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WAVELENGTH MODULATION SPECTRA OF PbS, PbSe, PbTe, AND SnSe

S. Kohn, Y. Petroff†, Y. R. Shen, and P. Yu‡

April 1972

Paper contributed to Conference on the Physics of IV-VI Compounds and Alloys to be held March 24-25,1972 at Philadelphia, Pennsylvania

LBL-456 Abstract

Wavelength Modulation Spectra of PbS, PbSe, PbTe, and SnSe.*

S. Kohn, Y. Petroff, P. Y. Yu, and Y. R. Shen, Department of Physics, University of California, Berkeley and IMRD, Lawrence Berkeley Lab., Berkeley, California 94720.--We have used the wavelength modulation technique to measure the derivative spectra dR/Rdω of single crystals of PbS, PbSe, PbTe, and SnSe between 1.5 and 6 eV at several temperatures from 5 to 300°K. The samples were cleaved and stored in the He atmosphere before measurements. As a consequence, surface contamination was avoided. We have observed all the structures previously detected by normal reflectivity and electroreflectance measurements. In addition, we have seen many new structures. The spectra generally become better resolved at low temperatures, but some of the structures show stronger temperature dependence than others in both the position and the strength. In particular, one component in the E_3-peak depends very strongly on temperature and becomes very pronounced through sharpening at low temperatures. We have interpreted the spectra in terms of interband transitions with the available band structures for these compounds.

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Optical properties of IV-VI compounds have been the subject of much investigation[1,2] In the visible and near uv, the observed spectra agree fairly well with those calculated from the available band structures.[3-7] However, the band structure calculations have predicted some fine structure in the spectra which cannot be easily observed in the ordinary reflectivity measurements because of their limited resolution. As is well known, derivative spectroscopy can effectively improve the resolution. Derivative reflectivity measurements on lead salts[8-10] and on $Pb_xSn_{1-x}Te$[11] alloys have actually been performed. Unfortunately, since these compounds have high dielectric constants and usually high carrier concentrations, their electroreflectance spectra appear to change with the dc bias, the modulation frequency, and the modulation amplitude.[8,9] This makes interpretation of the electroreflectance spectra very difficult. With wavelength-modulation reflectivity spectra, however, no such difficulty exists.[12] Using our wavelength-modulation spectrometer, we have obtained both the reflectivity spectra R and the logarithmic derivative spectra dR/RdE for PbS, PbSe, PbTe, and SnSe. The spectra cover the region from 1.5 to 6 eV in a temperature range from 5 to 300°K. To our knowledge, no reflectivity measurements on SnSe have ever been reported.

The detailed construction of the wavelength-modulation spectrometer has been described elsewhere.[12] We used in our measurements the particular mode of operation which yields simultaneously the spectra of $R(\lambda)$ and $dR(\lambda)/Rd\lambda$. The spectra were then converted into R(E) and dR(E)/RdE on a computer. With an appropriate Kramers-Kronig transformation, we were also able to obtain $\varepsilon_1(E)$, $\varepsilon_2(E)$, $d\varepsilon_1(E)/dE$, and $d\varepsilon_2(E)/dE$.

The surfaces of the samples under investigation were all prepared by cleavage. After cleaving, the sample was quickly transferred into the optical dewar and stored in He atmosphere. The spectra thus obtained were always reproducible.

The observed spectra for PbS, PbSe, PbTe, and SnSe at 5°K are presented in Figs. 1, 2, 3, and 4 respectively.[13] In Table I, the approximate positions of all the structure observed in the spectra are given, with the weak structure indicated by (W). The main reflectivity peaks in the spectra are denoted by E_1, E_2, and E_3 according to the notations of Cardona and Greenaway.[1] We notice that there are close similarities between the spectra of the lead salts. As observed by Cardona and Greenaway,[1] the main peaks in the reflectivity spectra are found to shift to lower energies as the compounds vary in the sequence of PbS, PbSe, and PbTe. We have, however, observed in the derivative spectra a number of distinct fine structure on top of the main peaks. These fine structure are generally not easily observable in the ordinary reflectivity spectra. They become less pronounced and usually shift together with the main peaks to higher energies as the temperature increases.

