Proc. XIX International School of Semiconducting Compounds, Jaszowiec 1990

AN INVESTIGATION OF OPTICAL VIBRATIONS IN Zn_3P_2*

J. MISIEWICZ,
Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

J.M. WROBEL† AND B.P. CLAYMAN
Department of Physics, Simon Fraser University, Burnaby, B.C. V5A1S6, Canada

(Received August 8, 1990)

Reflectivity and transmittivity spectra of Zn_3P_2 in the far infrared region were measured at several temperatures. Raman scattering spectra at 295 K were also measured. Results of these measurements were interpreted in terms of one-phonon and multi-phonon transitions.

PACS numbers: 63.20.-e, 78.30.Hv

1. Introduction

Zn_3P_2 is relatively little known but interesting compound due to both its application and its basic properties. Till now, only a few papers have been published in which the lattice modes of Zn_3P_2 were investigated [1–5].

TABLE I

Zone center infrared active phonons in Zn_3P_2 (in cm^{-1}).

Temperature 295 K								
TO	44	64	70.5	78	86	103	168.5	
LO	57	66	71	78.5	89	104.5	169	
TO	182.5	246	285	309.5	338	351		
LO	184	276	307	320	345	360		
Temperature 10 K								
TO	46.5	62	71	77	87.5	104	110.5	170.5
LO	58.5	63.7	71.5	78	94	105.5	112.5	172
TO	184	243	285	301.5	312.5	331.5	340	354
LO	186	274	309.5	301.5	323	333	348.5	363

*This work was supported in part by CPBP 01.04.I.2.7 and by a grant from the Natural Sciences and Engineering Council of Canada.

†Department of Physics, University of Missouri, Kansas City, M064110, USA.

Zn_3P_2 crystal structures is tetragonal and described by space group D_{4h}^{15} [6]. The unit cell is composed of 40 atoms producing 120 phonon branches, 117 optical and 3 acoustic modes. Optical measurements were performed on high-resistivity, low concentration samples ($p < 10^{15}\,\mathrm{cm}^{-1}$). Details of the experimental techniques as well as sample preparation method are presented elsewhere [4–5].

2. Results and discussion

Figure 1(a) presents reflectivity spectra in the reststrahlen region. As expected, a complicated structure is observed. In the first region (40–115 cm^{-1}) six peaks are visible at room temperature; their structure becomes clearer at low temperature. A relatively broad peak around 100 cm^{-1} splits into two independent ones. Very prominent features are located within 240–360 cm^{-1}. Five maxima are visible at 295 K and seven more sharpened at low temperature. Between these two ranges a relatively flat plot in the 150–180 cm^{-1} energy range can be found. Lowering the temperature causes two distinct maxima to appear.

TABLE II

Infrared overtones at Γ calculated from the data of Table I compared with transitions observed in VV Raman scattering (in cm^{-1}).

IR	88	128	141	156	172	206	337	365	492
calculated	114	122	142	157	178	209	338	368	
Raman									
observed	86.5	125	144	159	171	212	340	363	499

Group theory analysis gives the representation of infrared active one-phonon modes as $\Gamma^{\mathrm{IR}} = 9\Gamma_2^- + 15\Gamma_5^-$, so we should expect 9 single one-phonon and 15 double degenerated ones as infrared active. Performing Kramers-Kronig analysis of reflectivity spectra we determined energies of TO and LO infinite wavelength phonons (Table I). To explain the number of observed experimentally one-phonons, it is necessary to assume that some of theoretically degenerated modes (Γ_5^-) are split.

Transmittance spectra at several temperatures are presented in Fig. 1(b). From the temperature dependence of transmittance spectra we may expect that transitions located at approx. 500, 525, 560, 590, 625, 640, 660, 690 cm^{-1} are connected with sums of one-phonon transitions. A more detailed analysis of the temperature dependence of reflectivity and absorption spectra will be published [7]. An analysis of the Raman tensor shows that in the VV configuration $9\Gamma_1^+$ and $10\Gamma_3^+$ one-phonons should be visible and $16\Gamma_5^+$ doubly degenerated ones at VH configuration. Figure 2 presents Raman scattering spectra at room temperature. More prominent features, denoted in this figure by arrows, we connect with one-phonon transitions. The weaker ones we explain as multiphonon transitions.

