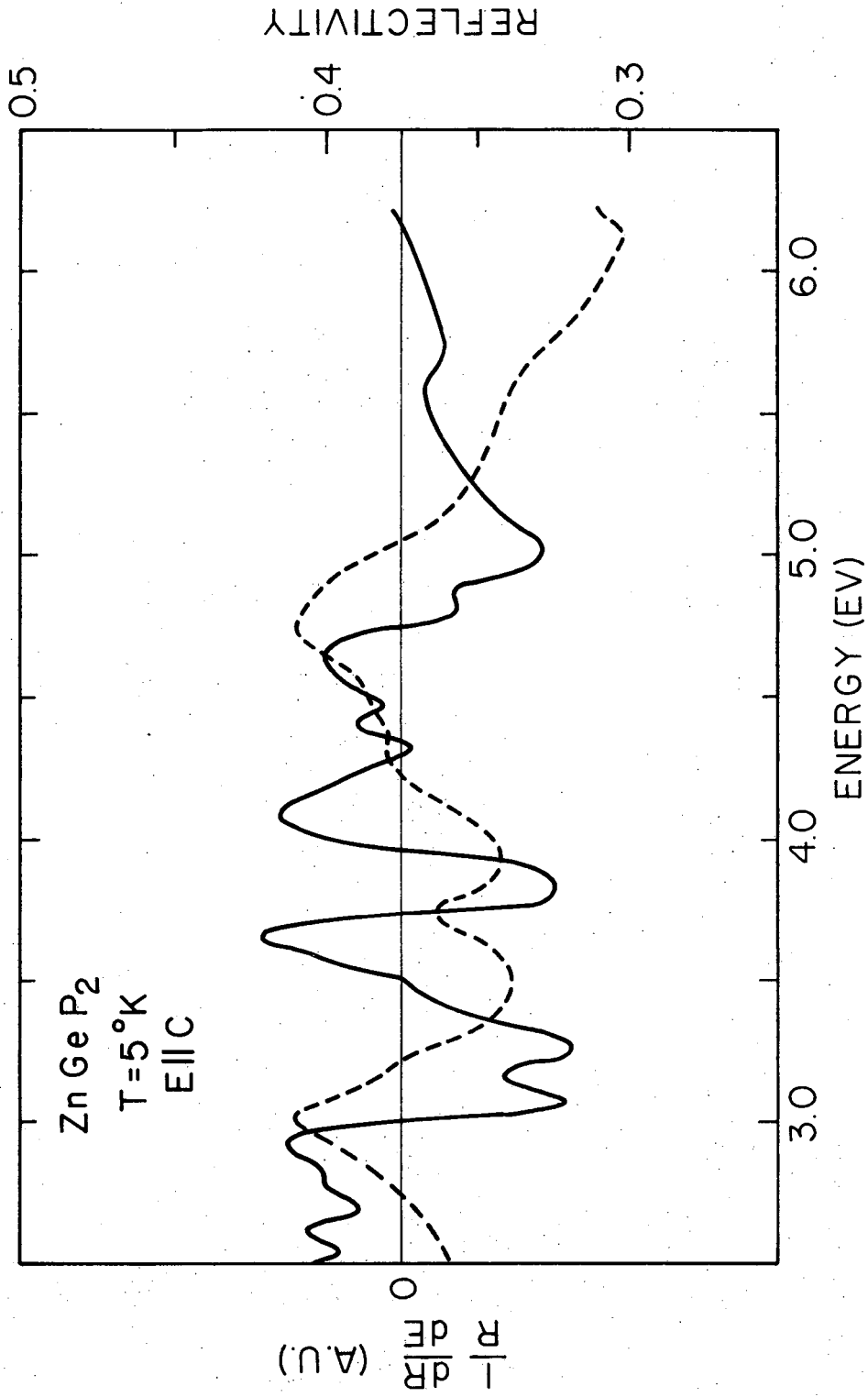
REFLECTOMETER FOR MEASUREMENTS AT $T = 1.8^{\circ}\text{K}$

