

# CHARACTER TABLES FOR THE ATOMIC VIBRATIONS IN SOME CUBIC CRYSTALS

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## 1. Introduction

IN an earlier paper in this symposium, a general group-theoretical method for dealing with lattice vibrations has been indicated. It has been shown that the solution of the normal vibration problem depends upon a knowledge of the character tables for some point groups which are associated with the different vectors\* of the translation group. In the present paper it is proposed to indicate the applications of that method to four crystals of the cubic system, *viz.*, zincblende, diamond, fluorspar and rock-salt. A complete analysis of the normal modes of these and other crystals has already been given in an earlier paper of this series, basing the discussion on purely intuitive geometric principles. Hence a group-theoretical discussion of simple cases like the vibrations of a simple cubic lattice, simple face-centred lattice, body-centred lattice, etc., is not needed here. To illustrate the principles, we propose here to put down the appropriate character tables and the nature of the normal modes for the four crystals mentioned above. All the cases considered here have a face-centred structure. The eight possible vectors for this case fall into three distinct sets, as is evident by a very simple application of the symmetry operations. The (1, 1, 1) vector forms a set by itself and (1, -1, -1); (-1, 1, -1); (-1, -1, 1) another set. The remaining four vectors, (-1, -1, -1); (-1, 1, 1); (-1, 1, 1) and (1, 1, -1) form a set by themselves and each can be carried over into the others by the symmetry operations. Thus the interesting feature in the face-centred system is that (-1, -1, -1) becomes equivalent to the other three. We now investigate these three cases separately.

## 2. Rock-salt, Zincblende, Diamond and Fluorspar Lattices

All these cases can be dealt with by the same methods. In the rock-salt lattice, we have two non-equivalent atoms in the positions:

	Na (0, 0, 0);	Cl: ( $\frac{1}{2}$ , 0, 0).
For zinc sulphide, Zn:	(0, 0, 0)	S: ( $\frac{1}{4}$ , $\frac{1}{4}$ , $\frac{1}{4}$ ).
For diamond,	C: (0, 0, 0)	C: ( $\frac{1}{4}$ , $\frac{1}{4}$ , $\frac{1}{4}$ ).
For fluorspar,	C: (0, 0, 0)	F: ( $\frac{1}{4}$ , $\frac{1}{4}$ , $\frac{1}{4}$ ) and ( $\frac{3}{4}$ , $\frac{3}{4}$ , $\frac{3}{4}$ ).

\* For an explanation of this symbology reference should be made to the previous paper.

So far as the symmetry group is concerned, it is  $O_h$  for all cases except ZnS, and excepting the centre of inversion, all the other operations, forming the group  $T_d$ , can be located at a lattice point and this feature is common to all the four cases given above. Zinc sulphide has no centre of inversion, while for rock-salt it can be located at either Na or Cl atom, for diamond at  $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$  and for fluorspar at  $(0, 0, 0)$ . This shows that the normal modes of all the cases given above can differ only with respect to the centre of inversion. Each of the 8 possible vectors will now be taken up one by one and the normal modes evaluated by the methods fully explained in the earlier paper.

(1, 1, 1) *Vector*.—This is left invariant by all the operations of the point-group symmetry. Excepting the case for ZnS, which has  $T_d$  symmetry, the others have  $O_h$  symmetry and the reduced character of the operations is easily found when acting on the non-equivalent dynamical variables in each unit cell.

$$n_i = \frac{1}{N} \sum \psi(R) \chi^i(R)$$

	E	$3C_2$	$8C_3$	$6\sigma$	$6S_4$	$i$	$3\sigma$	$8S_6$	$6C_2$	$6C_4$	$n_i$ (NaCl)	$n_i$ (C)	$n_i$ (ZnS)	$n_i$ (CaF <sub>2</sub> )
$A_{1g}$ ..	1	1	1	1	1	1	1	1	1	1	..	..	..	..
$A_{2g}$ ..	1	1	1	-1	-1	1	1	1	-1	-1	..	..	..	..
$E_g$ ..	2	2	-1	0	0	2	2	-1	0	0	..	..	..	..
$F_{1g}$ ..	3	-1	0	-1	1	3	-1	0	-1	1	..	1	..	..
$F_{2g}$ ..	3	-1	0	+1	-1	3	-1	0	+1	-1	..	..	..	1
$A_{1u}$ ..	1	1	1	1	1	-1	-1	-1	-1	-1	..	..	..	..
$A_{2u}$ ..	1	1	1	-1	-1	-1	-1	-1	+1	+1	..	..	..	..
$E_u$ ..	2	2	-1	0	0	-2	-2	1	0	0	..	..	..	..
$F_{1u}$ ..	3	-1	0	-1	1	-3	1	0	1	-1	..	..	..	..
$F_{2u}$ ..	3	-1	0	1	-1	-3	1	0	-1	1	2	1	2	2
NaCl $\psi$ ..	6	-2	0	2	-2	-6	2	0	-2	2				
Diamond $\psi$ ..	6	-2	0	2	-2	0	0	0	0	0				
ZnS $\psi$ ..	6	-2	0	2	-2	..	..	..	..	..				
CaF <sub>2</sub> $\psi$ ..	9	-3	0	3	-3	-3	+1	0	-1	1				

