GROUP THEORETICAL ANALYSIS OF LATTICE VIBRATIONS IN CAESIUM BROMIDE

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[Received, October, 26, 1968]

ABSTRACT

Employing Group theory[1], the nature of the normal modes of caesium bromide, at various critical points, is investigated The compatibility relations between the group of wave vectors and the complete phonon dispersion have been worked out.

The Method:

The caesium chloride structure is described by the space group O_h^1. The unit cell contains two atoms and hence at every wave vector **q**, there exist six normal modes of vibration. On account of symmetry, the same normal frequency may correspond to several normal modes especially at the critical points Γ, R, M, X, etc., of the reduced zone. To determine the degeneracy of the normal modes at a certain wave vector, the six dimensional mechanical representation of the normal vibrations should be reduced into the irreducible representations of the symmetry group of the wave vector. The dimension of the irreducible representation of **q** determine the degree of degeneracy of the normal modes. The number $N_j(q)$ determining the number of times the jth irreducible representation of **q** is contained in the reducible representation of the normal vibrations is given by

$$N_j(q) = \frac{1}{N_G} \sum_{\rho} \chi_j(\rho)\, \chi(\rho)$$

where the summation is over all the symmetry elements N_G of the space group of the wave vector **q**. Since caesium chloride structure belongs to the symmorphic space group, the group of the wave vectors corresponds to the known point groups. The characters of the normal vibrations for proper and improper rotations are given by

$$\chi(R_\phi) = (\pm 1 + 2\cos\phi) \sum_a n_a \exp(i\,\mathbf{q}\cdot\mathbf{a})$$

where n_a denotes the number of atoms in the basis cell which remain invariant or go over to equivalent atoms in the ath unit cell.

Tables I to V give the characters of the irreducible representations and the representation of the normal modes of the group of wave vectors at the various critical points. Tables (VI *a*) to (VI *d*) give us the compatibility relations between the various wave vectors.

From the tables, we find that at $\Gamma\,(q=0)$, there exist two triply degenerate normal vibrations corresponding to the optical and acoustic branches. The degeneracy of the optic modes at Γ_{15} is lifted on account of the Lyddane-Sachs-Teller relation. For wave vector along [001] direction, each Γ_{15} splits into $\Delta_1 \oplus \Delta_5$ and we have a pair of degenerate optical and acoustical branches coming under Δ_5. Similarly for waves along [111] direction, each Γ_{15} splits into Λ_1 and Λ_3 and hence, once again, we have pure longitudinal and pure transverse modes along this direction also. At the critical point R, however, we have two triply degenerate limiting vibrations, involving vibrations of planes of atoms of caesiums alone or bromines alone, coming under R'_{25} and R_{15}. Along [110] direction, the modes are non-degenerate except at the critical point M, where once again we have transverse modes along [001] directions and mixed degenerate modes in the [110] directions. Along the direction T (for all points with $q_x = q_y = \frac{1}{2}$), we have a pair of pure transverse modes. In these normal vibrations, the angle between the instantaneous positions of the two different atoms is always 90°.

TABLE 1

Character table for the group of the *a* vector at the point *M* and *Y*.

τ	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	I	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$N(M)$	$N(X)$
$\tau 1$	1	1	1	1	1	1	1	1	1	1	0	1
$\tau 2$	1	1	1	−1	−1	1	1	1	−1	−1	0	0
$\tau 3$	1	−1	1	1	−1	1	−1	1	1	−1	0	0
$\tau 4$	1	−1	1	−1	1	1	−1	1	−1	1	0	0
$\tau 5$	2	0	−2	0	0	2	0	−2	0	0	0	1
$\tau 1'$	1	1	1	1	1	−1	−1	−1	−1	−1	0	0
$\tau 2'$	1	1	1	−1	−1	−1	−1	−1	1	1	1	1
$\tau 3'$	1	−1	1	1	−1	−1	1	−1	−1	1	1	0
$\tau 4'$	1	−1	1	−1	1	−1	1	−1	1	−1	0	0
$\tau 5'$	2	0	−2	0	0	−2	0	2	0	0	2	1
$\chi(M)$	6	0	−2	0	−4	−6	0	2	0	4		
$\chi(X)$	6	4	−2	0	0	0	0	0	4	4		

TABLE 2

Character table for the group of q vector at the point Γ and R.