XBL 725 - 6336



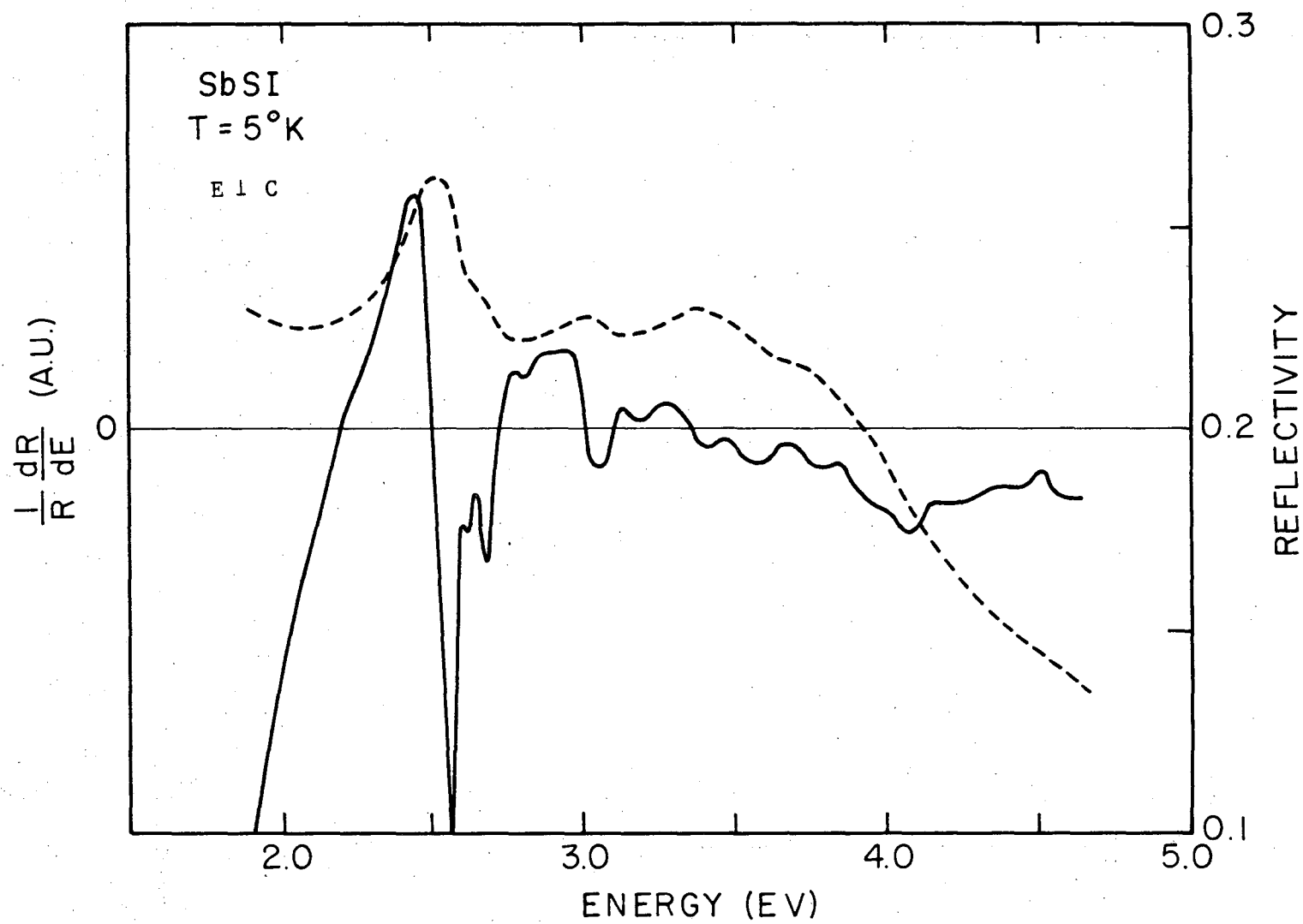
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Fig. 5