While the lead salts have the rock salt structure, SnSe has an orthorhombic structure.[13] As a result, the spectrum of SnSe does not closely resemble those of the lead salts. However, we can still group the structures in the spectrum of SnSe into E_2 and E_3 regions, especially if we believe that the reflectivity peaks of SnSe and PbSe should be only shifted slightly from each other, as in the case of SnTe and PbTe. The general characteristics of the SnSe spectrum are similar to those

of the lead salts.

To interpret our spectra, we use the following scheme. First, we use the reflectivity and pseudopotential band-structure calculation of Tsang and Cohen[14] to identify the structure in the spectrum of PbTe. Then, utilizing the fact that the spectra for these compounds are closely similar, we try to identify the structure in the spectra of PbS, PbSe, and SnSe.

Tsang and Cohen[14] have calculated $\varepsilon_1(E)$ and $\varepsilon_2(E)$ for PbTe from their empirical pseudopotential band-structure calculation. Their ε_2 spectrum agree well with the available spectra for PbTe except for some fine structures. More recently, using their ε_1 and ε_2, they have also calculated the logarithmic derivative dR/RdE for PbTe.[15] We have compared their theoretical spectrum with our experimental dR/RdE spectrum. Except for small differences in magnitudes and position of some of the structures, the agreement between the two spectra is remarkably good. In particular, the theoretical spectrum reproduces not only the major structure but also the fine structure in the experimental spectrum. We therefore believe that their assignment[14] of the structure in the spectrum of PbTe is basically correct. The E_2 peak is a composite peak due to critical point transitions between bands 5 and 7 at Σ and between bands 5 and 6 at Δ. The volume effect in the regions around these critical point transitions is also important and gives rise to the fine structures in the E_2 peak between 2 and 3 eV.[5,15] The E_3 peak is due to transitions between bands 4 and 6 near Δ and between bands 4 and 7 near Σ. The fine structures between 3.5 and 5.4 eV are probably due to the volume effect in the region around Λ (3-6,7)

and Σ (4-7). The E_4 peak with its fine structure at 5.9 eV is due to transitions in the region near X. The maximum of the E_4 peak is outside the range of our spectrometer.

Because of the close similarity between the band structures[3,4] and the observed reflectivity spectra of the four compounds under investigation, we tentatively assign the peaks and fine structure in the spectra of all four compounds by correspondence to the spectrum of PbTe. The assignment is given in Table I. Because the separations between various bands become wider as the compounds vary from PbTe to SnSe, PbSe, and then PbS, the peaks and the associated fine structure shift to higher energies accordingly. However, since SnSe has quite different crystal structure than the others and since there is no available band structure on SnSe, our assignment for the SnSe spectrum in Table I should be regarded as only suggestive.

We should mention that although the band structures of PbTe obtained by various authors[3-5,7] look qualitatively similar, they have appreciable quantitative difference. Since the band structure calculation of Tsang and Cohen for PbTe appears to explain our derivative reflectivity spectrum of PbTe fairly well, similar calculations for the other IV-VI compounds will tell us whether our tentative assignment of the structures in the reflectivity spectra of the other compounds is correct.

