We are now in a position to calculate $\mathscr{D}$ from equation (28), i.e.

$$\mathscr{D}_{\alpha\beta} = \sum_l \frac{1}{m} \Phi_{l,\alpha\beta} \exp(-i\mathbf{k}\cdot\mathbf{r}_l). \tag{39}$$

Thus, for example, the contributions to $m\mathscr{D}_{xx}$ are, using Figure 7, from atoms 1 and 5:

$$-\tfrac{1}{3}\gamma[\exp\{-i(k_xa+k_ya+k_za)\}+\exp\{i(k_xa+k_ya+k_za)\}],$$

from atoms 2 and 6:

$$-\tfrac{1}{3}\gamma[\exp\{-i(-k_xa+k_ya+k_za)\}+\exp\{i(-k_xa+k_ya+k_za)\}],$$

from atoms 3 and 7:

$$-\tfrac{1}{3}\gamma[\exp\{-i(k_xa-k_ya+k_za)\}+\exp\{i(k_xa-k_ya+k_za)\}],$$

from atoms 4 and 8:

$$-\tfrac{1}{3}\gamma[\exp\{-i(k_xa+k_ya-k_za)\}+\exp\{i(k_xa+k_ya-k_za)\}],$$

from atoms 9 and 12:

$$-R\gamma[\exp(-ik_x\cdot 2a)+\exp(ik_x\cdot 2a)],$$

from atom 0:

$$+2\gamma(\tfrac{4}{3}+R).$$

Hence

$$\mathscr{D}_{xx} = \frac{2\gamma}{m}\left(-\tfrac{4}{3}\cos k_xa\,\cos k_ya\,\cos k_za - R\cos 2k_xa +\tfrac{4}{3}+R\right). \tag{40}$$

Other elements of $\mathscr{D}$ can be just as readily obtained, for example,

$$\mathscr{D}_{xy} = \mathscr{D}_{yx} = +\tfrac{8}{3}\gamma \sin k_xa\,\sin k_ya\,\cos k_za. \tag{41}$$

Using definitions such as

$$c_x = \cos k_xa, \qquad s_x = \sin k_xa, \qquad c_{2x} = \cos 2k_xa,$$
$$\delta = 1+\tfrac{3}{4}R - c_xc_yc_z, \tag{42}$$

the elements of $\mathscr{D}$ can be considerably simplified. The final result is

$$\mathscr{D}(\mathbf{k}) = \frac{8\gamma}{3m}\begin{pmatrix} \delta-\tfrac{3}{4}Rc_{2x} & s_xs_yc_z & s_xc_ys_z \\ s_xs_yc_z & \delta-\tfrac{3}{4}Rc_{2y} & c_xs_ys_z \\ s_xc_ys_z & c_xs_ys_z & \delta-\tfrac{3}{4}Rc_{2z} \end{pmatrix}. \tag{43}$$

3.3 Two-atom unit cell

The principal difference in the equations, in the case of more than one atom per unit cell, is that we have three equations of motion for each of the atoms. If we allow l to label all atoms, of whichever sort (note this is the

alternative procedure to the óne adopted in section 2.4), then the force constant matrices will have the same form as before, but it will be necessary to label Φ and $\mathscr{D}$, and of course the masses m and the amplitudes $\mathbf{B}$, with the type of atom.

The reason for introducing $\mathbf{B}$ and $\mathscr{D}$ originally is that they must now take the form:

$$\mathbf{B}(\kappa) = m_\kappa^{\frac{1}{2}}\mathbf{A}(\kappa), \qquad \mathscr{D}(\kappa, \kappa') = (m_\kappa m_{\kappa'})^{-\frac{1}{2}} \sum_l \Phi_l(\kappa, \kappa')\exp(-i\mathbf{k}\cdot\mathbf{r}_l), \quad (44)$$

where κ and κ' label the n different atoms in the unit cell. The equations of motion are

$$\omega^2\mathbf{B}(\kappa) = \mathscr{D}(\kappa, \kappa)\cdot\mathbf{B}(\kappa) + \sum_{\kappa'\neq\kappa} \mathscr{D}(\kappa, \kappa')\cdot\mathbf{B}(\kappa'). \qquad (45)$$

Equations (45) can be written more compactly as

$$\omega^2\mathscr{B} = \mathscr{D}'\cdot\mathscr{B}, \qquad (46)$$

where $\mathscr{D}'$ is a $3n\times 3n$ matrix and $\mathscr{B}$ is a column vector whose elements are $B_x(1)$, $B_y(1)$, $B_z(1)$, $B_x(2)$, etc.

Again we need to specify the type of lattice before proceeding any further. One of the simplest types of crystal structure having two atoms per unit cell is the CsCl structure, whose atoms form a BCC lattice having one type of atom at the cube centre and the other type on the corners of the cube, as shown in Figure 7. We shall assume as before that all the forces are radial and also that the force constants are the same for the two species of atom, so that we need consider only the difference in masses for the two types of atom. (In practice of course it would be physically unrealistic to consider only two force constants for an ionic crystal such as CsCl where the forces are quite long ranged.)

The matrices Φ will have exactly the same form as before, except that now they must also be labelled with the species of atom, and the first eight will couple different types whereas the next six couple identical atoms. Thus some matrices will now be zero, as follows: $\Phi_l(1, 1) = \Phi_l(2, 2) = 0$, $l = 1\text{–}8$; $\Phi_l(1, 2) = \Phi_l(2, 1) = 0$, $l = 9\text{–}14$; and of course $\Phi_0(1, 2) = \Phi_0(2, 1) = 0$ by definition, and $\Phi_0(1, 1) = \Phi_0(2, 2) = (\frac{8}{3}\gamma + 2\gamma R)\mathbf{I}$, as before.