τ	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	I	$8S_6$	$3\sigma_h$	$6s_4$	$6\sigma_d$	$N(\Gamma)$	$N(R)$
$\tau 1$	1	1	1	1	1	1	1	1	1	1	0	0
$\tau 2$	1	1	1	−1	−1	1	1	1	−1	−1	0	0
$\tau 12$	2	−1	2	0	0	2	−1	2	0	0	0	0
$\tau 25'$	3	0	−1	−1	1	3	0	−1	−1	1	0	1
$\tau 15'$	3	0	−1	1	−1	3	0	−1	1	−1	0	0
$\tau 1'$	1	1	1	1	1	−1	−1	−1	−1	−1	0	0
$\tau 2'$	1	1	1	−1	−1	−1	−1	−1	1	1	0	0
$\tau 12'$	2	−1	2	0	0	−2	1	−2	0	0	0	0
$\tau 25$	3	0	−1	−1	1	−3	0	1	1	−1	0	0
$\tau 15$	3	0	−1	1	−1	−3	0	1	−1	1	2	1
$\chi(T)$	6	0	−6	12	−12	−6	0	6	−12	12		
$\chi(R)$	6	0	−6	0	0	0	0	0	−12	12		

TABLE 3

Character table for the group of q vector at the point Δ and T.

τ	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	$N(\Delta)$	$N(T)$
$\tau 1$	1	1	1	1	1	2	1
$\tau 1'$	1	1	1	−1	−1	0	0
$\tau 2$	1	−1	1	1	−1	0	0
$\tau 2'$	1	−1	1	−1	1	0	1
$\tau 5$	2	0	−2	0	0	2	2
$\chi(\Delta)$	6	4	−2	4	4		
$\chi(T)$	6	0	−2	0	4		

TABLE 4

Character table for the group of q vector at the point Σ, S and Z.

τ	E	C_2	σ_v	σ_v'	$N(\Sigma)$	$N(S)$	$N(Z)$
$\tau 1$	1	1	1	1	2	2	2
$\tau 3$	1	−1	1	−1	2	1	1
$\tau 2$	1	1	−1	−1	0	1	1
$\tau 4$	1	−1	−1	1	2	2	2
$\chi(\Sigma)$	6	−2	2	2			
$\chi(S)$	6	0	0	2			
$\chi(Z)$	6	0	0	2			

TABLE 5

Character table for the group of q vector at the point Λ.

τ	E	$2C_3$	$3\sigma_v$	$N(\Lambda)$
$\tau 1$	1	1	1	2
$\tau 2$	1	1	−1	1
$\tau 3$	2	−1	0	2
$\chi(\Lambda)$	6	0	6	

TABLE 6

Compatibility Relations at various critical points for the representations of caesium bromide.

(a) Compatibility Relations between Γ and Δ Λ, Σ

Γ	Δ	Λ	Σ
Γ_{15}	$\Delta_1 \oplus \Delta_5$	$\Lambda_1 \oplus \Lambda_3$	$\Sigma_1 \oplus \Sigma_3 \oplus \Sigma_4$

(b) Compatibility Relations between R and Λ, S, T

R	Λ	S	T
R_{25}'	$\Lambda_1 \oplus \Lambda_3$	$S_1 \oplus S_2 \oplus S_4$	$T_2' \oplus T_5$
R_{15}	$\Lambda_1 \oplus \Lambda_3$	$S_1 \oplus S_3 \oplus S_4$	$T_1 \oplus T_5$

(*c*) Compatibility Relations between M and T, Σ, Z

M	T	Σ	Z
M_2'	T_1	Σ_3	Z_3
M_3'	T_2'	Σ_3	Z_2
M_5'	T_5	$\Sigma_1 \oplus \Sigma_4$	$Z_1 \oplus Z_4$

(*d*) Compatibility Relations between X and Z, S, Δ

X	Z	S	Δ
X_1	Z_1	S_1	Δ_1
X_2'	Z_4	S_4	Δ_1
X_5	$Z_2 \oplus Z_4$	$S_2 \oplus S_4$	Δ_5
X_3'	$Z_1 \oplus Z_3$	$S_1 \oplus S_3$	Δ_5