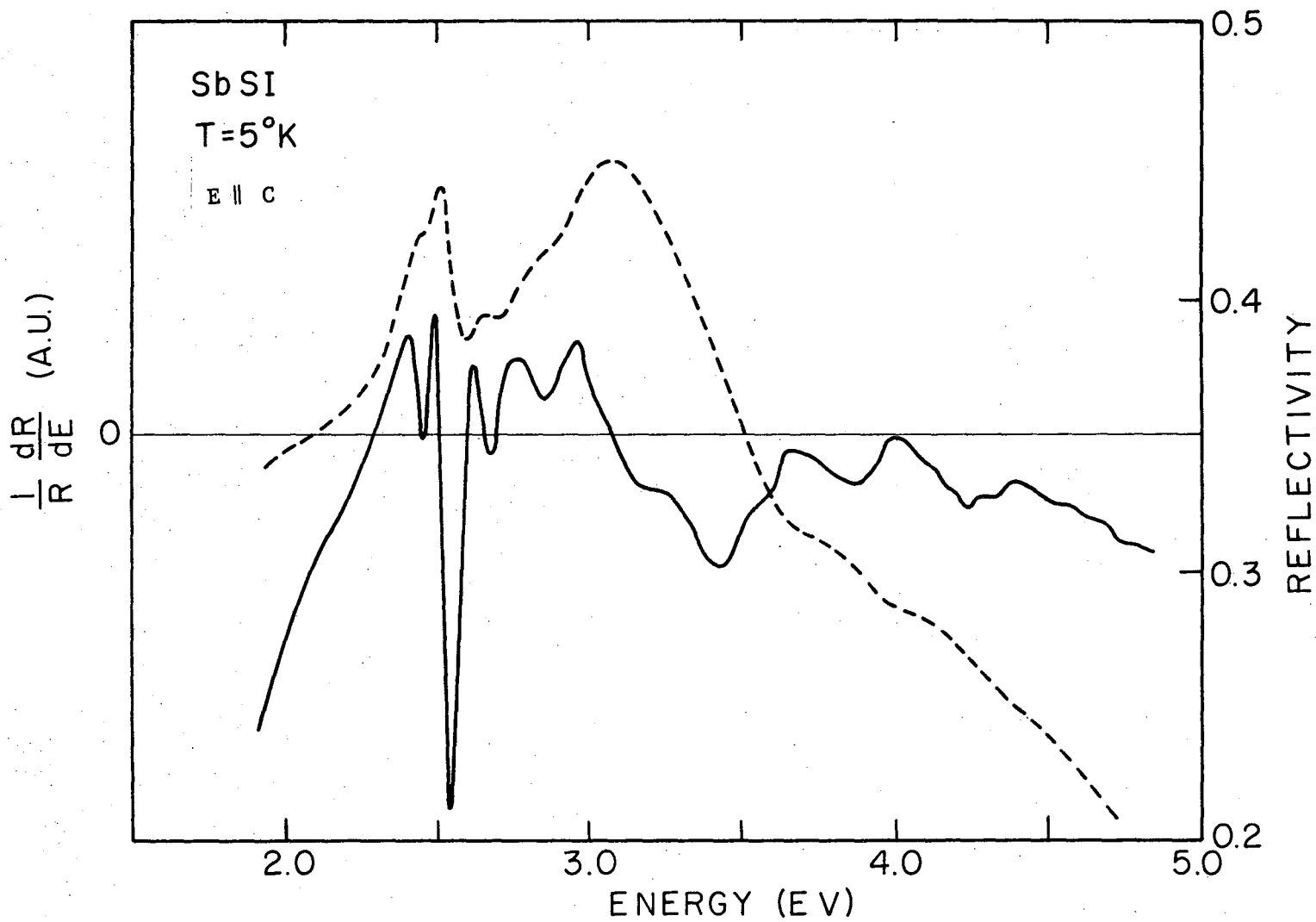
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Fig. 6



XBL7211-7220

Fig. 7



XBL7211-7219

Fig. 8

Table I

	A	B	C	D	Δ
CsBr	6.874	7.42	7.192	7.108	0.546
CsI	5.834	5.919	5.987	6.94	1.106

Table II

		<u>Theory</u>	<u>Experiment</u>
gap	Γ A	2.31 [*]	$\parallel \perp$
	B	2.27 [*]	\perp
	C	2.43 [*]	$\parallel \perp$
	X (16-17)	3.05	\parallel
	X (14-17)	3.36	\perp
First peak $E_1(1)+E_1(2)$	N (.2, .2, .4) (16-17)	3.37 [*]	$\parallel \perp$ 3.02 3.03
	N (.2, .2, .4) (15-17)	3.45 [*]	$\perp \parallel$ 3.08 (very weak)
Shoulder $E_1(3)+E_1(4)$	Vol. in N plane caused by strong interactions of the W-L line and the X- Σ line, some contribution comes from X (14-17)	3.55	$\parallel (\perp)$ 3.20 (3.18)
Small peak in \perp	The theory shows it but several bands are involved and very difficult to identify (N plane?)	3.75	\perp 3.41
Second peak $E_1(5)$	X (0,0,0.5) (12-17)	3.89	$\parallel (\perp)$ 3.74 (3.72)
$E_2^{\perp} (1)$	Γ (13-18)	4.77	\perp 4.17
$E_2^{\parallel} (1)$	Δ (.34, 0, 0) (15-17)	4.76	\parallel 4.3
$E_2^{\perp} (2)$	X (16-20) and along Σ	4.96	\perp 4.46
$E_2^{\parallel} (3)$	(0.47, 0.16, 0.06) (14-17) N (.2, .25, .5) (13-18)	5.05	\parallel 4.73
$E_2^{\perp} (3)$	N(.25, .25, .5) (14-20)	5.1	\perp 4.79
Shoulder	$\Delta(0.5, 0, 0)$ (15-18)	5.21	$\parallel (\perp)$ 4.92 (4.93)

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