The last four rows give the reduced character  $\psi$  of the operations when acting on dynamical variables of the four crystal lattices. The difference in the location of the inversion in NaCl and diamond is reflected by the fact

that in the former all the six modes are anti-symmetric with respect to inversion, while in the latter they separate out into symmetric and anti-symmetric modes.  $ZnS$  has no inversion and its six modes occur in  $F_{2u}$ . For  $CaF_2$ , the mode  $F_{2g}$  gives one triply degenerate normal mode symmetric with respect to inversion while two other modes with degeneracies 3 each come under  $F_{2u}$ . If we exclude translations, these give, as is at once evident from the character table, the following frequencies:

	Degeneracy
(1) An oscillation of the sodium lattice against the chlorines in $NaCl$ .. .. .	3
(2) A mutual oscillation of the interpenetrating lattices in diamond .. .. .	3
(3) A mutual oscillation of the zinc and sulphur lattices against one another in $ZnS$ .. .. .	3
(4) An oscillation of the $Ca$ and $F$ ions in $CaF_2$ which is symmetric with respect to inversion ( $F_{2g}$ ). Since the inversion is located at the calcium atoms, they must be at rest in this mode .. .. .	3
(5) A combined oscillation of all the calcium and fluorine atoms which is totally antisymmetric with respect to inversion ( $F_{2u}$ ). The translations also occur in $F_{2u}$ . Hence the only possibility left is that the fluorines go one way and the calciums go the other way .. .. .	3

This rigorous analysis can be compared with the treatment given in an earlier paper.

$(-1, -1, -1)$  vector referred to rhombohedral axes.—The vectors  $(-1, 1, 1)$ ;  $(1, -1, 1)$ ; and  $(1, 1, -1)$  referred to rhombohedral system are equivalent to  $(-1, -1, -1)$  and so there is a minimum degeneracy of 4 for frequencies of this set. We consider the  $(-1, -1, -1)$  vector only.

The symmetry operations keeping this invariant form the group  $D_{3d}$  in all cases except  $ZnS$  where it is simply  $C_{3v}$  without the inversion. The analysis is similar to the earlier treatment.

For  $ZnS$ , the appropriate character table consists of the first three columns and first three rows only. The distribution of frequencies in rock-salt and diamond is similar, with degeneracies 1, 2, 1, 2. The former two are symmetric with respect to inversion while the latter two are antisymmetric. Since  $ZnS$  has no centre of symmetry to distinguish the modes, we get a coupling between these two sets, which can be resolved only by forming the potential energy. For  $CaF_2$  there are two frequencies with degeneracies

	E	2 C <sub>3</sub>	3 σ	i	2 C <sub>3</sub> × i	3 σ × i	n <sub>i</sub> (NaCl)	n <sub>i</sub> (C)	n <sub>i</sub> (ZnS)	n <sub>i</sub> (CaF <sub>2</sub> )
A <sub>1g</sub> ..	1	1	1	1	1	1	1	1	2	1
A <sub>2g</sub> ..	1	1	-1	1	1	-1	..	..	..	..
E <sub>g</sub> ..	2	-1	0	2	-1	0	1	1	2	1
A <sub>1u</sub> ..	1	1	1	-1	-1	-1	1	1	..	2
A <sub>2u</sub> ..	1	1	-1	-1	-1	1	..	..	..	..
E <sub>u</sub> ..	2	-1	0	-2	1	0	1	1	..	2
(NaCl) ψ ..	6	0	2	0	0	0				
(Diamond) ψ ..	6	0	2	0	0	0				
(ZnS) ψ ..	6	0	2	..	..	..				
(CaF <sub>2</sub> ) ψ ..	9	0	3	-3	0	-1				

1 and 2 respectively which are symmetric with respect to the inversion. On the other hand, there are four frequencies with degeneracies 1, 2, 1, 2 and antisymmetric with respect to inversion. There is a coupling here between the two single frequencies, with a similar coupling for the double modes.