If we remember that the ratio of masses is $\rho = m_1/m_2$, and use the notation of (42), we obtain for $\mathscr{D}'$

$$\mathscr{D}'(\mathbf{k}) = \frac{8}{3}\gamma(m_1 m_2)^{-\frac{1}{2}}\begin{pmatrix} \rho^{-\frac{1}{2}}(1+r_x) & 0 & 0 & -c_xc_yc_z & s_xs_yc_z & s_xc_ys_z \\ 0 & \rho^{-\frac{1}{2}}(1+r_y) & 0 & s_xs_yc_z & -c_xc_yc_z & c_xs_ys_z \\ 0 & 0 & \rho^{-\frac{1}{2}}(1+r_z) & s_xc_ys_z & c_xs_ys_z & -c_xc_yc_z \\ -c_xc_yc_z & s_xs_yc_z & s_xc_ys_z & \rho^{\frac{1}{2}}(1+r_x) & 0 & 0 \\ s_xs_yc_z & -c_xc_yc_z & c_xs_ys_z & 0 & \rho^{\frac{1}{2}}(1+r_y) & 0 \\ s_xc_ys_z & c_xs_ys_z & -c_xc_yc_z & 0 & 0 & \rho^{\frac{1}{2}}(1+r_z) \end{pmatrix},$$

$$(47)$$

where the r's arise from the second-nearest-neighbour forces, and are defined by $r_x = \frac{3}{4}R(1 - c_{2x})$, etc.

3.4 Density of states

In order to make an analytical calculation of the density of states in three dimensions, it is necessary to integrate $(\nabla_k \omega)^{-1}$ (the three-dimensional equivalent of equation (11)) over a constant frequency surface in k-space. Since this is not normally feasible, the usual approach is to compute the density of states numerically by the method first described by Walker.[1] This is usually referred to as the 'root sampling method', since it builds up the density of states by finding the roots of the secular equation at a large number of points in the Brillouin zone.

Just as in one dimension, the allowed values of k are evenly distributed in k-space, with a density such that there are N states in the first Brillouin zone. The simplest approach is to solve the secular determinant over a cubic mesh of points in k-space, and to plot a histogram of the computed frequencies. In practice, there are important refinements which involve interpolation between the calculated points,[2,3] but the principle remains the same.

In one dimension the edge of the first Brillouin zone was simply the point at which the wavelength was twice the lattice spacing and all higher values of k could be reflected back into the first Brillouin zone by simply subtracting a *reciprocal lattice vector*, $2\pi/a$.

In three dimensions, we need to be concerned with planes of atoms. (As a matter of fact the dispersion curve calculations of section 2.1 will also hold for vibrations of planes of atoms for waves in high symmetry directions, provided that the γ_l are reinterpreted as the interplanar force constants.)

For the two-atom unit cell of the CsCl structure, whose space lattice is simple cubic, the Brillouin zone is also a cube (but with its faces a perpendicular distance $\pi/2a$ from the origin since the unit cell has a side of $2a$). For a one-atom BCC lattice, on the other hand, the most widely spaced planes of atoms are the (110) planes, with spacing $\sqrt{2}a$, so that the limiting wavelength is $2\sqrt{2}a$, and (remembering that the wave vector is defined as $|k| = 2\pi/\lambda$) the first Brillouin zone is that volume bounded by the 12 (110)-type planes, each a perpendicular distance $\pi/\sqrt{2}a$ from the origin.

It is not necessary to calculate frequencies over the whole Brillouin zone, of course. Just as in one dimension, we need only consider positive values of k_x, k_y, and k_z, which reduces calculations to the first octant. Moreover, symmetry reduces the calculations necessary still further. For a cubic lattice the x-, y-, and z-directions must be equivalent, so only one-third of the octant need be considered, and if we also remember that the (110) planes

have mirror symmetry, this divides the unique portion of the Brillouin zone in half again, to only 1/48 of the whole zone (e.g. that part lying between the [100]-, [110]-, and [111]-directions).

It is worth noting at this point that for the BCC lattice the [111] dispersion curves do not repeat outside the Brillouin zone boundary, but only after twice this distance. The reason is that the (111) planes are closely spaced, and can support waves of very short wavelength (i.e. large wave vector). However, these do not lie within the first Brillouin zone because they can be reflected back into the zone (in fact, on to the zone boundary on the line joining the [$\bar{1}\bar{1}$1]- and [001]-directions) by subtracting a [110] reciprocal lattice vector.

3.5 Van Hove critical points

If we refer back to the analytical expression for the density of states in one dimension (equation (12)) we can see that there is a singularity at $\omega = \omega_0$. The reason for this is easy to understand if we re-examine Figure 2. The density of points in k-space is uniform, so that at any point on the curve where the slope approaches zero there will be a very large density of points in ω-space. For the simple model illustrated in Figure 2 this occurs at the Brillouin zone boundary, where $\omega = \omega_0$. However, any point on a dispersion curve where the slope (i.e. the group velocity of the phonons) is zero will create a singularity in the density of states—for instance the point X in Figure 3—and these are known as *Van Hove singularities*.

In three dimensions a similar feature occurs wherever $\nabla_{\mathbf{k}}(\omega) = 0$, except that whereas in equation (12) the effect was proportional to $(|\omega^2 - \omega_0^2|)^{-\frac{1}{2}}$, in three dimensions the corresponding contribution is proportional to the less drastic $(|\omega^2 - \omega_0^2|)^{\frac{1}{2}}$. The latter frequency dependence does not create a singularity at ω_0, merely a cusp or critical point in the curve as the extra contribution starts or ceases. Nevertheless, one of the most characteristic features of a three dimensional density of states curve is the series of Van Hove critical points, or discontinuities in the slope of the curve, and in many cases these can be associated with points of zero slope on the phonon dispersion curves in high symmetry directions.

4. COMPUTER PROGRAM

4.1 Computation of the density of states

In a normal experimental determination of the density of states, the actual measurements are made on the dispersion curves in symmetry directions in the crystal. The commonest method is probably inelastic neutron scattering, although the pioneering work by Walker[1] was based on X-ray diffuse scattering measurements.

The force constants (typically five to nine constants are determined, including some non-radial forces) are then found by solving the secular determinant along the symmetry directions and varying the constants to obtain the best fit to the experimental data.

For the purposes of the simulation program to be described here, this approach is reversed, and the user sets the ratio of the two force constants being considered. This value is then used to generate a theoretical set of dispersion curves so that the effect of the two constants on the dispersion curves can be examined.

The final determination of the density of states follows the normal experimental approach, using the values chosen for the force constants in the secular determinant and evaluating the determinant over a mesh of points in **k**-space to build up a histogram of the density of states.

