

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part I. Diamond

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1. INTRODUCTION

THE investigation of the possible modes and frequencies of vibration of the atoms in diamond about their positions of equilibrium is a necessary step for the interpretation of the Raman and infra-red spectra of this solid. Such an investigation is also essential for the interpretation of the emission and absorption spectra of luminescent diamonds at low temperatures and indeed also the other physical properties in which the vibrations of the atoms are involved. The spectroscopic behaviour of diamond has during recent years been thoroughly investigated at Bangalore by the several distinct methods mentioned above. In particular, the present author has recently carried out a detailed experimental study (1946, 1947) of the infra-red absorption spectra of numerous samples of diamond. It has accordingly become necessary to consider in some detail, the nature of the vibration spectrum of this substance.

According to the new theory of crystal dynamics recently put forward by Sir C. V. Raman (1943), the structure of diamond is capable of nine independent normal modes of vibration out of which the frequencies of two are the same, thus giving rise to a spectrum having eight numerically different vibration frequencies. Following Nagendra Nath (1934), Bhagavantam (1943) and Chelam (1943) have derived expressions for the frequencies of vibration of the various modes. But their treatment of the problem with three constants alone to represent the interatomic forces is inadequate. A more general and rigorous dynamical treatment of the problem is obviously called for, and this has been carried out in the present work on the lines indicated by Sir C. V. Raman in his theory of the dynamics of crystal lattices.

2. DESCRIPTION OF THE MODES

The new theory of crystal dynamics leads to the result that the structure of a crystal consisting of p non-equivalent atoms in each unit cell is capable

of $(24p-3)$ modes of vibration, out of which $(3p-3)$ represent vibrations in which the dynamic repeating pattern is the unit cell of the crystal. The remaining $21p$ modes represent vibrations in which the dynamic repeating unit is a super-cell having twice the linear dimensions of the unit cell. In the case of a face-centred cubic lattice having one atom per unit cell, it can be shown that the normal and tangential oscillations of the octahedral planes of atoms and the normal and the tangential oscillations of the cubic planes of atoms having degeneracies of 4, 8, 3 and 6 respectively, correspond to the 21 degrees of freedom representing the vibrations of the superlattice. In a case like diamond where there are two non-equivalent atoms in the unit cell, there are two possibilities corresponding to every one of the above four distinct modes of the face-centred cubic lattice, since the two non-equivalent atoms in the unit cell can now move either in the same phase or in opposite phases. In addition, there will be one other frequency corresponding to the $(3p-3)$ modes, having a degeneracy of 3 which represents the oscillation of the two interpenetrating lattices of carbon atoms against each other, thus making up a total of nine independent modes having degeneracies of 4, 4, 8, 8, 3, 3, 6, 6 and 3. However, because of the numerical equivalence of the frequencies of the two triply degenerate modes of the superlattice, there will be only eight distinct frequencies in the vibration spectrum. The 45 degrees of freedom together with three transitions make up 48 which agrees with the number of degrees of freedom to be expected for the 16 atoms in a supercell having twice the linear dimensions of the unit cell. Table I

TABLE I

Sequence	Degeneracy	Oscillating units	Direction of motion	Relative phase of nearest layers	Operative Force-constant	Observed frequencies
I	3	The two lattices	Arbitrary	Opposite	$P-4Q+4S+8U-12\Sigma$	cm. ⁻¹ 1332
II	8	Octahedral planes	[011]	Opposite	$P-2Q-2R+4W+6\Sigma+6\Omega$	1250
III	6	Cubic	[011]	*Same	$P-4R-4S-12\Omega$	1232
IV	4	Octahedral	[111]	Same	$P+2Q-4R-8W-6\Sigma+12\Omega$	1149
V	3	Cubic	[100]	Opposite	$P+4S-8U$	1088
VI	3	Cubic	[100]	Same	$P+4S-8U$	1088
VII	4	Octahedral	[111]	Opposite	$P-2Q+4R-8W+6\Sigma-12\Omega$	1008
VIII	6	Cubic	[011]	*Opposite	$P+4R-4S+12\Omega$	752
IX	8	Octahedral	[011]	Same	$P+2Q+2R+4W-6\Sigma-6\Omega$	620

* See text for some explanatory remarks in these two cases.

contains a full description of the nine normal modes of vibration arranged in a descending sequence of the magnitudes of their frequencies determined as explained later.

