

## SHORT COMMUNICATIONS

## LATTICE DYNAMICS OF CESIUM FLUORIDE USING THREE-BODY FORCE SHELL MODEL

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THE lattice dynamics of a crystal is described by a frequency wave vector dispersion relation. The lattice dynamics of the NaCl structure has been discussed by several investigators, in particular by Kellermann<sup>1</sup>. The theory of lattice dynamics of ionic crystals has been developed using a shell model<sup>2</sup> and was subsequently modified<sup>3,4</sup>. The discrepancy in the original three-body force shell model<sup>4</sup> was later removed<sup>5</sup>. In the present investigation, this model with a new recent modification introduced<sup>6</sup> has been applied to cesium fluoride. The unique properties of cesium fluoride, like large electronic polarizability of Cs ion, light negative ion of NaCl structure, and availability of experimental values of elastic constants and phonon frequencies tempted us to theoretically investigate this alkali halide crystal.

## Theory

The TSM equations in the matrix form are given by:

$$-M\omega^2 U = (R + ZC'Z)U + (T + ZC'U)\omega$$

$$O = (YC'Z + T')U + (YC'Y + S)\omega.$$

with  $ZC'Z = Z[Z + 12f(a)]C + V$ ,

where  $R, S, T$  are matrices specifying short range core-core, shell-shell and core-shell interactions respectively and  $f(a)$  is related to overlap integrals of electron wave functions.  $V$  is the force constant derived from the purely three-body part of the lattice potential as expressed by Lundquists<sup>7</sup>. The other terms assume the usual meaning as given by Cowley *et al*<sup>8</sup>.

In the earlier approaches the  $R, S, T$ , elements have been set equal to one another and hence the phonon frequencies have been evaluated. In the present investigation we have started with a more general approach such that  $R \neq S \neq T$ . The  $R$  and  $C$

elements are calculated from the dimensionless coefficients of Kellermann<sup>1</sup>. The introduction of short range force constants  $A_1, B_1, A_{11}$  and  $B_{11}$ <sup>9</sup> enables one to calculate the  $T$  matrix elements. Further the variation in the  $T$  matrix elements with respect to the symmetry directions— $q$  are identical to the corresponding variations in the  $R$  elements. With this,  $S$  matrix elements are estimated using the relation  $2T - R = S$ . The  $V$  matrix elements are calculated using the coefficients (revised values) given by Verma and Singh. The secular equation to be solved and other details are the same as those given earlier<sup>6</sup>.

The availability of data such as the second order Raman spectrum, neutron scattering measurements, elastic and dielectric properties for CsF tempted us to study it on the basis of our modified model, that is,  $R \neq S \neq T$ . In this respect it is different from early studies on CsF<sup>10</sup>.

Table 1 presents the input data which are the elastic constants, the long wave optical frequencies and optical polarizability. The basic equations used for the calculation of the model parameters (table 2) from the elastic constants are the same as reported earlier<sup>5</sup>. The calculated values of phonon frequencies (table 3) show very good agreement with the experimental values<sup>11</sup>. This brings out the significance of the present approach. It may be mentioned that the treatment  $R \neq S \neq T$  has been applied to CsF for the first time.

Table 1 Input data\*

Elastic constants ( $10^{11}$ dy/cm <sup>2</sup> )	Lattice constant ( $10^{-8}$ cm)	Long wave optical frequency ( $10^{13}$ rad/sec)	Molecular polarizability ( $10^{-24}$ cm <sup>3</sup> )
$C_{11}$ 4.56	$a$ 3.004	$\omega_L$ 4.53	$\alpha$ 3.604
$C_{12}$ 1.15		$\omega_T$ 2.37	
$C_{44}$ 0.80			

\*Experimental values (Buhner<sup>11</sup>).

Table 2 Model parameters

$A$ : 10.10849	$a$ ( $df/da$ )	=	0.05309
$B$ : -0.94725	$Y_1$	=	-10.74433
$f(a)$ : -0.01558	$Y_2$	=	-1.58138

Table 3 Vibrational frequencies ( $10^{12}$  c/s)

Symmetry direction			Longitudinal frequencies				Transverse frequencies				
			Optical mode		Acoustic mode		Optical mode		Acoustic mode		
<i>q</i>	<i>q</i>	<i>q</i>									
0.2	0	0	4.4625	(4.50)	0.6786	(0.69)	2.4207	(2.44)	0.4122	(0.40)	
0.4	0	0	4.3862	(4.26)	1.2432	(1.22)	2.4625	(2.47)	0.5972	(0.58)	
0.6	0	0	3.8126	(3.69)	1.6208	(1.56)	2.4954	(2.49)	0.7308	(0.76)	
0.8	0	0	3.2050	(3.02)	1.6021	(1.59)	2.4987	(2.50)	0.7708	(0.76)	
1	0	0	4.0285		1.4327	(1.45)	2.5032	(2.50)	0.8382	(0.82)	
0.2	0.2	0	4.1876	(4.01)	0.7892	(0.81)	T <sub>1</sub> 2.3302	(2.38)	0.5369	(0.52)	
							T <sub>2</sub> 2.4602	(2.44)	0.2689	(0.40)	
0.4	0.4	0	3.8702	(3.89)	1.4362	(1.41)	T <sub>1</sub> 2.4295	(2.44)	0.8289	(0.83)	
							T <sub>2</sub> 2.5434	(2.52)	0.6342	(0.70)	
0.6	0.6	0	3.5206	(3.74)	1.5021	(1.54)	T <sub>1</sub> 2.4596	(2.45)	0.8259	(0.94)	
							T <sub>2</sub> 2.5687	(2.53)	1.3021	(1.19)	
0.1	0.1	0.1	4.3858	(4.54)	0.5416	(0.54)	2.4205	(2.38)	0.3252	(0.32)	
0.2	0.2	0.2	4.4062	(4.41)	0.9082	(0.91)	2.4354	(2.43)	0.5304	(0.52)	
0.3	0.3	0.3	4.3708	(4.36)	1.3455	(1.33)	2.4385	(2.43)	0.7908	(0.76)	
0.4	0.4	0.4	4.3438	(4.30)	1.6302	(1.59)	2.5002	(2.46)	0.8994	(0.87)	
0.5	0.5	0.5	4.2802	(4.24)	1.6442	(1.59)	2.5488	(2.53)	0.8740	(0.85)	

Values in parentheses are experimental values<sup>11</sup>.

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## REVISED VAN DER WAALS RADIUS FOR HYDROGEN

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THE availability of a large amount of crystallographic structural data through the Cambridge structural data base has been used for a variety of purposes. In particular, since the data base also covers structures analysed by neutron diffraction, the precise location of hydrogens in such studies has led to interesting analyses, such as C-H...O, C-H...N type of hydrogen bonds<sup>1</sup> and revision of C-H bond lengths, precise molecular geometry and related features<sup>2</sup>. More recently, Nyburg and Faerman<sup>3</sup> reported the effective non-bonding (van der Waals) shapes of non-metallic elements such as N, O, F, S, Cl, Se, Br and I atoms.

The value currently in use<sup>4</sup> for the van der Waals radius of hydrogen is 1.2 Å and even in the discussion of the C-H...X type of hydrogen bonds, this value is being used in the literature<sup>1</sup>.

A survey of non-bonded H...H contact distances from organic structures was carried out using the