4.2 Program details

Since numerical values are of less interest than the shape of the various curves, the program output consists entirely of curves, with arbitrary scales on the axes, plotted on the line printer (although it would be quite a simple task for the reader to alter the printing subroutines to have the output generated on a graph plotter). This means that it is unnecessary to specify values for the lattice spacing, force constant, or atomic mass, as it is only the ratios of the force constants and masses that affect the shape of the curves.

The program is based on the two subroutines D1 and D2, which set up the dynamical matrices for the one-atom and two-atom cases respectively. Each subroutine then calls a standard library subroutine to evaluate the secular determinant, whose eigenvalues are the squares of the frequencies of the normal modes of vibration. The program has been developed using the NAG subroutine F02AAF, which solves the simple eigenvalue problem $\mathbf{A} \cdot \mathbf{x} = \lambda \mathbf{x}$ for a real symmetric matrix. Any similar subroutine may be used instead, but it should be noted that the NAG subroutine returns the eigenvalues in ascending order. This fact is utilized in the main program, so if the subroutine chosen does not do this, it will be necessary to sort the values immediately after the subroutine call.

After reading in the necessary data (described in the next subsection) the program calculates the frequencies of the three normal modes at equal intervals of k, along the three symmetry directions [100], [110], and [111]. The subroutine PRDC then outputs the dispersion curves, in graphical form, on the line printer. The ω- and k-axes both have annotated scales with arbitrary units, but the respective scales are the same for all three sets of dispersion curves. Where the curves, or individual points on them, are degenerate, they are denoted by stars instead of crosses. For the one-atom case, the [111] dispersion curves do not repeat outside the Brillouin zone (as
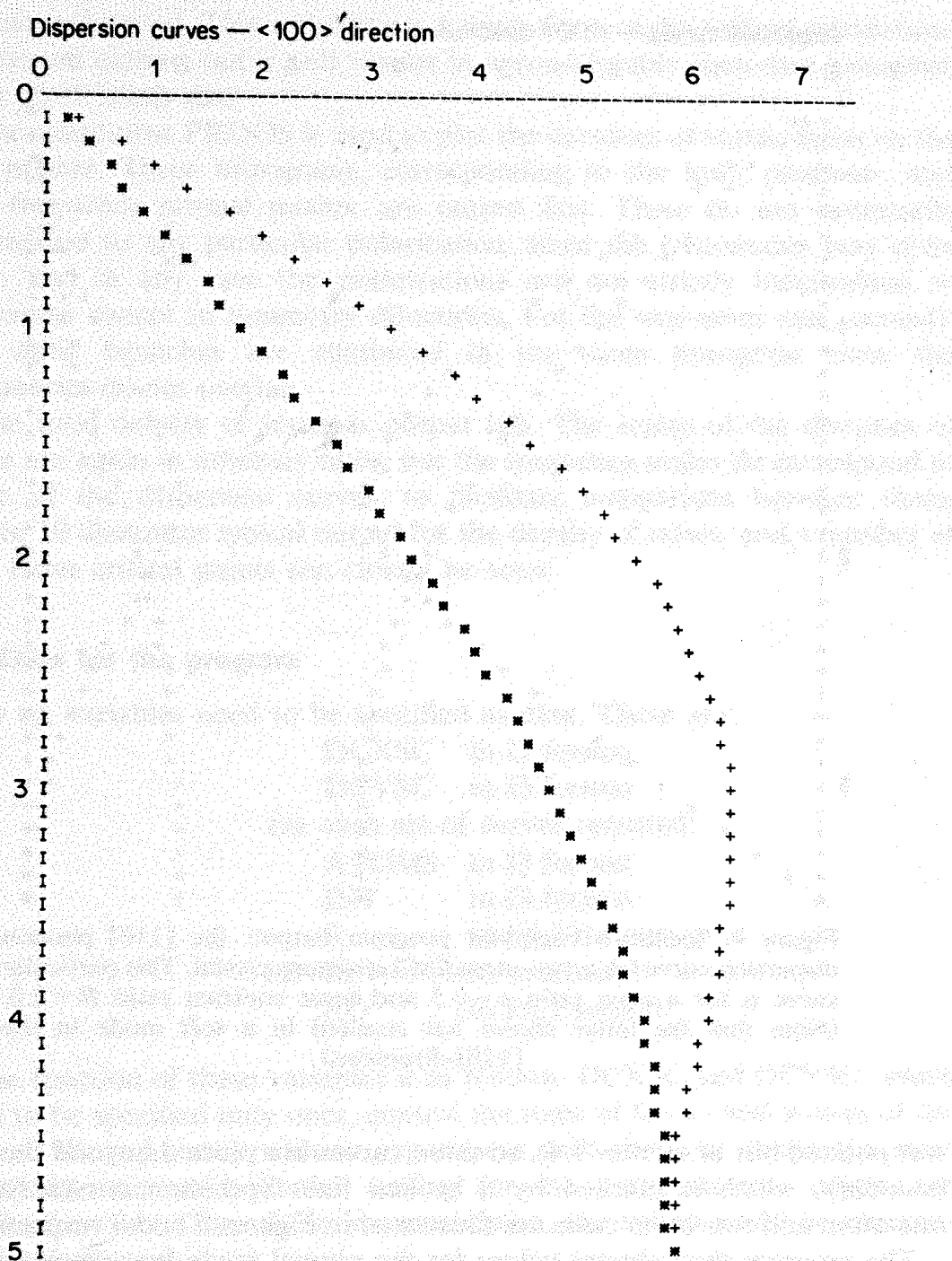
Figure 8. Specimen computer program output: the [100] phonon dispersion curve for a one-atom BCC crystal lattice. This particular curve is for the force constant ratio $R = 0.8$. DCXSC and DCYSC have been specified as 25 and 75 respectively; these values are smaller than would normally be specified for a line printer, but would be suitable for a terminal
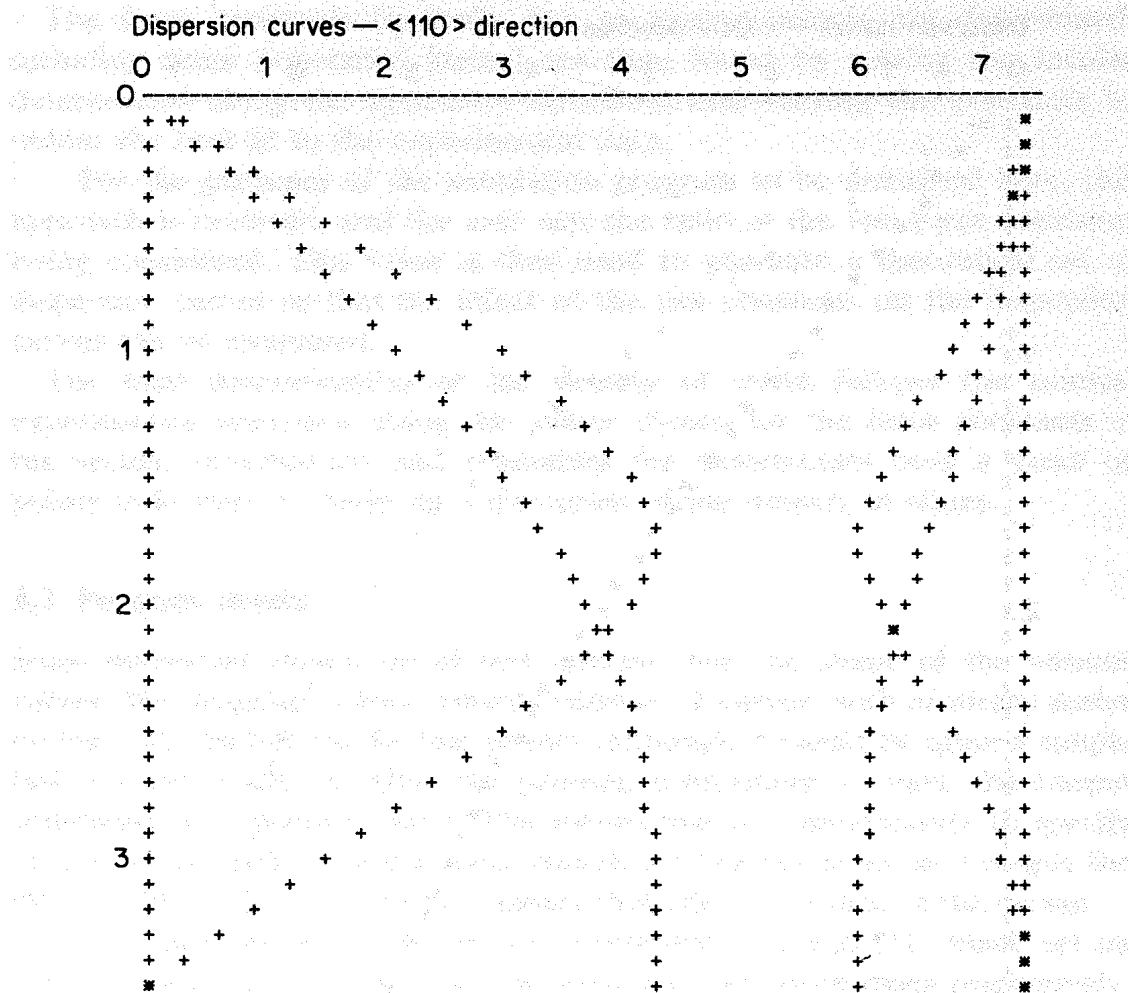
```
Dispersion curves — <110> direction
     0        1        2        3    .   4        5        6        7
 0 ────────────────────────────────────────────────────────────────
     + ++                                                           *
     +    + +                                                       *
     +      + +                                                    +*
     +       +  +                                                  *+
     +         +  +                                               +++
     +          +   +                                             +++
     +            +   +                                           ++ +
     +              +   +                                        +  + +
     +               +    +                                      + +  +
 1 +                  +      +                                   +  +  +
     +                    +     +                                 +  +  +
     +                      +      +                             +  +   +
     +                        +      +                          +   +   +
     +                          +      +                        +   +   +
     +                           +      +                       +   +   +
     +                            +       +                    +   +    +
     +                              +       +                  +  +     +
     +                                +       +                +  +     +
     +                                 +       +              +  +      +
 2 +                                    +  +                 + +       +
     +                                    ++                  *        +
     +                                    + +                ++        +
     +                                   +   +              +  +       +
     +                                  +      +           +    +      +
     +                                 +        +          +     +     +
     +                              +            +         +      +   +
     +                           +                +        +       + +
     +                        +                    +       +        ++
     +                     +                        +       +       ++
 3 +               +                                +        +       ++
     +           +                                  +        +       ++
     +        +                                     +        +       *
     +     +                                        +        +       *
     + +                                            +       +        *
     *                                              +        +       *
```

