FIZIKA VOLUME 10 SUPPLEMENT 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics of Condensed Matter, Kruševac, September, 18-22, 1978

RAMAN SPECTRA ANALYSIS OF V_2-VI_3 LAYERED SEMICONDUCTORS

P.M.Nikolić, [+]LJ.A.Miljković, B.Lavrenčič [*]

Institute of Physics, Electrotechnical Faculty Belgrade University, [+]Philosophy Faculty of Niš University and Institute "Jožef Štefan", Ljubljana[*], 11000 Beograd, P.O.Box 57, Yugoslavia.

ABSTRACT

Raman spectra were investigated for single crystal samples of bismuth and antimony chalcogenide V_2-VI_3 compounds. With the help of Adams tables Raman ($2A_{1g}+2E_g$) and infrared active ($2A_u+E_u$) modes were calculated. The obtained results were compared with the literature data which were in disagreement for infrared modes.

1. INTRODUCTION

There has been increased interest in the last several years in the lattice dynamics of bismuth and antimony chalcogenide compounds[1,2,3,4]. Their free carrier concentrations are very high ($\sim 10^{21}$ cm^{-3}) so there are some special experimental problems when reflectivity measurements are performed. Much earlier the specific heat and the thermal conductivity were investigated[5,6,7] in papers mainly refering to Bi_2Te_3 and Bi_2Se_3.

2. EXPERIMENTAL

Single crystal specimens of various V_2-VI_3 compounds were made using the standard Bridgeman technique. The samples could be easily cleaved, parallel to c plate, and shiny mirror like surfaces were obtained. The lattice parameters were determined using X-ray work. Then they were compared with the literature data so that the composition was confirmed.

Raman spectra were taken from freshly cleaved surfaces using an Ar^+ laser. Back scattered light was analysed by a double monochromator and a photon counting system.

The Raman frequencies (cm^{-1}) obtained for three V_2-VI_3 compounds are given in table 1.

TABLE 1. Experimental Raman frequencies (cm^{-1}) for Bi_2Se_3, Bi_2Te_3 and Sb_2Se_3

	A_{1g}	E_g	A_{1g}	E_g
Bi_2Se_3	193	136	88	39
Bi_2Te_3	159	115	73	50
Sb_2Se_3	190	118	83	45

We also tried to measure the infrared and far infrared reflectivity of all three compounds. In the far infrared region the reflectivity was above 90% so we could not detect any resonance. In the infrared range at about 900 cm^{-1} we observed a well exposed plasma effect for Bi_2Se_3, but not for the other two compounds.

3. ANALYSIS AND DISCUSSION OF RESULTS

The studied V_2-VI_3 chalcogenide compounds crystallise in a rhombohedral lattice which corresponds to a hexagonal cell with the space group D^5_{3d} ie $R\bar{3}m$. The atomic layers are periodically arranged along the c axis in five layers, for instance for Bi_2Te_3 this arrangement can be represented:

Te - Bi - Te - Bi - Te

These atoms have the following position using the well known Wyckoff notation

1 Te (a): 000
2 Bi (c):±(xxx) with x_{Bi}=o.392
3 Te (c):±(xxx) with x_{Te}=0.788

According to the literature data[4] there are 12 optical modes and among them four are Raman active ($2A_{1g}+2E_g$) and four are infrared active ($2A_{1u}+2E_u$).

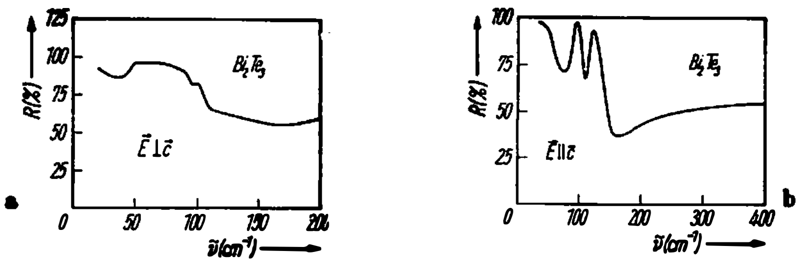
Using Adams[8] Newton tables for factor group and point group analysis we recalculated the number of infrared and Raman active modes. The Adams-Newton table for D^5_{3d} space group is given in table 2.

TABLE 2

	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
	$\alpha_{xx}+\alpha_{yy}$ α_{zz}	R_z	$\alpha_{xx}-\alpha_{yy}$ $\alpha_{xy}\alpha_{yz}\alpha_{zx}$	-	T_z $(E\|\|z)$	T_x, T_y $(E\perp z)$
2 V 2Bi 2c	1	0	1	0	1	1
1 $VI^{(1)}$ $2Se_1$ 1a	0	0	0	0	1	1
2 $VI^{(2)}$ $2Se_2$ 2c	1	0	1	0	1	1
N(tot)	$2A_{1g}$	-	$2E_g$	-	$3A_{2u}$	$3E_u$
$T_{acoustic}$	-	-	-	-	A_{2u}	$2E_u$
$T_{opt.}$	$2A_{1g}$				$2A_{2u}$	E_u

Using this table and knowing that there are three acoustic modes we calculated that there are four Raman active modes ($2A_{1g}+2E_g$) and only three infrared active modes ($2A_{2u}+E_u$).

Richter et al[4] also reported four infrared experimental optical modes which are shown in figures 1.a and 1.b for Bi_2Te_3. The reflectivity for $\vec{E}\perp\vec{c}$ does not show well exposed peaks.



(a) (b)

Figure 1. Far infrared reflectivity for Bi_2Te_3 (After W.Richter[4]).

According to our analysis only three modes should exist for both polarisations so we think that the reflectivity peak found at about 100 cm^{-1} is an artefact.

Our Raman scattering experimantal results given in table 1 are not in perfect agreement with Richter's[4] data either. First of all our data are more complete because Richter did non observe E_g modes at all. Secondly our frequencies are generally lower than those from literature. Here one should mention that Richter had to use an averaging device to get Raman peaks distinguished from the level of noise. We did not need to average our experimental results because the peaks were well exposed.

In conclusion one can say that V_2-VI_3 compounds with very high carrier concentrations are very difficult to study experimentally. Therfore discrepances in the results are not unexpected.

REFERENCES

1. Jenkins J.O., Rayne J.A,Ure R.W.,Phys.Rev.B5,3171,1972.
2. Unkelbach K.H. et al.Phys.Stat.Sol(b),60,k41,1973.
3. Köhler H., Becker R.C., Phys.Stat.Sol.(b),61,533,1974.
4. Richter W, Köler and Becker C.R.,Phys.Stat.Sol.(b),84,619,1977.
5. Satterthwaite C.B., Ure R.W.,Phys.Rev.108,1164,1957.
6. Goldsmid H.J., Proc.Phys.Soc.72,117,1958.
7. Walker P.A., Proc.Phys.Soc.,76,113, 1960.
8. Adams D.M., Newton D.C., Tables for factor group and point group analysis, Beckman, Croydon,1970.