In measuring the reflectivity spectrum of PbS as a function of temperature, we observed a pronounced sharpening in the fine structure at 5.08 eV as the temperature decreases. This sharpening is observable even between liquid nitrogen and liquid helium temperatures. This is shown in Fig. 5. No other structure in the spectra of all four compounds

has a similar behavior. The sample used in this measurement was n-type with a carrier concentration of $\sim 10^{16}/cm^3$ as obtained from Hall effect measurements. However, when we repeated the measurement on an n-type sample with a carrier concentration of $\sim 10^{18}/cm^3$, this 5.08-eV structure became less pronounced at low temperature, and did not show appreciable change as the temperature varied from 80 to 5°K. This result, similar to what was observed for the E_1 peaks of Ge[16], indicates that this structure is not simply due to band transitions. The strong temperature dependence together with the dependence on the carrier density seems to suggest that the structure may be due to excitonic effect. According to Herman et al.[4] the E_3 peak is due to M_1 and M_2 critical point transitions at Σ and Δ, and hence, based on the Toyozawa model,[17] hyperbolic excitons can exist in the E_3 peak. One may use the high dielectric constant of PbS to argue against the idea of excitons in PbS.[18] However, in our case, the excitons involving electrons in the high conduction bands may see a smaller effective dielectric constant than even the high-frequency dielectric constant ε_∞. The free carriers tend to screen the attractive interaction between electrons and holes, and this would explain why the excitonic effect decreases with higher carrier concentration in our observation.

In conclusion, we have shown that the wavelength modulation reflectivity spectra of PbS, PbSe, PbTe, and SnSe generally exhibit more detailed structure than ordinary reflectivity spectra. The spectra of all four compounds are similar. Assignment of the structure in the spectra is based on the recent pseudopotential calculations of Tsang and Cohen for PbTe. A fine structure in the E_3 peak of PbS was found

to depend on carrier concentration and strongly on temperature. It is proposed that this structure can be associated with a hyperbolic exciton.

ACKNOWLEDGEMENTS

We would like to thank Professor M. L. Cohen and Dr. Y. W. Tsang for letting us use the theoretical curve prior to publication and for helpful discussions.

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	PbTe		PbSe			PbS			SnSe	Critical Point Assignment (c)
	This paper	Other work	This Paper	Other work		This paper	Other work			
				(a)	(b)		(a)	(b)		
		1.24		1.53	1.59	1.9	1.85	1.85		$\Sigma(5\rightarrow6)$
E_1 region				1.78		2.15	1.98			$L(5\rightarrow7)$
						2.46				
							(a)			
	2.16(W)		1.97(W)			3.35	3.3			
	2.25(W)		2.18(W)						2.0	
									2.3	
			2.84(W)						2.6	$\Sigma(5\rightarrow7)$
E_2 region	2.36	(b)		(a)	(b)		(a)	(b)		
	2.56(W)	2.18	3.12	3.0	2.95	3.66	3.7	3.49	3.2	$\Delta(5\rightarrow6)$
				3.3		4.01	4.0			
				3.8		4.5	4.6			
						5.08				
		(b)		(a)	(b)			(b)		
E_3 region	3.47	3.34	4.47	4.6	4.65	5.31		5.27	4.3	$\Delta(4\rightarrow6)$
	4.83(W)		5.22			5.75(W)			5.58	$\Sigma(4\rightarrow7)$
	5.9									

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Note: Structures marked by (W) after them correspond to weak shoulders in the reflectivity spectrum

TABLE I

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‡ IBM Postdoctoral Fellow

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For SnSe, only measurements with E ⊥ C have been performed due to its layer structure.

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FIGURE CAPTIONS

Fig. 1. Reflectivity and logarithmic derivative of the reflectivity for PbS at T = 5°K.

Fig. 2. Reflectivity and logarithmic derivative of the reflectivity for PbSe at T = 5°K.

Fig. 3. Reflectivity and logarithmic derivative of the reflectivity for PbTe at T = 5°K.

Fig. 4. Reflectivity and logarithmic derivative of the reflectivity for SnSe at T = 5°K.

Fig. 5. Reflectivity and logarithmic derivative of the reflectivity for PbS at different temperatures, showing the fine structure at 5.08 eV.