Figure 9. Specimen computer program output: the [110] phonon dispersion curve for a two-atom CsCl structure crystal. This particular curve is for a mass ratio $\rho = 0.5$ and force constant ratio $R = 0.0$. (Note that the latter choice has resulted in a soft mode in the [110]-directions)

was pointed out in section 3.4), so these curves are plotted beyond the zone boundary, which is marked by a broken line. Specimen curves for the one-atom and two-atom cases are illustrated in Figures 8 and 9 respectively.

The program then obtains values for the normal mode frequencies over a mesh of points in the irreducible portion of the Brillouin zone, giving only half weighting to points on the sides of the portion, since they are shared with the neighbouring portion. As the frequencies are calculated, they are immediately stored in histograms, which when completed form the densities of states for each of the modes of vibration. Instead of forming a simple histogram, each frequency value is made to contribute to the two frequency intervals centred above and below it, the contributions being weighted according to the closeness of the frequency value to the centre of the

frequency interval. This weighting is a crude form of the refined calculations mentioned earlier, but it still results in a considerably smoother histogram for a given mesh size.

The subroutine PRDOS is used to plot the densities of states, again on the line printer. Three histograms, corresponding to the low-, medium-, and high-frequency normal modes, are output first. These do not necessarily correspond to any particular polarization, since the frequencies may cross over, and in any case the polarizations are not strictly longitudinal or transverse except in symmetry directions. For the two-atom case, acoustic and optic branches are combined in the same histogram since the frequencies do not overlap.

The total density of states is output last. The scales of the densities of states are again in arbitrary units, but the frequency scales do correspond to those of the dispersion curves, to facilitate comparison between them. Figure 10 illustrates typical output for the density of states, and a number of Van Hove critical points can clearly be seen.

