# Study of Zone Center Phonons in $CdWO_4$

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## Abstract

*Raman and the infrared wave numbers in $CdWO_4$ in monoclinic phase having space group P2/c, have been investigated by applying short-range force constant model. The calculation of zone center phonons has been made with eight stretching and five bending force constants. The calculated Raman and infrared wavenumbers are in good agreement with the observed ones. The potential energy distribution has also been investigated for determining the significance of contribution from each force constant toward the Raman and the infrared wave numbers.*

## 1. Introduction

Metal tungstates has been studied due to many applications [1-2]. Tungstates $AWO_4$ crystallize in either the tetragonal scheelite structures or the monoclinic wolframite structures depending on the size of cation A i.e tungstates of relatively large bivalent cations crystallize in scheelite structure and of smaller bivalent cations exhibit the wolframite structure. $CdWO_4$ has the wolframite crystal structure.

Phonon properties of $CdWO_4$ are very important and have not been studied widely. R.Lacomba et al. [3] had studied $CdWO_4$ compound with the help of Raman spectroscopy and density functional theory. In infrared modes they have calculated two frequencies which are very near to each other i.e 252.9 $cm^{-1}$ and 255.1 $cm^{-1}$ by ab-initio method which is not generally possible in experiment. Also there is not a good agreement between their calculated values and experimentally observed higher infrared modes. Hence in this paper we have presented the calculated values of Raman and infrared modes using short range force constant model in P2/c structure with eight stretching and five bending force constants, which are in very good sync with the experimental results. Also all the infrared modes have been assigned properly. The PED (potential energy distribution) has also been investigated which determined the contribution of each force constant towards the Raman and infrared wavenumbers.

## 2. Structure

$CdWO_4$ crystallizes in a monoclinic structure. Lattice parameters are a = 5.028 Å, b = 5.862 Å, c = 5.067 Å, β=91.50°, V=149.3 $Å^3$ and Z=2 [1]. Atomic co-ordinates are taken from the work of J. Macavei et al. [4]. The total no. of zone center phonon modes present for each species of space group is Ƭtotal =8 $A_g$ +10 $B_g$ +8 $A_u$+10 $B_u$. Out of these normal modes, $1A_u$+$2B_u$ are acoustical and rest are optical modes.Out of thoes 8 $A_g$ + $10B_g$ are Raman active and 7 $A_u$ + $8B_u$ are infrared active.

## 3. Theory

The frequency of normal mode vibrations is determinate by solving the secular equation using Wilson's GF matrix method [5]. If F is the potential energy matrix and G is the inverse kinetic energy matrix, then the secular equation can be written as $\det | FG - E\lambda | = 0$, where $\lambda = 4\pi^2c^2\nu^2$ and E is the unit matrix, c is velocity of light and ν is the wave number. The stretching forces between two atoms were assumed to be obeying the Hook's law. The input parameters used for the calculation are the lattice parameter, masses of the atoms, symmetry coordinates [2] and the available Raman and infrared wavenumbers [3,6].

## 4. Results and discussion

In this work we have calculated the Raman and infrared wavenumbers given in Table 1 by using force constants (N/cm) given below
K1(W-O2):3.681; K2(W-O1):1.775; K3(Cd-O1): 0.669; K4(W-O1):1.102; K5(Cd-O2):0.400; K6(Cd-

O2): 0.351; K7(O2-O2):0.117; K8(W-Cd):2.509; H1(O1-Cd-O2): 0.277; H2(O1-W-O2):0.089; H3(O1-W-Cd):0.452; H4(W-O1-W):1.609; H5(Cd-W-O1):0.593.

The calculated Raman and infrared modes are compared with the experimently results of Lacomba et al.[3] and Daturi et al.[6]. Higher infrared modes calculated by Lacomba et al. [3] are not in good agreement with the experimental values [6] of the infrared modes. But it is clear from Table 1 that present calculations provide a very good agreement with the experimental results of the Raman and the infrared modes. It can be seen from Table 1 that our calculated results are better than the theoretically calculated results of Lacomba et al.[3]. The PED for each mode has also investigated in this work. The interpretations drawn from the PED are described below.

