Lattice Dynamical Investigations for Insulating Cs_2CdBr_4 in Orthorhombic Phase

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Abstract

Cs_2CdBr_4 is widely used for acousto-optic devices by operating the laser radiation in a wide range of spectra. It undergoes several successive phase transitions upon cooling. Low temperature phases of Cs_2CdBr_4 were found to be non-polar ferro-elastic but at room temperature and atmospheric pressure, it crystallizes in orthorhombic phase having space group Pnma. In the present paper, we have applied a short-range force constant model to calculate the Raman and infrared wave numbers of Cs_2CdBr_4 in the orthorhombic phase at zone centre. The calculated Raman and infrared wave numbers are found to be in a satisfactory match with the experimentally observed Raman and infrared wave numbers. Calculations on the zone centre phonons have been made with three bending and thirteen stretching force constants. We have also calculated the significant contribution of each force constant towards the Raman and the infrared wave numbers by investigating the potential energy distribution.

"1. Introduction"

Cs_2BX_4 (B= Hg, Cd; X= Cl, Br) crystals belong to the halide family with the β-K_2S0_4 structure [1]. Cs_2CdBr_4 crystals of this family possess high acousto-optic figure of merit and hence were found to be good acousto-optic material [2]. At room temperature, Cs_2CdBr_4 crystallizes in orthorhombic phase having space group Pnma with four formula units per unit cell. Upon cooling, it undergoes several successive phase transitions like the other compounds of this family and the low temperature phases of Cs_2CdBr_4 were found to be non-polar ferro-elastic (centro-symmetric) [3].

Shchur et al. [4] assigned some of the Raman and infrared modes at zone centre for the compound Cs_2CdBr_4. Therefore, in the present paper, we have calculated and assigned all the Raman and infrared zone centre modes of Cs_2CdBr_4 in their orthorhombic phase having space group Pnma using normal coordinate analysis based on G-F matrix method. The so calculated Raman and infrared wave numbers agrees well with the available experimental results [4].

"2. Structure"

Cs_2CdBr_4 undergoes several successive phase transitions upon cooling and the low temperature phases of Cs_2CdBr_4 were found to be non-polar ferro-elastic [3]. Cs_2CdBr_4 exhibits the same crystal structure as does the β-K_2S0_4 [1] at room temperature and crystallizes in orthorhombic structure having space group Pnma (No. 62-D_{2h}^{16}) having four formula units. The unit cell contains four $CdBr_4^{2-}$ tetrahedra and eight corresponding Cs^+ ions. The lattice parameters (in Å) for Cs_2CdBr_4 are a = 10.235, b = 7.946, c = 13.977 [4]. The site symmetry, atomic coordinates [4] are given in Table 1. Using factor group analysis, Phonon contribution of each atom at Γ point for Cs_2CdBr_4 is given below:

$\Gamma_{Cs1} = \Gamma_{Cs2} = \Gamma_{Cd} = \Gamma_{Br1} = \Gamma_{Br2} = 2A_g + 2B_{2g} + B_{3g} + B_{1g} + A_u + B_{2u} + 2B_{3u} + 2B_{1u}$

$\Gamma_{Br3} = 3A_g + 3B_{2g} + 3B_{3g} + 3B_{1g} + 3A_u + 3B_{2u} + 3B_{3u} + 3B_{1u}$.

So the total number of zone centre modes present for each species of the space group will be

$\Gamma = 13A_g + 8B_{1g} + 13B_{2g} + 8B_{3g} + 8A_u + 13B_{1u} + 8B_{2u} + 13B_{3u}$.

Out of these, $1B_{1u}$, $1B_{2u}$, $1B_{3u}$ are acoustical, $13A_g$, $8B_{1g}$, $13B_{2g}$ are Raman active, $12B_{1u}$, $7B_{2u}$, $12B_{3u}$ are infrared active, and $8A_u$ are silent modes.