4.3 Data for the program

Only six variables need to be specified as data. These are:

DCXSC   in I3 format
DCYSC   in I3 format

for each set of curves required:

ATOMS   in I3 format
INT   in I3 format
R   in F6.2 format

for the two-atom case only:

RO   in F6.2 format.

The function of these variables is as follows: DCXSC and DCYSC, which need to be specified only once, control the scale of the x- and y-axes of the output. The user may wish to experiment with these to obtain the most presentable size and relative scaling for the particular line printer (or terminal) in use. Once these are established, the values could be incorporated into the program.

ATOMS should be given the value 1 or 2 respectively to simulate the appropriate lattice—one-atom BCC or two-atom CsCl structure. The program will plot as many sets of curves as required and a value for ATOMS of zero must be specified to terminate the program.

INT sets the scale of the mesh for the density of states calculation. Obviously, the greater the number of mesh points the smoother the resulting histograms, but the number of points, and resulting computing time, will increase roughly as INT cubed. The user is left to set the size of the mesh

Figure 10. Specimen computer program output: the phonon densities of states. These particular curves are for a one-atom BCC lattice with $R = 0.8$ (a) Densities of states for the low-, medium-, and high-frequency polarizations; (b) total density of states
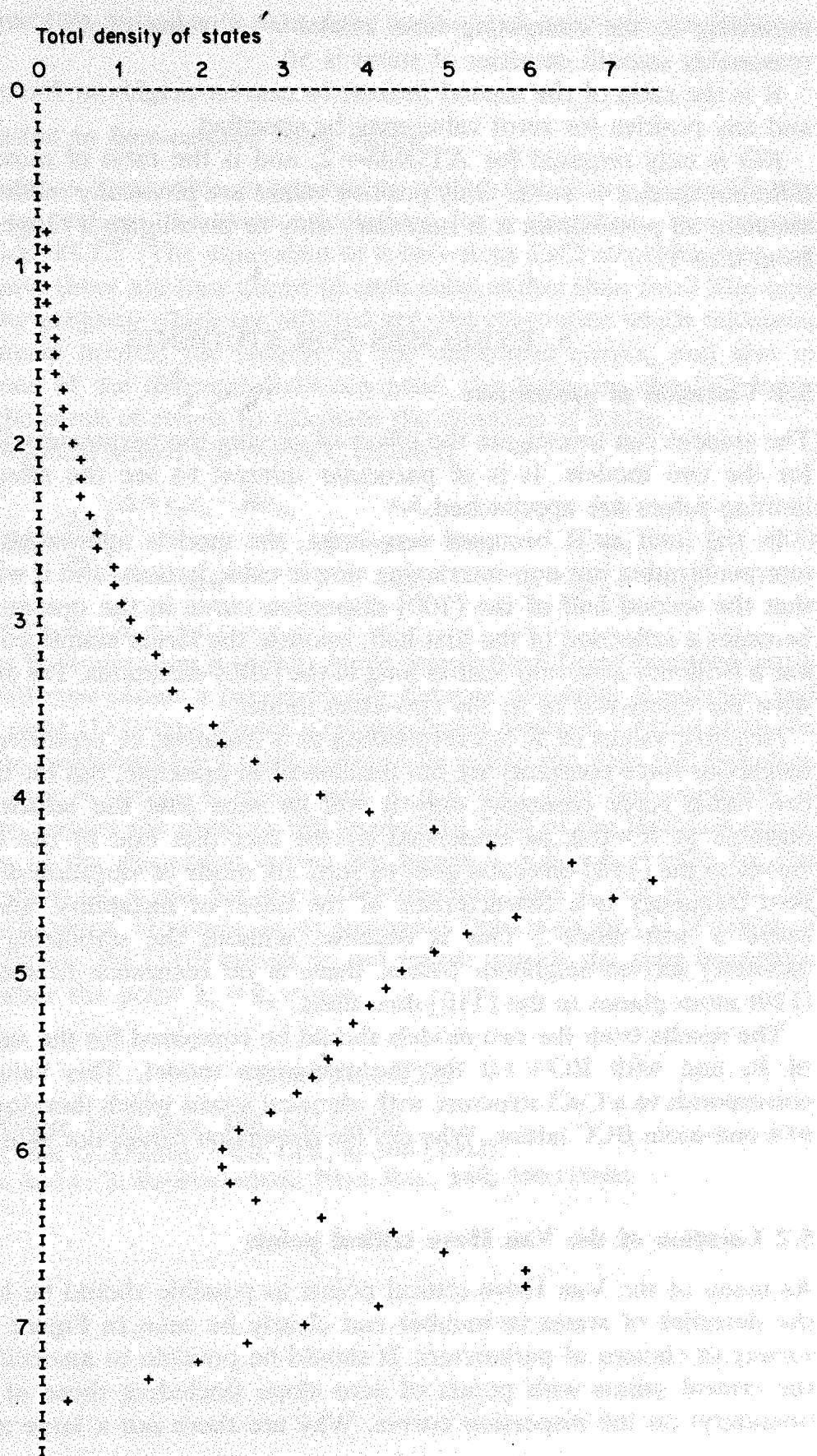
Figure 10b

according to the computing time available—a value of INT which gives reasonably smooth densities of states is 50.

R is the ratio of the second nearest to nearest-neighbour force constant, and any positive (or zero) value may be specified.

RO is only required for ATOMS = 2, and is the ratio of masses of the different species of atom. Only positive values are physically realistic, and to simulate all possibilities it is necessary only to investigate a range of values from 0 to 1.

5. EXERCISES FOR STUDENTS

5.1 Variation of parameters

The student can investigate the effect of varying the parameters R and RO for the two models. It is of particular interest to see the effects as the limiting values are approached.

In the limit as R becomes very large, the models approximate to two interpenetrating but non-interacting simple cubic lattices, and it will be seen that the second half of the [100] dispersion curve in the one-atom model becomes a reflection of the first half, because the larger simple cubic lattice has a Brillouin zone only half as long in the [100]-directions. Try and predict what the effect will be in the two-atom model.