For the high frequency mode i.e. 827 $cm^{-1}$ of Ag mode, 830 $cm^{-1}$ of Bg mode, 834 $cm^{-1}$ of Au mode, 876 $cm^{-1}$ of Bu mode, the force constant W-O1-W contributes in a dominant way. For frequencies 700 $cm^{-1}$ of Ag, 699 $cm^{-1}$ of Bg , 699 $cm^{-1}$ of Au and 698 $cm^{-1}$ of Bu , W-O2 force constant was found as leading force constant.

From theoretical calculations, W-O1 force constant plays an important role for frequencies 493 $cm^{-1}$ of Ag, 508 $cm^{-1}$ of Bg, 500 $cm^{-1}$ of Au and 508 $cm^{-1}$ of Bu.

Force constant Cd-W-O1 plays a very significant role in frequencies 388 $cm^{-1}$ of Ag, 392 $cm^{-1}$ of Bg, 383 $cm^{-1}$ of Au and 376 $cm^{-1}$ of Bu. Force constant W-Cd is of utmost importance for frequencies 291 $cm^{-1}$ of Ag, 278 $cm^{-1}$ of Bg, 309 $cm^{-1}$ of Au and 310 $cm^{-1}$ of Bu.

Frequencies 244$cm^{-1}$ of Ag, 245 $cm^{-1}$ of Bg, 232 $cm^{-1}$ of Au and 244 $cm^{-1}$ of Bu are mainly contributed by Cd-O2 force constant. For lower frequencies i.e 125 $cm^{-1}$ of Ag, 74 $cm^{-1}$ of Bg, 127 $cm^{-1}$ of Au and 83 $cm^{-1}$ of Bu force constant O1-W-O2 dominates.

Daturi et al [6] had observed experimentally only seven frequencies of Bu mode. The present calculation has mentioned the remaining one frequency i.e. 310 $cm^{-1}$ of Bu mode which is found to be in agreement with the experimental result of similar compounds [7] . Lacomba et al had not calculated frequency of this range in Bu mode.

It is important to mention that the bond between W – Cd is very important for explaining the lower set of frequencies. When this bond is not considered the lower frequencies of Bu mode become very small in comparison to the experimental value.

Table 1. Calculated and observed Raman and infrared active zone center modes ($cm^{-1}$) for $CdWO_4$

| Species | Exp.[3] | Exp.[6] | Present cal. | Cal.[3] |
|---|---|---|---|---|
| Ag | 897 | 896 | 827 | 864 |
| | 707 | 706 | 700 | 684 |
| | 546 | 547 | 493 | 530 |
| | 388 | 387 | 388 | 357 |
| | 306 | 307 | 291 | 287 |
| | 229 | 229 | 244 | 220 |
| | 177 | 177 | 150 | 177 |
| | 100 | 99 | 125 | 97 |
| Bg | 771 | 771 | 830 | 742 |
| | 688 | 687 | 699 | 655 |
| | 514 | 514 | 508 | 490 |
| | 352 | 351 | 392 | 338 |
| | 269 | 269 | 278 | 252 |
| | 249 | 248 | 245 | 238 |
| | 148 | 148 | 191 | 142 |
| | 134 | 133 | 153 | 126 |
| | 118 | 117 | 119 | 111 |
| | 78 | 77 | 74 | 67 |
| Au | - | 835 | 834 | 839 |
| | - | 693 | 699 | 627 |
| | - | 455 | 500 | 471 |
| | - | 354 | 383 | 379 |
| | - | 310 | 309 | 322 |
| | - | 230 | 232 | 270 |
| | - | 131 | 127 | 121 |
| | - | 0.0 | 0.0 | 0.0 |
| Bu | - | 884 | 876 | 744 |
| | - | 595 | 698 | 524 |
| | - | 510 | 508 | 421 |
| | - | 408 | 376 | ---- |
| | - | ---- | 310 | ---- |
| | - | 260 | 244 | 253,255 |
| | - | 161 | 165 | 145 |
| | - | 107 | 83 | 105 |
| | - | 0.0 | 0.0 | 0.0 |
| | - | 0.0 | 0.0 | 0.0 |



## 5. References

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