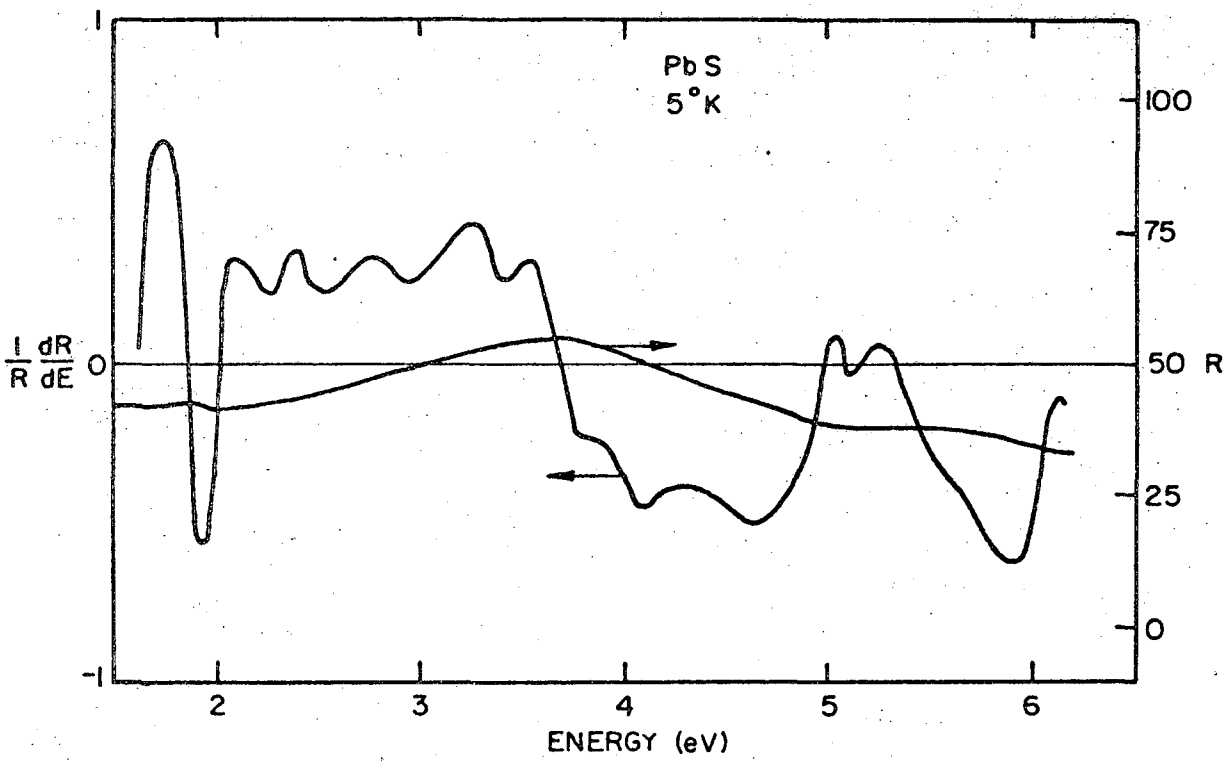

Fig. 1

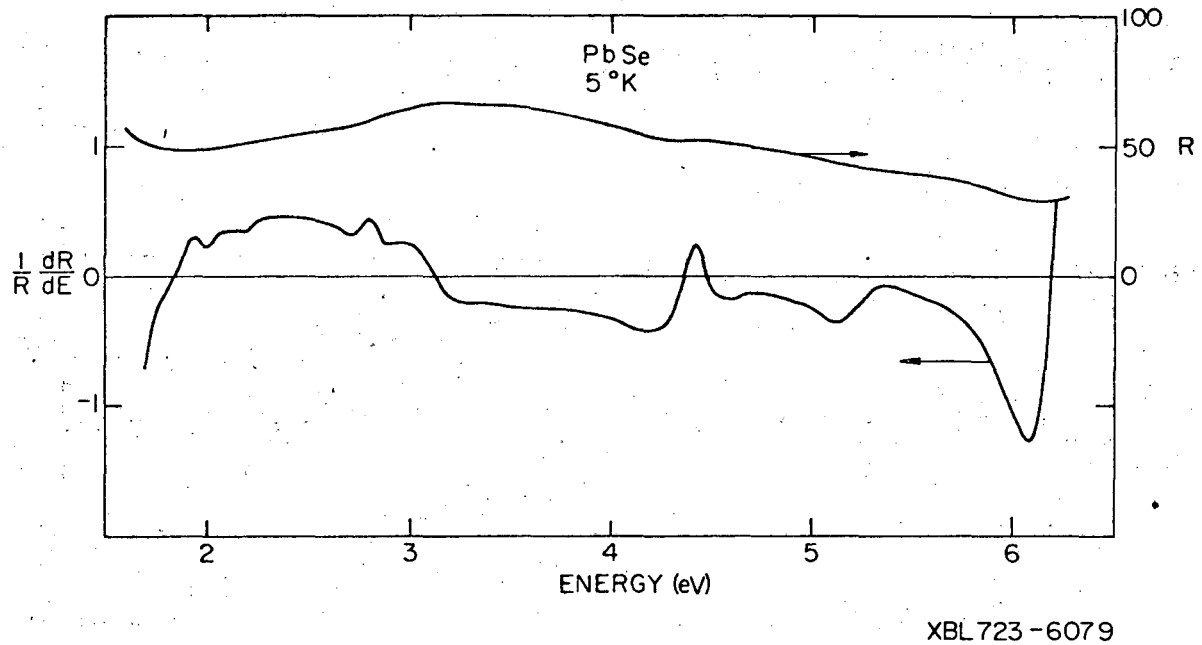
PbSe
5°K
100
50 R
0
1
0
-1
$\frac{1}{R}\frac{dR}{dE}$
2
3
4
5
6