"Table 1. Site symmetry, atomic coordinates"

Atom	Site	x/a	y/b	z/c
Cs_1	4c	0.1236	0.25	0.0960
Cs_2	4c	-0.0170	0.25	0.6762
Cd	4c	0.2225	0.25	0.4236
Br_1	4c	-0.0243	0.25	0.4119
Br_2	4c	0.3204	0.25	0.5926
Br_3	8d	0.3209	-0.0094	0.3426

"3. Theory"

Lattice dynamical calculations on Cs_2CdBr_4 in its orthorhombic phase have been carried out by applying Wilson GF matrix method [4]. Wilson's method of obtaining the normal frequencies and the normal coordinates of any system is to obtain eigen values and eigen vectors of the matrix GF, where G is the inverse kinetic energy matrix that involves the masses and certain spatial relationships of the atoms and consequently, brings the kinetic energies into the equation, and F is the potential energy matrix of the system. F matrix has been constructed using short range force constant model. The magnitude of short range forces generally diminishes after the second neighbor, therefore, interatomic interactions up to only second neighbor are considered in the present calculation. In the present work, two types of short range forces are considered, viz, stretching forces (K_1–K_{13}) and bending forces (H_1–H_3) in Table 2. To account for the transverse vibrations in the lattice, we have also included the bending forces along with stretching forces for the present calculation.

The secular equation for calculating the normal frequencies is given as

$$\text{Det}\,[GF - E\lambda] = 0 \qquad (1)$$

Here, E is the unit matrix with the same order as that of the G and F matrices, and $\lambda = 4\pi^2 c^2 v^2$, where c is the light velocity and v is the wave number.

The system such as crystal lattice possesses the translational symmetry. Therefore, the G or F matrix of infinite order will be repetition of sub-matrices of a finite size. By summing these sub-matrices multiplied by a proper set of phase factors, the G or F matrix can be constructed. These phase factors are unity for the lattice vibrations which are active in the infrared or Raman region Therefore, G or F matrix for these optically active vibrations can be obtained by adding the G or F matrix for a Bravais cell to the sum of all the G or F matrices representing the interactions between the Bravais cell and the neighboring Bravais cells.

The input parameters used for the whole calculation are the lattice parameters [4], masses of the atoms, fractional coordinates of the atoms [4], calculated symmetry coordinates [6] and the experimentally available Raman and infrared wavenumbers [4]. Also, thirteen stretching force constant for the nearest neighbors, Cd–Br_2, Cd–Br_1, Cd–Br_3, Cs–Br_3, Cs–Br_2, Cs–Br_2, Cs–Br_3, Cs–Br_1, Cs–Br_3, Cs–Br_2, Cs–Br_3, Cs–Br_2, and Cs–Br_1 and three bending force constants for angles, Br_1–Cd–Br_3, Br_2–Cd–Br_3, and Br_3–Cd–Br_3 are used in the calculation. The force constants were evaluated by fitting the observed 23 Raman modes and 27 infrared modes [4] and their values are given in Table 2.

"4. Results and discussion"

"Table 2. Stretching and bending force constants and their corresponding values"

Force constant	Between atoms	Interatomic distance (Å)/angle	Force constant Values (N/cm)
K_1	Cd–Br_2	2.5312	0.929
K_2	Cd–Br_1	2.5340	0.859
K_3	Cd–Br_3	2.5752	0.620
K_4	Cs–Br_3	3.6184	0.596
K_5	Cs–Br_2	3.6348	0.206
K_6	Cs–Br_2	3.6456	0.180
K_7	Cs–Br_3	3.6604	0.117
K_8	Cs–Br_1	3.6949	0.091
K_9	Cs–Br_3	3.8188	0.103
K_{10}	Cs–Br_2	4.0144	0.409
K_{11}	Cs–Br_3	4.0647	0.077
K_{12}	Cs–Br_2	4.0717	0.121
K_{13}	Cs–Br_1	4.1809	0.068
H_1	Br_1–Cd–Br_3	110.718	0.022
H_2	Br_2–Cd–Br_3	105.210	0.028
H_3	Br_3–Cd–Br_3	106.340	0.042