TABLE 7

Symmetry Coordinates for the normal modes of caesium bromide

Critical point	Irreducible representation	Symmetry coordinate a	b	c
Γ	Γ_{15}	$x_1 + x_2$	$y_1 + y_2$	$z_1 + z_2$
		$x_1 - x_2$	$y_1 - y_2$	$z_1 - z_2$
R	R_{15}	x_1	y_1	z_1
	R_{25}'	x_2	y_2	z_2
M	M_2'	z_1		
	M_3'	z_2		
	M_5'	$x_1 + y_1$	$x_1 - y_1$	
		$x_2 + y_2$	$x_2 - y_2$	
X	X_1	x_2		
	X_2'	x_1		
	X_5'	$y_2 + z_2$	$y_2 - z_2$	
	X_5	$y_1 + z_1$	$y_1 - z_1$	

TABLE 7—(*concld*)

Critical point	Irreducible representation	Symmetry coordinate a	b	c
Σ	Σ_1	$x_1 + y_1$ $x_2 + y_2$		
	Σ_2	z_1 z_2		
	Σ_4	$x_1 - y_1$ $x_2 - y_2$		
Δ	Δ_1	x_1 x_2		
	Δ_5	$y_1 + z_1$ $y_2 + z_2$	$y_1 - z_1$ $y_2 - z_2$	
A	A_1	$x_1 + y_1 + z_1$ $x_2 + y_2 + z_2$		
	A_3	$2x_1 - y_1 - z_1$ $2x_2 - y_2 - z_2$	$y_1 - z_1$ $y_2 - z_2$	
T	T_1	z_1		
	T_2	z_2		
	T_3	$x_1 + y_2$ $x_2 + y_1$	$x_1 - y_2$ $x_2 - y_1$	
S	S_1	x_2 $y_1 + z_1$		
	S_2	$y_2 - z_2$		
	S_3	$y_1 - z_1$		
	S_4	$y_2 + z_2$ x_1		
Z_1	Z_1	y_1 x_2		
	Z_2	z_2		
	Z_3	z_1		
	Z_4	x_1 y_2		

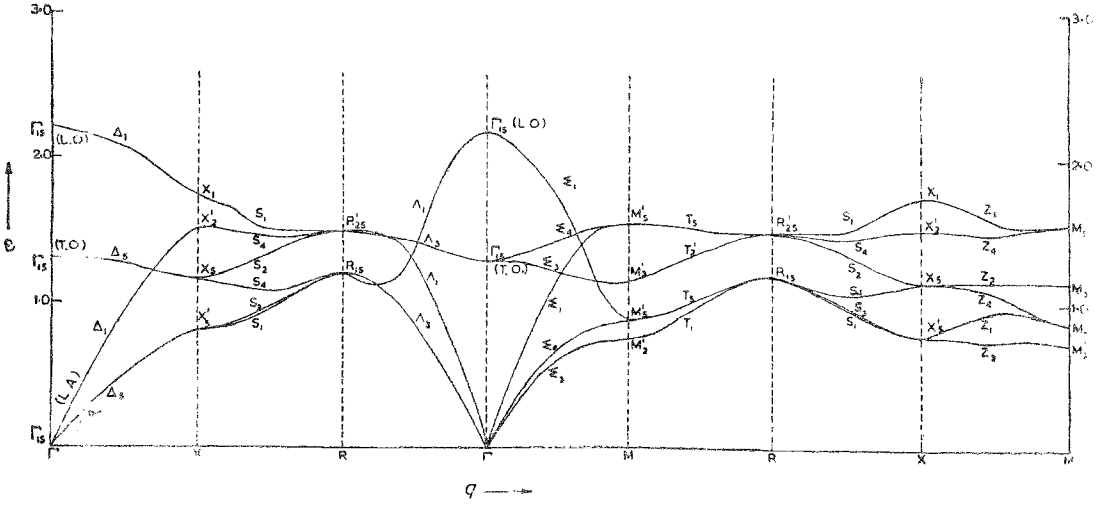

FIG. 1

Dispersion curves for caesium bromide

The character of the normal modes can be easily studied from Table 7, which gives us the symmetry coordinates of the normal modes. Employing these symmetry coordinates and the shell-model calculations of the lattice vibrations in caesium bromide,[2] the complete dispersion curves along these critical points have been plotted as in Fig. 1. The critical point phonons are consistent with the Raman modes and the second order Raman and Infrared spectra[3].

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