ENERGY (eV)
XBL723-6079

Fig. 2

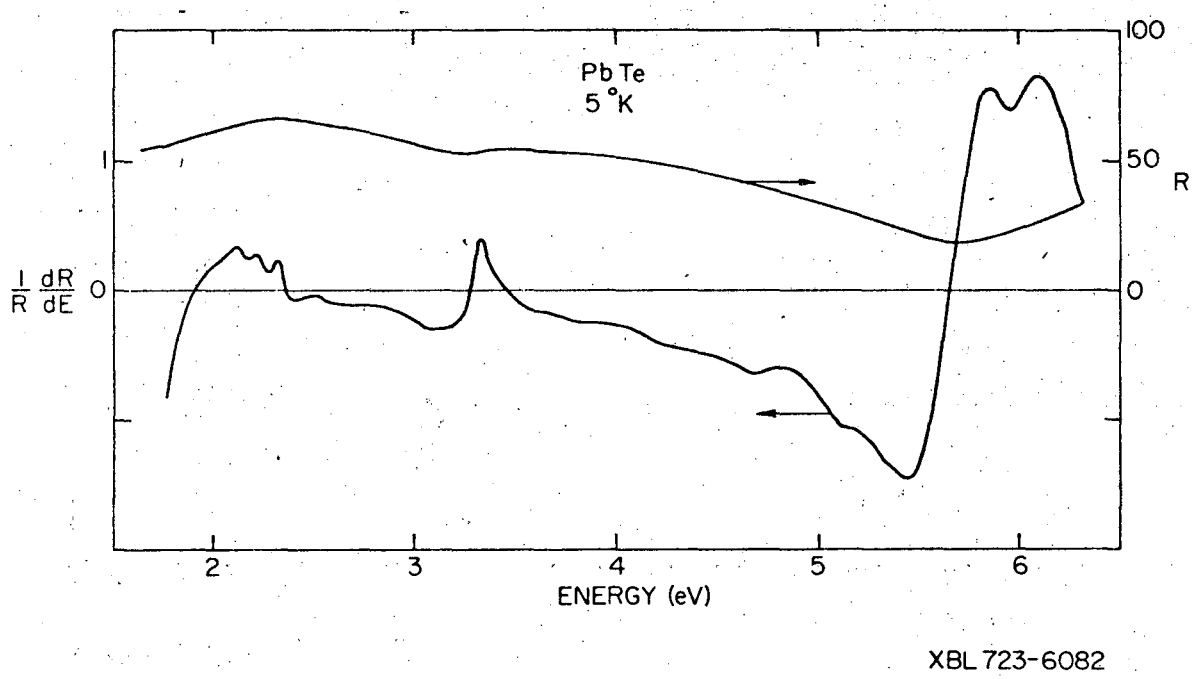
PbTe
5 °K
100
50
R
0
1
$\frac{1}{R}\frac{dR}{dE}$ 0
2
3
4
5
6
ENERGY (eV)
XBL 723-6082