"Table 3. Comparison between the calculated and experimental frequencies and corresponding PED"

Species	Present Frequencies (cm^{-1})	Experimental frequencies (cm^{-1}) [4]	Potential Energy Distribution (PED)
A_g,1	204	194	K_1- 63%, K_2- 29%
A_g,2	193	-	K_2- 15%, K_3- 39%, K_4- 36%
A_g,3	166	173	K_1- 16%, K_2- 47%, K_4- 28%
A_g,4	109	-	K_3- 28%, K_6-21%, K_7- 24%
A_g,5	94	-	K_6- 36%, K_{12}- 26%
A_g,6	81	81	K_3- 14%, K_8- 11%, K_9- 22%
A_g,7	69	69	K_5- 30%, K_{12}- 16%, H_3- 29%
A_g,8	66	-	K_{11}- 62%
A_g,9	47	42	K_8- 55%, K_{13}- 12%
A_g,10	43	-	(K_7, H_2)- 14%, K_9- 24%, (K_{10}, K_{12})- 12%
A_g,11	32	-	K_7- 24%, H_1-27%
A_g,12	26	28	(K_5, K_6)- 20%, H_2- 18%
A_g,13	15	21	K_{11}- 19%, H_3- 38%
B_{2g},1	204	-	K_1- 63%, K_2- 30%
B_{2g},2	193	187	K_2- 14%, K_3- 40%, K_4- 36%
B_{2g},3	165	172	K_1- 16%, K_2- 47%, K_4- 28%
B_{2g},4	103	-	K_3- 17%, K_6-38%, K_7- 14%, K_{12}- 11%
B_{2g},5	92	-	K_3- 31%, K_4- 17%, K_9- 12%
B_{2g},6	88	-	K_7- 21%, K_9- 26%, K_{12}- 17%
B_{2g},7	69	65	K_5- 21%, K_{11}- 36%
B_{2g},8	64	-	K_5- 31%, K_8- 18%, K_{11}- 26%
B_{2g},9	51	52	K_5- 10%, K_8- 33%, H_1- 18%
B_{2g},10	47	-	K_6- 17%, K_{12}- 30%,H_3- 28%
B_{2g},11	40	-	K_7- 28%, K_9- 23%, K_{10}- 13%
B_{2g},12	25		K_7- 18%, H_2- 38%, H_3- 17%
B_{2g},13	08	22	K_9- 11%, K_{11}- 22%, K_{12}- 14%, H_3- 18%
B_{3g},1	185	181	K_3- 66%, K_4- 32%