3. THE EQUATIONS OF MOTION

Since in any particular normal mode of vibration of any conservative dynamical system, all the particles vibrate with the same frequency, it is enough, in our present case, if we consider the equation of motion of any one atom, in order to obtain expressions for the frequencies of vibration of all the different modes. It is necessary here to decide as to how many of the neighbouring atoms are to be taken account of in deriving the equations of motion of a particular atom. There can be no question that the influence of the neighbouring atoms decreases rapidly as we go to the more and more distant ones. There is therefore no reason why we should not confine our attention to a limited number of neighbours in framing the equations of motion of a particular atom. In the present treatment, we shall take account of the influence of 28 atoms nearest to the one under consideration, these falling into three groups comprised of 4, 12 and 12 atoms respectively, situated at the same distance from the particular atom. We shall suppose this latter to be situated at the origin of a Cartesian co-ordinate system having its three axes along the three cube directions. Also let the suffix 0 represent this atom in what follows. Then the four atoms (1 to 4) situated at the ends of the tetrahedral axes are the nearest neighbours. The point 0 is common to twelve cube faces, four of them parallel to YZ, four to ZX and the remaining four to the XY planes of the co-ordinate system. The twelve atoms at the face centres of these twelve cube faces (5 to 16) represent the next-nearest neighbours of atom 0. The positions of the twelve atoms (17 to 28) can be arrived at by the translations of the four nearest neighbours, by the length of the edge of the unit cube along x , y and z axes in positive or negative directions according as atom 0 is situated in positive or negative directions of the co-ordinate system with respect to these atoms. The co-ordinates of all the 28 neighbours in fractions of the length of the edge of the unit cube, are contained in Table II.

Let x, y, z denote the displacements of the atom 0 and x_i, y_i, z_i , the displacements of the 28 neighbours from their equilibrium positions at any instant of time t . Then, if m denotes the mass of the carbon atom, the three equations of motion of atom 0 are:—

$$m \frac{d^2x}{dt^2} - x F_{xo}^{xo} = \sum_1^{28} x_i F_{xi}^{xo} + \sum_1^{28} y_i F_{yi}^{xo} + \sum_1^{28} z_i F_{zi}^{xo} \quad (1)$$

$$m \frac{d^2y}{dt^2} - y F_{yo}^{yo} = \sum_1^{28} x_i F_{xi}^{yo} + \sum_1^{28} y_i F_{yi}^{yo} + \sum_1^{28} z_i F_{zi}^{yo} \quad (2)$$

$$m \frac{d^2z}{dt^2} - z F_{zo}^{zo} = \sum_1^{28} x_i F_{xi}^{zo} + \sum_1^{28} y_i F_{yi}^{zo} + \sum_1^{28} z_i F_{zi}^{zo} \quad (3)$$

TABLE II
Showing the Co-ordinates of the 29 atoms

Atom No.	x	y	z	Atom No.	x	y	z
0	0	0	0	2	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$
1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	4	$-\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$
3	$-\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	6	0	$-\frac{1}{2}$	$-\frac{1}{2}$
5	0	$\frac{1}{2}$	$\frac{1}{2}$	8	0	$-\frac{1}{2}$	$\frac{1}{2}$
7	0	$\frac{1}{2}$	$-\frac{1}{2}$	10	$\frac{1}{2}$	0	$-\frac{1}{2}$
9	$\frac{1}{2}$	0	$\frac{1}{2}$	12	$-\frac{1}{2}$	0	$\frac{1}{2}$
11	$-\frac{1}{2}$	0	$-\frac{1}{2}$	14	$\frac{1}{2}$	$-\frac{1}{2}$	0
13	$\frac{1}{2}$	$\frac{1}{2}$	0	16	$-\frac{1}{2}$	$-\frac{1}{2}$	0
15	$-\frac{1}{2}$	$\frac{1}{2}$	0	18	$\frac{1}{4}$	$-\frac{3}{4}$	$\frac{1}{4}$
17	$-\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	20	$-\frac{3}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$
19	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{3}{4}$	22	$\frac{1}{4}$	$-\frac{1}{4}$	$\frac{3}{4}$
21	$\frac{1}{4}$	$\frac{3}{4}$	$-\frac{1}{4}$	24	$-\frac{1}{4}$	$-\frac{3}{4}$	$-\frac{1}{4}$
23	$\frac{3}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	26	$\frac{3}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$
25	$-\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	28	$-\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{3}{4}$
27	$-\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$				