Similarly to reflectivity data, it seems to be necessary to assume that some of theoretically degenerated modes (Γ_5^+) are split. Zn_3P_2 crystal possesses inversion symmetry, so due to mutual exclusion rule the same transitions should not be observed in infrared and Raman spectra. Almost all, from the total number

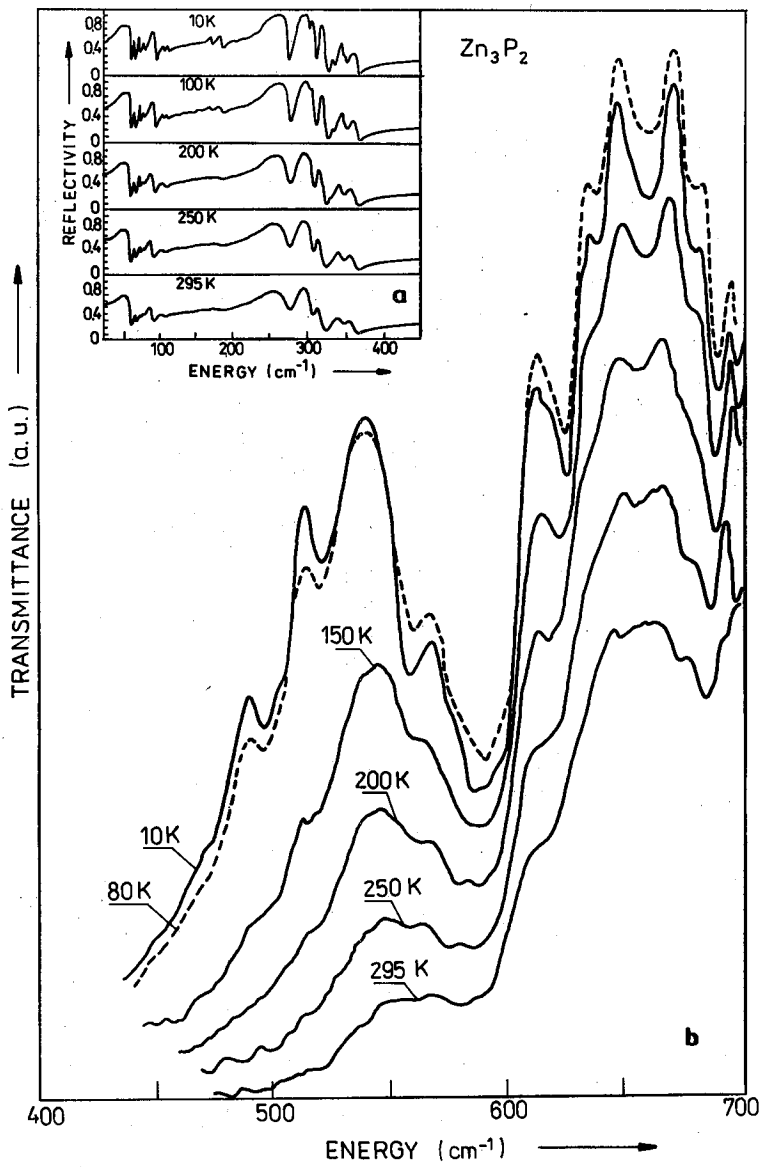

Fig. 1. (a) Reflectivity spectra of Zn_3P_2 within reststrahlen region as a function of temperature; (b) transmittance spectra of Zn_3P_2 at several temperatures.