The symmetry characters of the modes are at once evident from the character table. Those under A<sub>1g</sub> are totally symmetric with respect to (x, y, z) and for a state of vibration represented by the (-1, -1, -1) vector, this can only be in a direction normal to the (111) planes. All the normal co-ordinates of an atom 'r' involve the term x<sub>r</sub> + y<sub>r</sub> + z<sub>r</sub>. For rock-salt, this is a vibration of the (111) planes. Being symmetric with respect to inversion, the sodiums are at rest, and alternate (111) planes of chlorine atoms move oppositely and normal to themselves. The same description holds good for the diamond lattices. For zincblende, alternate (111) planes contain zinc and sulphur atoms respectively, and the exact relative magnitude through which they move depends upon the forces between them. Hence they occur coupled together with two frequencies under A<sub>1g</sub>. In fluorspar a similar motion of (111) planes occurs except that the calciums must be at rest in A<sub>1g</sub> because of the symmetric nature with respect to inversion.

Coming to A<sub>1u</sub> the modes of rock-salt are the same as the above case for A<sub>1g</sub> except that it is the chlorine atoms which are at rest, with the sodium atoms moving. Diamond has a similar vibration which is now antisymmetric with respect to inversion. Alternate (111) planes now go two against two, thus ++ --, etc. For zinc sulphide, there is no distinction between A<sub>1u</sub> and A<sub>1g</sub>, while for fluorspar we have two coupled modes both antisymmetric with respect to inversion. This is natural, since a motion with

the two fluorines going the same way leaves a twofold option for the calcium atom. Either the calcium can move in the same way or opposite way with respect to fluorine. Thus  $\overset{\rightarrow}{\text{F}} \overset{\rightarrow}{\text{Ca}} \overset{\rightarrow}{\text{F}}$  or  $\overset{\rightarrow}{\text{F}} \overset{\leftarrow}{\text{Ca}} \overset{\rightarrow}{\text{F}}$  are possible and both are antisymmetric with respect to the inversion at the calcium atom.

The representations  $E_{1g}$  and  $E_{1u}$  are double. It is easily seen from the group characters that they involve co-ordinates like  $x_r - y_r$ ,  $y_r - z_r$  or  $z_r - x_r$  of an atom. They involve motions of the (111) planes in two directions in their own planes and these two directions are equivalent. For rock-salt, the same motion as described earlier takes place with either the chlorines at rest or the sodiums at rest. Alternate (111) planes move tangentially and in opposite phases in this motion. For diamond also, a similar motion takes place, and it is either symmetric or antisymmetric with respect to inversion. In the former case the alternate planes move as  $+ - - +$  and in the second case they move as  $+ + - -$ , etc. In zincblende alternate (111) planes of the same sort move in opposite phases tangentially. As there is no inversion to distinguish the modes further, we get a coupled mode or  $E_g$ . In fluorspar,  $E_g$  gives a doubly degenerate mode which is uncoupled with any other. It is symmetric with respect to inversion and so calciums must be at rest with the fluorines going in opposite ways. Here also alternate (111) planes of fluorines move tangentially. For  $\text{CaF}_2$  we get in  $E_u$  two coupled modes with degeneracy two each. As explained for the case of  $A_{2u}$ , this is natural, as the calcium atoms can move in the same or opposite ways with respect to the fluorines. The direction of motion however is tangential here unlike  $A_{2u}$ . This completes a description of all the modes for similar motions occurring for  $(1, \bar{1}, 1)$   $(1, 1, \bar{1})$  and  $(\bar{1}, 1, 1)$  planes corresponding to the three other vectors. Thus we get an extra degeneracy of four for every frequency belonging to  $(-1, -1, -1)$ . The distribution for this branch can hence be represented as

(1) Rock-salt:	Distinct frequencies with degeneracies	4, 4, 8, 8
(2) Diamond	” ”	4, 4, 8, 8
(3) Zincblende	” ”	<u>4, 4</u> , <u>8, 8</u>
(4) Fluorspar	” ”	4, 8, <u>4, 4</u> , <u>8, 8</u>

We now turn to the final vector  $(1, -1, -1)$ . A detailed description of the geometric modes for this vector can be given as above, but we content ourselves here by merely indicating the character table and the number of the appropriate normal modes with their degeneracies. This vector is left invariant by the elements

- (i) the identity;
- (ii) the three two-fold rotations about the  $x$ ,  $y$  and  $z$  axes,  $3C_2$ ;

(iii) a reflexion  $\sigma_1$  in a plane passing through  $x$  axis and bisecting the other two;

(iv) the products of  $\sigma_1$  with  $3C_2$  i.e.,  $3C_2 \sigma_1$ .