Negative values of R (corresponding to a negative, or repulsive, second-neighbour force constant) are not disallowed in principle, but for the case of two radial force constants only it will be seen that the lattice becomes unstable at R = 0.0, as evidenced by the fact that one of the dispersion curves in the [110]-direction goes to zero. (A mode of vibration dropping to zero frequency is a characteristic of the onset of instability, and is often called a 'soft mode'.) This is because, without the stabilizing effect of (positive) second-neighbour forces, there is no resistance to shear of the (110) atom planes in the [$\bar{1}$10]-directions.

The results from the two models should be compared for the same values of R, and with RO = 1.0 for the two-atom model. This value of RO corresponds to a CsCl structure with identical atoms which therefore reduces to a one-atom BCC lattice. Why are the dispersion curves not identical?

5.2 Location of the Van Hove critical points

As many of the Van Hove critical points as possible should be located on the densities of states (a number can clearly be seen in Figure 10) for a variety of choices of parameters. It should be possible to associate most of the critical points with points of zero slope (including those at the zone boundary) on the dispersion curves. Why are there not a large number of

critical points associated with zero slope positions elsewhere in the Brillouin zone?

5.3 Extension to face-centred cubic lattice

Readers with a reasonable programming ability should try to modify the program to perform the same calculations for a one-atom, face-centred cubic lattice (FCC). (The equivalent of a two-atom CsCl structure does not exist because there are four atoms to each cube, rather than two.) The only parts of the program which are affected are: the subroutine which calculates the dynamical matrix; the lengths of the dispersion curves; and also in consequence of the different Brillouin zone, the limits on the DO loops creating the mesh of points to calculate the densities of states.

The dynamical matrix for the FCC lattice is

$$\mathscr{D}(\mathbf{k}) = \frac{2\gamma}{m} \begin{pmatrix} \Delta + c_y c_z - Rc_{2x} & s_x s_y & s_x s_z \\ s_x s_y & \Delta + c_x c_z - Rc_{2y} & s_y s_z \\ s_x s_z & s_y s_z & \Delta + c_x c_y - Rc_{2z} \end{pmatrix}, \quad (48)$$

where $\Delta = 2 + R - (c_x c_y + c_y c_z + c_z c_x)$.

The first Brillouin zone is slightly more complicated, being bounded partly by six (100)-type planes a perpendicular distance π/a from the centre, and partly by eight (111)-type planes a perpendicular distance $\sqrt{3}\pi/2a$ from the centre. The conditions for a mesh point to lie within the zone will therefore be $k_x + k_y + k_z \leqslant 3\pi/2a$, $k_x \leqslant \pi/a$ and $k_z \leqslant k_y \leqslant k_x$ (the last condition is imposed to restrict the mesh to the irreducible 1/48 of the Brillouin zone). The limits of the dispersion curves are hence $k_x = k_y = k_z = \pi/2a$ for the [111]-direction, $k_x = \pi/a$ for the [100]-direction, and $k_x = k_y = 3\pi/4a$ for the [110]-direction. However, in an analogous fashion to the [111] curves of the BCC lattice, the [110] curves do not repeat outside the zone boundary, but only after the point $k_x = k_y = \pi/a$.

REFERENCES

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2. G. Gilat and G. Dolling, *Phys. Lett.*, **8**, 304 (1964).
3. G. Gilat and L. J. Raubenheimer, *Phys. Rev.*, **144**, 390 (1966).

LATTICE DYNAMICS PROGRAM

```
      INTEGER ATOMS,INT,KX,KY,KZ,K,LIM,INT1,INT2,INT3,DIR,J,I,L,M,WINT,
     1.      IFAIL,DCYSC,DCXSC,DOSXSC,CH(120)
      REAL PI,R,WMAX,NWMAX,WT,WFRAC,QX,QY,QZ,W(3,6,200),NW(6,200),
     1    N(200),RO,NMAX
      COMMON CH
C
C     ATOMS MUST BE SET TO 1 FOR THE CASE OF THE SINGLE ATOM, B.C.C.
C     LATTICE AND 2 FOR THE CASE OF THE TWO ATOM CSCL LATTICE.
C     J IS THUS THE NUMBER OF BRANCHES OF THE DISPERSION CURVES.
C     R IS THE RATIO OF SECOND-NEAREST TO NEAREST NEIGHBOUR FORCE
C     CONSTANTS. IN THE LATTER CASE, RO IS THE RATIO OF ATOMIC MASSES.
C     R MUST BE .GE. ZERO FOR THE MODELS CHOSEN, AND RO MUST BE .GT.
C     ZERO. VALUES OF RO .LE. ONE WILL COVER ALL EVENTUALITIES.
C     INT IS AN INTEGER, THE NUMBER OF POINTS IN K-SPACE IN EACH
C     DIRECTION TO BE USED IN THE CALCULATIONS OF THE DENSITY OF
C     STATES.
C
      IFAIL=0
      PI=4.0*ATAN(1.0)
      READ(1,1001)DCXSC
C
C     DCXSC CONTROLS THE SCALE OF THE K AXIS OF THE DISPERSION
C     CURVES. 40 IS SUGGESTED AS A SUITABLE VALUE, BUT IN ANY CASE IT
C     SHOULD NOT EXCEED 57 UNLESS THE SIZE OF ARRAY W IS CHANGED.
C
      READ(1,1001)DCYSC
C
C     DCYSC CONTROLS THE SCALE OF THE W AXIS OF ALL THE CURVES
C     AND THE Y AXIS OF THE DENSITIY OF STATES CURVES.
C     117 IS SUGGESTED AS A SUITABLE VALUE FOR A 120 CHARACTER
C     LINE PRINTER, BUT IN ANY CASE IT MUST BE AT LEAST 3 LESS
C     THAN THE AVAILABLE NUMBER OF CHARACTERS, IT MUST BE
C     DIVISIBLE BY 3, AND IT SHOULD NOT EXCEED 120 UNLESS THE
C     DIMENSION OF CH AND THE FORMAT STATEMENTS WHERE IT IS
C     PRINTED ARE ALTERED ACCORDINGLY.
C
  100 READ(1,1001)ATOMS
 1001 FORMAT(I3)
      IF (ATOMS.EQ.0) GOTO 199
      READ(1,1001)INT
      READ(1,1002)R
 1002 FORMAT(F6.2)
      WRITE(2,1003)
 1003 FORMAT(//////)
      WRITE(2,1005)
 1005 FORMAT(48H DISPERSION CURVES AND DENSITIES OF STATES FOR A)
      IF (ATOMS.EQ.2) GOTO 101
      J=3
      WRITE(2,1006)
 1006 FORMAT(33H MONATOMIC B.C.C. CRYSTAL LATTICE)
  101 CONTINUE
      IF (ATOMS.EQ.1) GOTO 102
      J=6
      READ(1,1002)RO
      WRITE(2,1007)
 1007 FORMAT(35H DIATOMIC CSCL TYPE CRYSTAL LATTICE)
```