F_{x0}^{i0} , F_{y0}^{i0} and F_{z0}^{i0} are the restoring forces along the three directions for unit displacements of atom 0. The contribution by any atom to each of the above three equations consists of three different terms. The three terms on the right hand side of equation (1) represent the forces produced in the x direction on atom 0, due to displacements of atom i in the x , y or z direction respectively. Similarly the terms on the right hand side of equations (2) and (3) represent the forces along the y and z directions respectively due to x , y and z displacements of atom i . Since the summation is to be carried out over all the 28 neighbours, the three equations contain $(28 \times 9 + 3) = 255$ force components. Actually, however, the number of independent force constants appearing in the equations is reduced considerably by reason of the high degree of symmetry of the crystal. The exact manner in which this reduction is carried out is described below.

It is well known that every crystal by virtue of its symmetry is characterised by a set of symmetry operations which have the property of transforming the entire crystal into itself. In what follows, we shall deal only with symmetry operations which leave the position of atom 0 unchanged. This restriction is essential because we are concerned here with the forces produced at the point 0 due to displacements of the neighbouring atoms. Any symmetry operation can now result only in the interchange among themselves of the individual groups of atoms (4, 12 and 12) which are equidistant from 0. All the atoms of each such group belong to one or the other of the two interpenetrating lattices of carbon atoms. It is also easy to see that digonal rotations about the three cubic axes passing through 0 and reflections in the

six planes of symmetry containing atom 0 and belonging to the tetrahedral group of operations, are sufficient to enable us to bring into coincidence any atom of a particular group with any other atom of the same group.

In the general case of interaction between any two atoms, there will be nine force-components as mentioned above, because corresponding to each one of the three displacements of one of the atoms, there will be a component of the force produced along all the three directions on the second atom. In order to illustrate the manner in which some of the force-components transform among themselves, we shall associate every one of the neighbouring atoms of 0 with three vectors F_{xi} , F_{yi} and F_{zi} corresponding to the three displacements, and the atom 0 with three vectors F^{xo} , F^{yo} and F^{zo} corresponding to the directions of the force components. Every force component will then be connected with two vectors, one corresponding to the direction of the force component on atom 0 and the other corresponding to the direction of displacement of the atom producing the force. For example, the force component F_{zi}^{yo} is associated with the two vectors F^{yo} and F_{zi} . If, by the application of a symmetry operation, the two vectors associated with a force component due to an atom i are transformed into the two vectors associated with a force component due to another atom j , then the magnitudes of the two force components will be the same. For instance, if the two vectors F^{yo} and F_{zi} are transformed respectively into F^{zo} and F_{xj} , then $F_{zi}^{yo} = F_{xj}^{zo}$ (in magnitude only). The two components have the same sign if by the application of the particular operation, the signs of both the vectors associated with one of the force components remain the same and also when both of them are reversed. If however, the sign of one of the vectors is reversed while the sign of the other remains the same, then the two force components will be of opposite sign. In this manner we can determine the relative signs of the force components due to a particular group of atoms. In order to fix the absolute signs of the components with respect to our co-ordinate system, we can consider those components having both their vectors along the positive directions or both along the negative directions of the co-ordinate system, to be negative. Obviously then, the force on any atom P which is proportional to its own displacement, for which the directions of the displacement and of the force are opposite will be positive.