B_{3g},2	168	172	K_{10}- 96%
B_{3g},3	109	-	K_3- 19%, K_4- 43%, K_7- 12%
B_{3g},4	68	68	(K_7,K_9)- 31%, H_2- 17%
B_{3g},5	61	-	K_9- 12%, K_{13}- 68%
B_{3g},6	45	43	K_{11}- 58%, K_{13}- 14%
B_{3g},7	33	-	K_7- 16%, H_1- 60%
B_{3g},8	15	22	(K_9, H_1)- 26%, K11- 19%, H_2- 17%
B_{1g},1	185	183	K_3- 66%, K_4- 32%
B_{1g},2	168	174	K_{10}- 96%
B_{1g},3	102	-	K_3- 24%, K_4- 55%
B_{1g},4	79	-	K_7- 40%, K_9- 23%, K_{13}- 21%, H_1- 14%
B_{1g},5	61	66	K_7- 11%, K_9- 19%, K_{13}- 52%
B_{1g},6	49	43	K_{11}- 64%, H_2- 11%, H_3- 17%
B_{1g},7	22	39	K_7- 45%, K_9- 50%
B_{1g},8	16	21	K_{11}- 24%, H_2- 65%
B_{2u},1	185	183	K_3- 66%, K_4- 32%
B_{2u},2	168	-	K_{10}- 96%
B_{2u},3	101	-	K_3- 25%, K_4- 55%
B_{2u},4	80	70	K_7- 40%, K_9- 26%, K_{13}- 17%, H_1- 14%
B_{2u},5	63	61	K_9- 20%, K_{13}- 54%, H_2- 12%
B_{2u},6	45	47	K_9- 80%, H_2- 12%
B_{2u},7	31	34	K_7- 39%, K_9- 12%, H_2- 33%
B_{2u},8	0	0	-
B_{3u},1	204	198	K_1- 65%, K_2- 26%
B_{3u},2	194	191	K_2- 21%, K_3- 37%, K_4- 25%
B_{3u},3	163	-	K_1- 19%, K_2- 45%, K_4- 30%
B_{3u},4	109	-	K_3- 37%, K_4- 11%, K_7- 19%
B_{3u},5	100	-	K_5- 21%, K_6- 37%, K_{12}- 12%
B_{3u},6	80	85	K_6- 12%, K_7- 19%, K_9- 23%, K_{12}- 16%, H_3- 18%
B_{3u},7	72	75	K_5- 10%, (K_9, K_{11})- 21%, H_2- 14%
B_{3u},8	64	65	K_{11}- 46%, K_{12}- 18%, H_3- 19%
B_{3u},9	50	49	K_8- 62%
B_{3u},10	44	43	K_5- 11%, K_9- 17%, H_1- 14%, H_2- 24%
B_{3u},11	29	32	(K_{11}, H_1)- 11%, H_3- 41%
B_{3u},12	13	-	K_6- 11%, K_7- 17%, H_1- 44%, H_2- 13%
B_{3u},13	0	0	-
B_{1u},1	204	199	K_1- 65%, K_2- 26%
B_{1u},2	194	184	K_2- 22%, K_3- 38%, K_4- 34%
B_{1u},3	163	173	K_1- 20%, K_2- 44%, K_4- 30%
B_{1u},4	102	-	K_3- 45%, K_4- 21%, K_5- 17%
B_{1u},5	101	-	K_6- 41%, K_7- 17%, K_{12}- 16%
B_{1u},6	83	-	K_6- 16%, K_7- 23%, K_9- 31%, H_3- 15%
B_{1u},7	70	71	K_5- 18%, K_{11}- 29%, K_{12}- 23%
B_{1u},8	66	64	K_9- 17%, K_{11}- 31%
B_{1u},9	54	58	K_5- 11%, K_8- 47%, H_1- 17%
B_{1u},10	41	44	K_6- 21%, K_8- 12%, K_{12}- 10%, H_2- 14%
B_{1u},11	33	31	H_2- 20%, H_3- 38%
B_{1u},12	26	-	K_5- 22%, K_7- 21%, H_2- 16%, H_3- 12%
B_{1u},13	0	0	-

The force constants used in the calculation for the Raman and infrared modes are given in Table 2. The calculated values are compared with the experimentally determined Raman and infrared modes by Shchur et al. [4] in Table 3. It is confirmed from the Table 3 that there is good agreement between the theory and the experiment for all the Raman as well as infrared modes. The potential energy distribution (PED) for each mode is also investigated to determine the contribution of different force constants to various frequencies and the interpretations drawn from the PED are described below.