LATTICE DYNAMICS PROGRAM

```
  102 CONTINUE
      WRITE(2,1008)R
 1008 FORMAT(42H RATIO OF INTERATOMIC FORCE CONSTANTS = 1:,F8.4)
      IF (ATOMS.EQ.2) WRITE(2,1009)RO
 1009 FORMAT(28H RATIO OF ATOMIC MASSES = 1:,F8.4)
      WMAX=0.0
C
C     INTEGER COUNTERS K, KX, KY, KZ WILL BE USED TO CONTROL LOOPS OVER
C     MESHES IN K-SPACE. QX, QY, QZ WILL BE USED FOR THE ACTUAL VALUES
C     OF THE PRODUCT KA. THUS FOR THE ATOMS=1 CASE, THE MAXIMUM VALUE
C     OF EACH Q WILL BE PI ALONG THE <100> DIRECTIONS, AND PI/2 FOR THE
C     <110> AND <111> DIRECTIONS. HOWEVER, SINCE IN THE <111> DIRECTIONS
C     THE DISPERSION CURVES DO NOT REPEAT OUTSIDE THE BRILLOUIN ZONE
C     THESE ARE ALLOWED TO RUN TO THE REPEAT DISTANCE PI, AND THE EDGE
C     OF THE BRILLOUIN ZONE IS MARKED BY A BROKEN LINE ON THE PRINT-OUT.
C         FOR ATOMS=2 THE MAXIMUM VALUE OF EACH Q IS PI/2.
C
      INT1=DCXSC*2/ATOMS
      DO 103 K=1,INT1,1
         QX=FLOAT(K)*PI/FLOAT(INT1*ATOMS)
         QY=0.0
         QZ=0.0
         IF (ATOMS.EQ.1) CALL D1(1,K,QX,QY,QZ,R,W,IFAIL)
         IF (ATOMS.EQ.2) CALL D2(1,K,QX,QY,QZ,R,RO,W,IFAIL)
         IF (IFAIL.EQ.1) GOTO 199
         IF (WMAX.LT.W(1,J,K)) WMAX=W(1,J,K)
C
C     THE SUBROUTINE F02AAF IN THE SUBROUTINES D1 AND D2 RETURNS THE
C     EIGENVALUES OF W**2 IN ASCENDING ORDER, SO FINDING THE MAXIMUM
C     VALUE OF W(DIR,J,K) FOR ALL DIR AND K IS SUFFICIENT TO FIND THE
C     MAXIMUM FREQUENCY.
C
  103 CONTINUE
      INT2=IFIX(FLOAT(DCXSC)*SQRT(2.0))
      DO 104 K=1,INT2,1
         QX=FLOAT(K)*PI*0.5/FLOAT(INT2)
         QY=QX
         QZ=0.0
         IF (ATOMS.EQ.1) CALL D1(2,K,QX,QY,QZ,R,W,IFAIL)
         IF (ATOMS.EQ.2) CALL D2(2,K,QX,QY,QZ,R,RO,W,IFAIL)
         IF (IFAIL.EQ.1) GOTO 199
         IF (WMAX.LT.W(2,J,K)) WMAX=W(2,J,K)
  104 CONTINUE
      INT3=IFIX(FLOAT(DCXSC)*SQRT(3.0)*2.0/FLOAT(ATOMS))
      DO 105 K=1,INT3,1
         QX=FLOAT(K)*PI/FLOAT(INT3*ATOMS)
         QY=QX
         QZ=QX
         IF (ATOMS.EQ.1) CALL D1(3,K,QX,QY,QZ,R,W,IFAIL)
         IF (ATOMS.EQ.2) CALL D2(3,K,QX,QY,QZ,R,RO,W,IFAIL)
         IF (IFAIL.EQ.1) GOTO 199
         IF (WMAX.LT.W(3,J,K)) WMAX=W(3,J,K)
  105 CONTINUE
      WRITE(2,1010)
 1010 FORMAT(////37H  DISPERSION CURVES - <100> DIRECTION)
      CALL PRDC(INT1,1,J,DCYSC,W,WMAX)
```