In the case of diamond we find that in addition to the force P , the forces due to the displacements of the nearest neighbours of any atom can be represented by two constants Q and R , of the next-nearest neighbours by five constants S , T , U , V and W , and of the atoms 19 to 28 by five constants α , β , γ , δ and ϵ . A description of the 255 force-components appearing in the three equations (1), (2) and (3) is contained in Tables III, IV and V.

TABLE III

Force-components acting in the x-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	<i>x</i>	<i>y</i>	<i>-y</i>	<i>z</i>	<i>-z</i>
P ..	0
Q ..	1 to 4
R	1, 4	2, 3	1, 3	2, 4
S ..	5 to 8
T	5, 8	6, 7	5, 7	6, 8
U ..	9 to 16
V	9, 12	10, 11	13, 15	14, 16
W	13, 16	14, 15	9, 11	10, 12
α ..	18, 19, 21, 22, 24, 25, 27, 28
β	18, 27	21, 24	19, 25	22, 28
γ	19, 28	22, 25	18, 24	21, 27
δ ..	17, 20 23, 26
ϵ	17, 26	20, 23	17, 23	20, 26

The exact manner in which the force-components are reduced to 13 independent constants can be understood from these tables. Table III for example, describes the force-components acting on atom 0 due to all possible displacements of the 29 atoms capable of producing a force on atom 0 in the *x*-direction. The symbol at the head of each column in Table III denotes the direction of displacements of the atoms which result in a force-component along the positive direction of the *x*-axis on atom 0. The symbol at the head of each row denotes the magnitude of the force per unit displacement. If we take for instance atom 12, the three X components of force on atom 0 due to *x*, *y* and *z* displacements of the former along the positive directions of the axes are:—

$$F_{x12}^{z0} = U, F_{y12}^{z0} = V \text{ and } F_{z12}^{z0} = -W$$

The negative sign occurs in the last equation because it is seen from Table III that the *z*-displacement vector of atom 12 is negative. Thus Table III

TABLE IV
Force-components acting in the y-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	<i>x</i>	$-x$	<i>y</i>	<i>z</i>	$-z$
P	0
Q	1 to 4
R ..	1, 4	2, 3	..	1, 2	3, 4
S	9 to 12
T ..	9, 12	10, 11	..	9, 10	11, 12
U	5 to 8 & 13 to 16
V ..	5, 8	6, 7	..	13, 14	15, 16
W ..	13, 16	14, 15	..	5, 6	7, 8
α	17, 19, 20, 22, 23, 25, 26, 28,
β ..	17, 26	20, 23	..	19, 22	25, 28
γ ..	19, 28	22, 25	..	17, 20	23, 26
δ	18, 21, 24, 27
ϵ ..	18, 27	21, 24	..	18, 21	24, 27

directly gives us the values of the 85 *x*-components, Table IV the 85 *y*-components and Table V the 85 *z*-components of force acting on atom 0. The 255 force-components being known, we can at once write down the equations of motion of any normal mode of vibration, by substituting the proper displacements of the various atoms (taking care to insert the correct signs) involved in the particular normal mode.

4. THE EXPRESSIONS FOR THE FREQUENCIES OF VIBRATION

In order to express the frequencies of vibration of the different normal modes in terms of the force constants, it is necessary to substitute the displacements of the different atoms from the equilibrium configuration in any particular normal mode, in the three equations 1, 2 and 3 and solve them for the frequency. It should be borne in mind that the *x*, *y* and *z* displacements of any atom are numerically equal to the corresponding displacements of every other atom in the structure. The method of solution can be best

TABLE V

Force-components acting in the z-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	<i>x</i>	$-x$	<i>y</i>	$-y$	<i>z</i>
P	0
Q	1 to 4
R ..	1, 3	2, 4	1, 2	3, 4	..
S	13 to 16
T ..	13, 15	14, 16	13, 14	15, 16	..
U	5 to 12
V ..	5, 7	6, 8	9, 10	11, 12	..
W ..	9, 11	10, 12	5, 6	7, 8	..
α	17, 18, 20, 21, 23, 24, 26, 27
β ..	17, 23	20, 26	18, 21	24, 27	..
γ ..	18, 24	21, 27	17, 20	23, 26	..
δ	19, 22, 25, 28
ϵ ..	19, 25	22, 28	19, 22	25, 28	..