Fig. 3

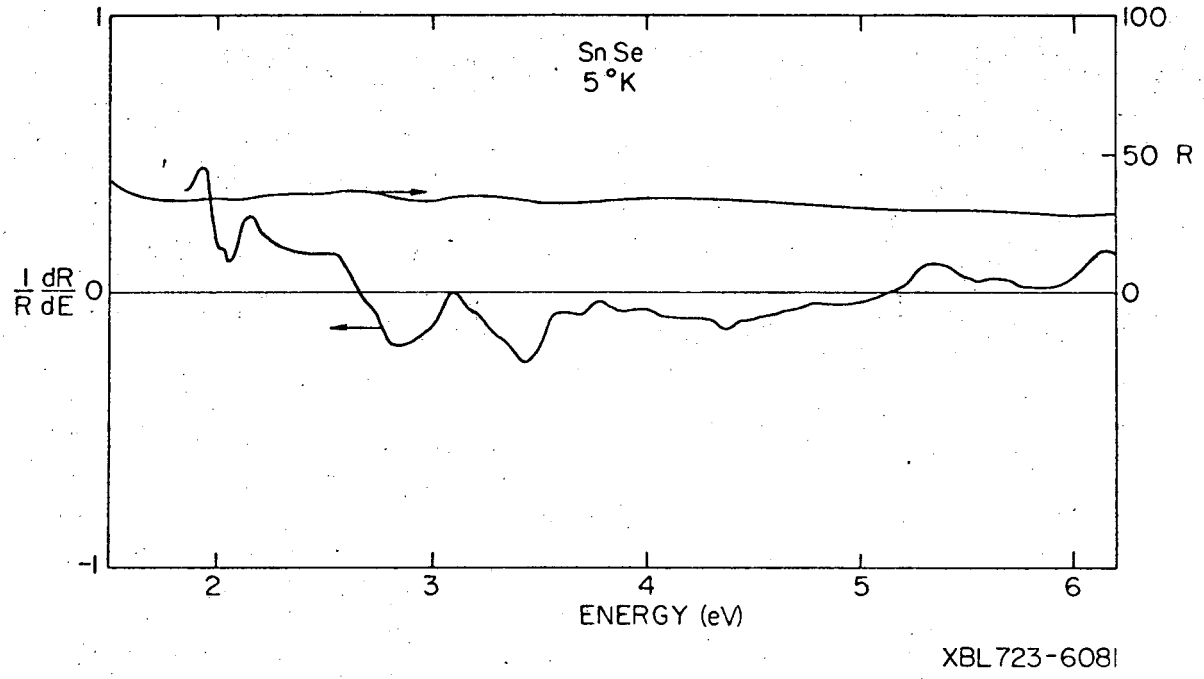
Sn Se
5 °K
1
0
-1
100
50 R
0
$\frac{1}{R}\frac{dR}{dE}$
2
3
4
5
6
ENERGY (eV)
XBL723-6081