It is clear from the potential energy distribution that the force constants K_1 to K_4 contribute significantly to the higher frequencies of each mode. K_1 (Cd–Br_2) and K_2 (Cd–Br_1) are the dominating force constants for the highest frequency of the modes which are 13 in number (i.e. 204 cm^{-1} of A_g, 204 cm^{-1} of B_{2g}, 204 cm^{-1} of B_{3u}, 204 cm^{-1} of B_{1u}) and K_2 (Cd–Br_1), K_3 (Cd–Br_3) and K_4 (Cs–Br_3) are dominant force constants for the next higher frequency of these modes (i.e. 193 cm^{-1} of A_g, 193 cm^{-1} of B_{2g}, 194 cm^{-1} of B_{3u}, 194 cm^{-1} of B_{1u}) and K_1 (Cd–Br_2), K_2 (Cd–Br_1) and K_4 (Cs–Br_3) contributes towards the 3rd higher frequency of these modes (i.e. 166 cm^{-1} of A_g, 165 cm^{-1} of B_{2g}, 163 cm^{-1} of B_{3u}, 163 cm^{-1} of B_{1u}). By the contribution of the first three force constants i.e. K_1 (Cd–Br_2), K_2 (Cd–Br_1) and K_3 (Cd–Br_3) towards the higher frequencies of the modes which are thirteen in number (i.e. A_g, B_{2g}, B_{3u}, and B_{1u}), we may conclude that the tetrahedra group $CdBr_4^{2-}$ contributes more significantly to the higher frequencies of these modes. On the other hand, force constants K_3 (Cd–Br_3) and K_4 (Cs–Br_3) are the dominant force constants for the highest frequency of each mode which are 8 in number (i.e. 185 cm^{-1} of B_{3g}, 185 cm^{-1} of B_{1g} and 185 cm^{-1} of B_{2u}). Force constant K_{10} (Cs–Br_2) is much dominating force constant for the next higher frequency of these modes (i.e. 168 cm^{-1} of B_{3g}, 168 cm^{-1} of B_{1g} and 168 cm^{-1} of B_{2u}). Force constant K_3 (Cd–Br_3) and K_4 (Cs–Br_3) are the main contributors for the 3rd higher frequency of these modes (i.e. 109 cm^{-1} of B_{3g}, 102 cm^{-1} of B_{1g} and 101 cm^{-1} of B_{2u}). For the frequency region of 110–70 cm^{-1} of A_g, B_{2g}, B_{3u} and B_{1u} modes, Cs–Br vibrations dominate. The stretching force constants K_4 (Cs–Br_3), K_5 (Cs–Br_2), K_6 (Cs–Br_2), K_7 (Cs–Br_3), K_9 (Cs–Br_3), K_{11} (Cs–Br_3), and K_{12} (Cs–Br_2) contribute towards this frequency region. As we move towards the lower frequency region of all the modes, Cs-Br stretching vibrations dominate than any other vibrations and bending force constants also contribute significantly for the much lower frequencies.

"5. Conclusions"

All the Raman and IR modes for Cs_2CdBr_4 at the zone centre have been calculated by using the short range force constant model and are compared with the experimental results [4] which are in good agreement. Potential energy distribution for each mode is also investigated to know the contribution of each force constant towards them.

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"7. References"

[1] D. Altermatt, H. Arend, A. Niggli, and W. Petter, "New tetrahedrally coordinated A_2CdBr_4 compounds (A = Cs, CH_3NH_3)" *Mat. Res. Bull.*, ScienceDirect, Nov. 1979, pp.1391-1396.
[2] T. Dudoc, I. Martynyuk-Lototska, I. Trach, G. Romanyuk, M. Romanyuk, and R. Vlokh, "Dispersion of Refractive Indices in Cs_2CdBr_4 and Cs_2HgBr_4 Crystals" *Ukr J. Phys Opt.*, Feb. 2005, pp. 24-26.
[3] V I Torgashev, Yu I Yuzyuk, L A Burmistrova, F Smutny, and P Vanek, "Raman spectra of Cs_2CdBr_4 single crystals" *J. Phys.: Condens. Matter*, IOP Science, May 1993, pp. 5761-5772.
[4] Ya Shchur, S Kamba, and J Petzelt, "Lattice dynamics simulation of Cs_2CdBr_4 crystal", *J. Phys.: Condens. Matter*, IOP Science, Feb. 1999, pp. 3615–3628.
[5] T. Shimanouchi, M. Tsuiboi, and T. Miyazawa, "Optically active lattice vibrations as treated by the GF-matrix method", *J. Chem. Phys.*, AIP, Nov. 1961, pp. 1597-1612.
[6] S. Garg, M. M. Sinha, and H. C. Gupta, "Lattice dynamical investigations for Raman and the infrared frequencies of Cs_2HgCl_4" *International Journal of Modern Physics: conf. proc.*World Scientific, pp. 694-700.