This is the symmetry group  $D_{2d}$  for a crystal with no centre of inversion such as ZnS. The addition of a centre of inversion in rock-salt and fluorspar brings in eight operations more  $D_{2d} \times i$  and the total group is of order 16. In diamond, however, the inversion does not commute with all the operations in  $D_{2d}$ , particularly the three twofold rotations  $P_1, P_2, P_3$  about the three cubic axes. Its association with these elements brings in translation operations thus

$$i P_1 i^{-1} = P_1 \tau_x \text{ or } i P_1 i^{-1} P_1^{-1} = \tau_x, \quad (2)$$

Since  $i^{-1} = i$  and  $P_1^{-1} = P_1$  this can be written as

$$(iP_1)^2 = \tau_x; (iP_2)^2 = \tau_y; (iP_3)^2 = \tau_z. \quad (3)$$

Hence the space group keeping the vector  $(+1, -1, -1)$  invariant in diamond lattice cannot be resolved as the product of a point group and a translation group. The simplified formula (17) in the paper on general theory is not directly applicable here and we have to derive the full character table for the space group. All these complications can be avoided, if, for a moment, we regard the two non-equivalent atoms in diamond as being different. Consequently there will be no centre of inversion here and the pattern is exactly the same as for ZnS. Afterwards, when the normal modes for ZnS are written down, we can, if we choose, bring in the inversion and easily see what modification it can bring in the normal modes.

	E	$P_1$	$P_2, P_3$	$\sigma_1, \sigma_1 P_1$	$P_2 \sigma_1, P_3 \sigma_1$	$n_i$
$A_1$ ..	1	1	1	1	1	..
$A_2$ ..	1	1	1	-1	-1	..
$B_1$ ..	1	1	-1	1	-1	2
$B_2$ ..	1	1	-1	-1	1	..
E ..	2	-2	0	0	0	2
$\psi$ ..	6	-2	-2	2	-2	..

We thus have two single modes (coupled) and two double modes (coupled). If the inversion is now introduced, the coupling is removed with the modes separating out according as they are, or are not, symmetric with respect to inversion. We have here a process of building up the representations of a group from its subgroups. The full method is explained in the paper on general theory. Since the inversion brings in the translations,

we first choose the group  $D_{2d} \times$  translations for diamond. According to Clifford's work each representation of this group we need here, is merely the direct product of the representations for  $D_{2d}$  and the representation (1, -1, -1) of the translation group.

Here  $\chi(\tau_x) = -\chi(\tau_y) = -\chi(\tau_z) = 1$  (5)

Hence  $\chi(P_1\tau_x) = \chi(P_1)$ ;  $\chi(P_2\tau_y) = -\chi(P_2)$ ;  $\chi(P_3\tau_z) = -\chi(P_3)$  (6)

for all representations associated with this vector. We now append the inversion and derive the group table for  $D_{2d} \times \{E, i\}$ . Taking the representation  $B_1$  it is easily seen that it is sent into the representation  $A_1$  by the inversion. This is because the inversion changes  $P_1, P_2, P_3$  into  $P_1\tau_x, P_2\tau_y$  and  $P_3\tau_z$  the characters for which, however, are equal to  $\chi(P_1), -\chi(P_2)$  and  $-\chi(P_3)$  from (6).

Thus  $\chi(P_1) \rightarrow \chi(P_1)$      $\chi(P_2) \rightarrow -\chi(P_2)$      $\chi(P_3) \rightarrow -\chi(P_3)$

as a result of the inversion. Thus  $A_1$  and  $B_1$  are equivalent under the inversion and they give rise to a double representation in the space group. The degeneracy of the mode under  $B_1$  is thus increased and as a consequence the coupling is removed. The representation E however is left invariant by the inversion and so we do not get any new combination of representations. This gives rise to two representations in the space group, one which is symmetric, and the other antisymmetric with respect to inversion. Accordingly, the distribution of the six normal modes in diamond lattice for this vector is 2, 2, 2. From the symmetry characters of  $A_1, B_1$  and E the normal modes can be derived. They will be found to be identical with the descriptions given earlier.

For fluorspar and rock-salt, the inversion is also located at a lattice point and so commutes with the point group  $D_{2d}$ . Hence there is no need to bring in a space group, and the appropriate character table is given by the direct product of  $D_{2d}$  and the inversion group with two representations  $\chi(i) = \pm 1$ . The further analysis is then exactly the same as above and there is no real need to put it down here again. The distribution of the modes is the same as given in the earlier paper.

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### Summary

In this paper, the character tables for groups associated with vectors defining normal modes are given for four cubic crystals based on a face-centred Bravais lattice, viz., rock-salt, diamond, zincblende and fluorite. The method of deriving normal modes from these tables, described in an earlier paper, is illustrated here.