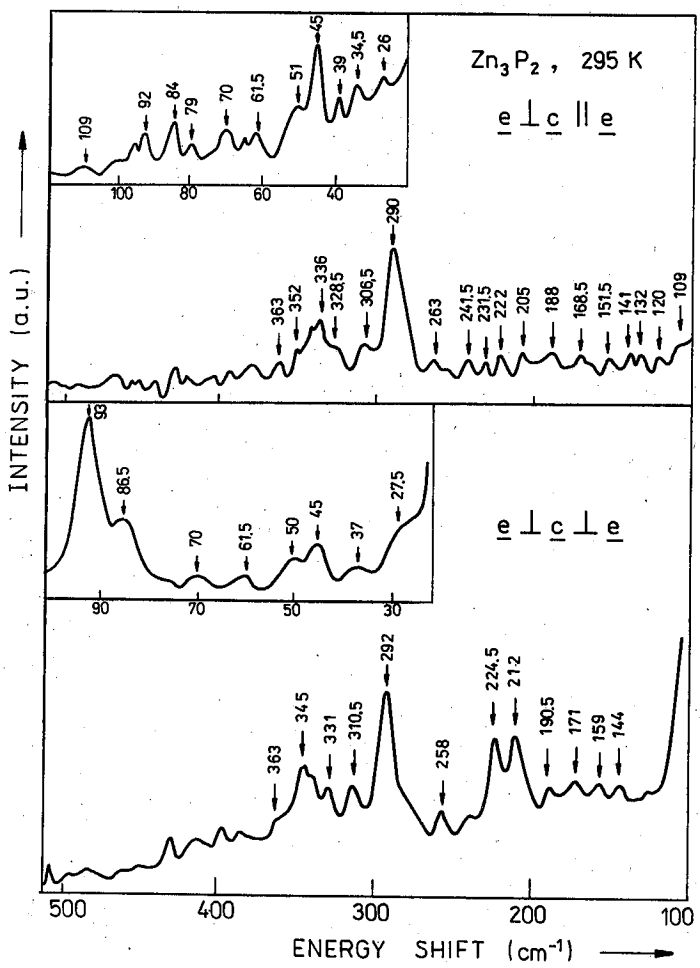

Fig. 2. Raman scattering spectra of Zn_3P_2 at room temperature in two configurations: $e \perp c \parallel e$ (VH) and $e \perp c \perp e$ (VV); arrows denote energies of one-phonon transitions.

of one-phonon energies observed in Raman scattering and determined from reflectivity spectra ones are different (compare the data from Tab. I and Fig. 2), so this rule seems to be well satisfied. Group theory predicts no overtones of infrared active phonons at Γ allowed in infrared but they should be Raman active in VV configuration (Table II).

Understanding of the phonon spectra in Zn_3P_2 needs more investigations e.g. temperature dependence of Raman scattering, detailed study of multiphonon absorption as a function of temperature as well as neutron scattering experiments.

Acknowledgments

The authors are indebted to Dr D. Heiman, of the Francis Bitter National Magnet Lab at MIT (USA), who made it possible to perform the Raman scattering measurements.

References

[1] R.S. Radautsan, N.N. Syrbu, J.J. Nebola, V.J. Volodina, *Sov. Phys. Solid State* **19**, 1290 (1977).

[2] J. Misiewicz, B. Sujak–Cyrul, A. Bartczak, *Solid State Commun.* **58**, 677 (1986).

[3] J. Misiewicz, J.M. Wrobel, B.P. Clayman, F. Królicki, in *Proc. 16th School Phys. Semicond. Comp. Jaszowiec 1987, Acta Phys. Pol.* **A73**, 407 (1988).

[4] J. Misiewicz, J.M. Wrobel, B.P. Clayman, *Solid State Commun.* **66**, 747 (1988).

[5] J. Misiewicz, *J. Phys. Condens. Matter* **1**, 9283 (1989).

[6] M.V. Stackelberg, P. Paulus, *Z. Phys. Chem.* **28B**, 427 (1935).

[7] J. Misiewicz, J.M. Wrobel, B.P. Clayman, to be published.