explained by illustrating it with a particular case. In mode 2 of Table I representing the tangential motion of the octahedral planes of atoms, if we assume the motion to be in the *yz* plane, then the *x* displacements of all the atoms are zero. The *y* displacements are given by

$$y = y_1 = y_7 = y_8 = y_{10} = y_{12} = y_{14} = y_{15} = y_{20} \text{ to } y_{28}$$

$$= -y_2 \text{ to } -y_6 = -y_9 = -y_{11} = -y_{13} = -y_{16} = -y_{17} \text{ to } -y_{19}$$

and the *z* displacements are given by $z_i = ky_i$, *k* being an arbitrary constant.

Equation 1 becomes zero, while 2 and 3 are reduced to

$$m \frac{d^2y}{dt^2} = (P - 2Q + 2kR - 4kW + 4\alpha - 2k\beta - 2k\gamma + 2\delta - 2k\epsilon) y \quad (4)$$

$$km \frac{d^2y}{dt^2} = (kP + 2kQ + 2R - 4W + 4k\alpha - 2\beta - 2\gamma + 2k\delta - 2\epsilon) y \quad (5)$$

On subtracting (5) from (4) the constant k vanishes, showing that the frequency is the same for all values of k including our particular value ($k = -1$) and we get

$$m \frac{d^2y}{dt^2} = y \{P - 2Q - 2R + 4W + 2(2\alpha + \delta) + 2(\beta + \gamma + \epsilon)\} \quad (6)$$

The frequency of vibration is therefore given by

$$4\pi^2\nu^2c^2m = (P - 2Q - 2R + 4W + 6\Sigma + 6\Omega) \quad (7)$$

where $\Sigma = \frac{1}{3}(2\alpha + \delta)$ and $\Omega = \frac{1}{3}(\beta + \gamma + \epsilon)$ and ν and c are respectively the frequency in wavenumbers and the velocity of light. In a similar manner, the expressions for all the modes can be obtained easily and are contained in column 6 of Table I. Table I also contains a detailed description of all the modes in columns 2 to 5. There is however an ambiguity with regard to the description of the relative phases of nearest layers in the case of the modes III and VIII. The ambiguity arises because the cubic planes of atoms in diamond are arranged at equal intervals. This fact does not make any difference with regard to the description of modes V and VI because the expressions for the frequencies of these two modes are the same. The ambiguity in the case of III and VIII can be cleared up if we consider any two neighbouring layers for which the phases of motion are the same, and then describe the direction of motion in the two cases, with respect to the plane of the valence bonds joining the two layers. In such a case the direction of motion in III will be perpendicular to the plane of the bonds and in VIII parallel to the plane.

It will be noticed that the constants T and V do not appear in any of the equations. These represent two of the three transverse force-constants due to the displacements of the twelve next-nearest neighbours previously described as situated at the face centres of the twelve cube faces originating from the point 0. Owing to the nature of the displacements of these atoms in the various normal modes, they cancel out from the frequency formulæ.

5. THE FORCE CONSTANTS

In addition to the eight expressions for the frequencies of vibration of the various modes, we can obtain one more relation between the constants which corresponds to the translation of the entire crystal having zero frequency. Substituting the values of the force components appearing in equations 4, 5 or 6, we obtain for the case of diamond

$$(P + 4Q + 4S + 8U + 12\Sigma) = 0 \quad (8)$$

We have now got nine expressions involving the eight constants P, Q, R, S, U, W, Σ and Ω . The constants are therefore perfectly determinate if

the frequencies corresponding to each one of the different modes are taken from the results of the experimental investigations on the vibration spectrum of diamond. The identification of the frequencies contained in column 8 of Table I with the different modes has been carried out with the help of the sequence contained in the same table. The two low frequencies appearing as the last two in Table I have not been measured very accurately. But, a combination of these two has been found to occur at about 1370 cm.^{-1} in infra-red absorption and in luminescence and absorption at low temperatures in the visible region. The eight constants appearing in the equations have therefore been determined by using the values of the six accurately known frequencies and the fact that the sum of the low frequencies is at about 1370 cm.^{-1} . The values of the constants obtained are contained in Table VI.