Fig. 4

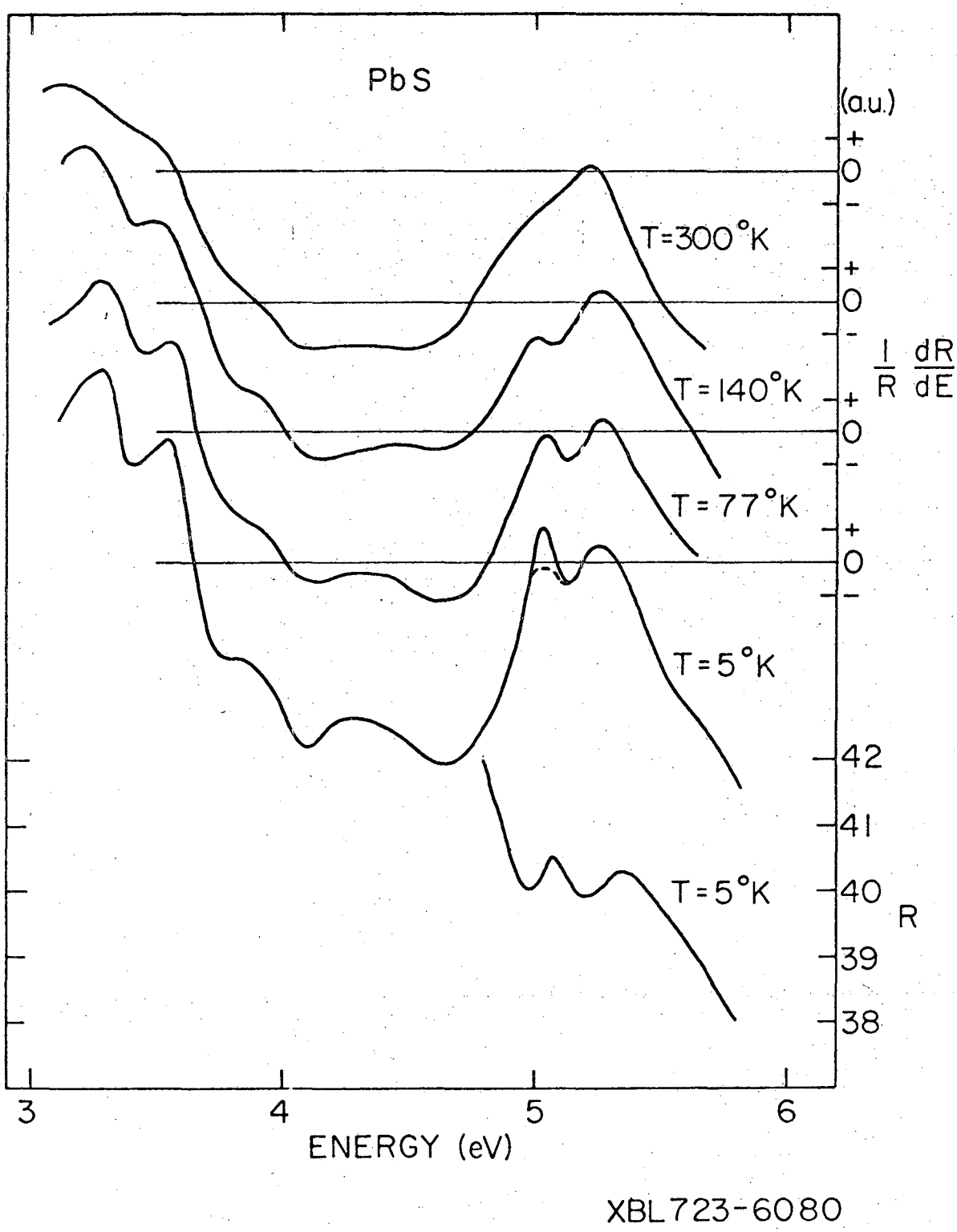
PbS
(a.u.)
+
0
-
T=300°K
+
0
-
T=140°K
+
0
-
T=77°K
+
0
-
T=5°K
T=5°K
42
41
40
39
38
R
1/R dR/dE
3
4
5
6
ENERGY (eV)
XBL723-6080

Fig. 5

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