TABLE VI

Numerical values of the force-constants $\times 10^{-5}$ dynes per cm.

Atom 0	Atoms 1 to 4		Atoms 5 to 16			Atoms 17 to 28	
P	Q	R	S	U	W	Σ	Ω
7.35	-1.39	-0.858	-0.005	-0.131	-0.114	-0.06	+0.005

The fourth, fifth and sixth columns of Table VII show the frequencies calculated from abbreviated formulæ containing only the force constants

TABLE VII

Calculated values of the frequencies

Sequence	Degeneracy	Operative Force-constant	Frequencies from abbreviated formulæ			Complete Formulæ
			P only	P, Q, R	P, Q, R S, U, W	
I	3	$P-4Q+4S+8U-12\Sigma$	cm. ⁻¹ 1020	cm. ⁻¹ 1351	cm. ⁻¹ 1294	cm. ⁻¹ 1332
II	8	$P-2Q-2R+4W+6\Sigma+6\Omega$	1020	1294	1269	1250
III	6	$P-4R-4S-12\Omega$	1020	1234	1236	1232
IV	4	$P+2Q-4R-8W-6\Sigma+12\Omega$	1020	1064	1123	1149
V & VI	3+3	$P+4S-8U$	1020	1020	1088	1088
VII	4	$P-2Q+4R-8W+6\Sigma-12\Omega$	1020	973	1038	1008
VIII	6	$P+4R-4S+12\Omega$	1020	744	746	752
IX	8	$P+2Q+2R+4W-6\Sigma-6\Omega$	1020	635	582	620

shown, the number of neighbouring atoms taken into account being respectively 0, 4 and 16. The last column gives the experimentally observed

values which are also those given by the complete expressions taking all the force constants for the 28 neighbouring atoms into account. The values of the constants assumed are in every case those shown in Table VI.

It will be noticed from Table VI that P, Q and R are numerically by far the largest constants, as is to be expected since the four nearest atoms are linked directly by valence bonds to the atom under consideration, while the other atoms are only indirectly connected with it. Further, all the constants except P and Ω are seen to be negative. This could have been foreseen from equation (8), since P being taken as positive, then by the nature of the case the quantities Q, S, U and Σ should be negative, while the constants R and W come out negative by reason of the convention adopted regarding their sign. Table VI further shows that P is greater than 4Q, as could also have been foreseen from relation (8). The constant S comes out as practically negligible, and this is not surprising since it represents the forces on any atom due to others situated in the same cubic plane but not directly linked with it, the direction of both force and displacement being normal to the plane.

Column 5 of Table VII shows that the three constants P, Q, R suffice to give a tolerable fit with the experimentally observed values. The relative values of P, Q and R determine the sequence of the frequencies calculated from the formulæ, and this is the same as that of the observed frequencies provided that numerically $2R > Q > R$, as is actually the case. That Q would be numerically greater than R could have been expected since the former is the longitudinal and the latter the transverse component of the force exerted by one atom on another linked to it by a valence bond. If $2R < Q$, mode IV would have a lower frequency than mode VII which would scarcely have been possible in view of the much larger bond-length variations involved in the former mode.

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SUMMARY

Exact expressions have been derived for the frequencies of the nine normal modes of vibration of the diamond structure, which take account of the forces of interaction between each atom and its 28 nearest neighbours. The formulæ involve 8 independent constants together with an additional relation between them, and the constants are thus perfectly determinate

if the frequencies are known. The interactions decrease very rapidly with the increase of distance and their magnitudes and directions as evaluated from the observed frequencies are also otherwise in accord with theoretical expectations.

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