LATTICE DYNAMICS PROGRAM

```
      WRITE(2,1011)
 1011 FORMAT(//37H  DISPERSION CURVES - <110> DIRECTION)
      CALL PRDC(INT2,2,J,DCYSC,W,WMAX)
      WRITE(2,1012)
 1012 FORMAT(//37H  DISPERSION CURVES - <111> DIRECTION)
      CALL PRDC(INT3,3,J,DCYSC,W,WMAX)
C
C     THE IRREDUCIBLE PORTION OF THE BRILLOUIN ZONE IS SPECIFIED BY
C     THE CONDITION KZ<KY<KX. THE BRILLOUIN ZONE BOUNDARY FOR ATOMS=2
C     (SIMPLE CUBIC) IS SIMPLY A CUBE OF SIDE PI/2. THUS ALLOWING VALUES
C     OF QX UP TO PI/2 TERMINATES ON THE BRILLOUIN ZONE BOUNDARY.
C        THE BRILLOUIN ZONE FOR ATOMS=1 (F.C.C. RECIPROCAL LATTICE) IS
C     A (110) PLANE, I.E. IT IS SPECIFIED BY QX+QY=PI. THUS ALLOWING
C     QX VALUES UP TO PI, AND SPECIFYING QY<QX AND ALSO QY<<(PI-QX)
C     TERMINATES ON THE ZONE BOUNDARY. IT IS NECESSARY TO GIVE POINTS ON
C     THE ZONE BOUNDARY, OR THE BOUNDARIES OF THE IRREDUCIBLE PORTION,
C     REDUCED WEIGHTING OF ONE HALF. HOWEVER, IF KZ IS GIVEN HALF
C     INTEGER VALUES, TWO OF THE THREE SIDES, AND ALL THE EDGES OF THE
C     PORTION ARE AVOIDED, WHICH SIMPLIFIES THE POINTS OF REDUCED
C     WEIGHTING TO THOSE FOR QY=QX OR (PI-QX), AND QX=PI/2 (THE LATTER
C     ONLY MATERIALLY AFFECTS THE ATOMS=2 CASE).
C
      DO 106 WINT=1,200,1
         N(WINT)=0
         DO 106 I=1,6,1
            NW(I,WINT)=0
  106 CONTINUE
      DOSXSC=0
      INT2=INT
      IF (ATOMS.EQ.2) INT2=INT/2
      DO 107 KX=1,INT2,1
         QX=FLOAT(KX)*PI/FLOAT(INT)
         LIM=KX
         IF (KX.GT.INT/2) LIM=INT-KX
C
C     SETS LIM AS THE APPROPRIATE BOUNDARY FOR KY.
C
         DO 107 KY=1,LIM,1
            QY=FLOAT(KY)*PI/FLOAT(INT)
            DO 107 KZ=1,KY,1
               QZ=(FLOAT(KZ)-0.5)*PI/FLOAT(INT)
               IF (ATOMS.EQ.1) CALL D1(1,1,QX,QY,QZ,R,W,IFAIL)
               IF (ATOMS.EQ.2) CALL D2(1,1,QX,QY,QZ,R,RO,W,IFAIL)
               IF (IFAIL.EQ.1) GOTO 199
C
C     IT IS UNNECESSARY THIS TIME TO FILL ALL ELEMENTS OF THE ARRAY W
C     SINCE THE VALUES WILL IMMEDIATELY BE USED TO INCREMENT THE
C     APPROPRIATE ARRAY ELEMENTS OF THE DENSITY OF STATES.
C
               WT=1.0
               IF (KY.EQ.LIM.OR.KX.EQ.INT2) WT=0.5
               DO 107 I=1,J,1
                  W(1,I,1)=FLOAT(DCYSC-1)*W(1,I,1)/WMAX
                  WINT=IFIX(W(1,I,1))
                  IF (DOSXSC.LT.WINT+2) DOSXSC=WINT+2
C
```

LATTICE DYNAMICS PROGRAM

```
C      THE SCALE OF THE X AXIS (WHICH IS W IN THIS CASE) IS MADE THE
C      SAME AS THE Y AXIS (ALSO W) OF THE DISPERSION CURVES.
C      THE SCALE LENGTH OF THE X AXIS IS SET TO THE LARGEST VALUE OF
C      FREQUENCY ANYWHERE IN THE BRILLOUIN ZONE IN CASE THERE ARE ANY
C      FREQUENCIES GREATER THAN WMAX, WHICH IS THE GREATEST FREQUENCY
C      IN ANY SYMMETRY DIRECTION.
C
               WFRAC=W(1,I,1)-FLOAT(WINT)
               NW(I,WINT+1)=NW(I,WINT+1)+(1.0-WFRAC)*WT
               NW(I,WINT+2)=NW(I,WINT+2)+WFRAC*WT
C
C      TO GENERATE A SMOOTHER DENSITY OF STATES, RATHER THAN PLOT A
C      SIMPLE HISTOGRAM EACH CALCULATED FREQUENCY IS DIVIDED BETWEEN
C      THE TWO HISTOGRAM POINTS ABOVE AND BELOW, WEIGHTED ACCORDING TO
C      HOW CLOSE THE FREQUENCY IS TO EITHER POINT.
C
  107 CONTINUE
      NWMAX=0.0
      NMAX=0.0
      DO 108 WINT=1,200,1
         DO 109 I=1,3,1
            IF (ATOMS.EQ.2) NW(I,WINT)=NW(I,WINT)+NW(I+3,WINT)
            N(WINT)=N(WINT)+NW(I,WINT)
            IF (NWMAX.LT.NW(I,WINT)) NWMAX=NW(I,WINT)
  109    CONTINUE
         IF (NMAX.LT.N(WINT)) NMAX=N(WINT)
  108 CONTINUE
      CALL PRDOS(NW,NWMAX,N,NMAX,DCYSC,DOSXSC)
      GOTO 100
  199 STOP
      END




      SUBROUTINE D1(DIR,K,QX,QY,QZ,R,W,IFAIL)
      INTEGER DIR,K,I,J,IFAIL
      REAL QX,QY,QZ,R,DIAG,W(3,6,200),D(3,3),S(3),C(3),W2(3),
     1     WKSPC(3)
C
C      THIS SUBROUTINE SETS UP THE 3*3 DYNAMICAL MATRIX FOR THE ONE ATOM
C      UNIT CELL, AND USES A STANDARD LIBRARY SUBROUTINE F02AAF TO FIND
C      THE EIGENVALUES OF THE SECULAR DETERMINANT. ANY SIMILAR SUB-
C      ROUTINE WHICH FINDS THE EIGENVALUES OF A REAL SYMMETRIC MATRIX
C      MAY BE USED INSTEAD, AND THE EIGENVECTORS ARE NOT REQUIRED.
C
      C(1)=COS(QX)
      C(2)=COS(QY)
      C(3)=COS(QZ)
      S(1)=SIN(QX)
      S(2)=SIN(QY)
      S(3)=SIN(QZ)
      DIAG=1.0+0.75*R-C(1)*C(2)*C(3)
      D(1,1)=DIAG-0.75*R*COS(2.0*QX)
      D(2,2)=DIAG-0.75*R*COS(2.0*QY)
```

LATTICE DYNAMICS PROGRAM

```
       D(3,3)=DIAG-0.75*R*COS(2.0*QZ)
       D(1,2)=S(1)*S(2)*C(3)
       D(2,3)=C(1)*S(2)*S(3)
       D(3,1)=S(1)*C(2)*S(3)
       D(2,1)=D(1,2)
       D(3,2)=D(2,3)
       D(1,3)=D(3,1)
       CALL F02AAF(D,3,3,W2,WKSPC,0)
C
C      THE PARAMETERS OF F02AAF(D,N,N,W2,WKSPC,IFAIL) ARE AS FOLLOWS:
C      D IS THE DYNAMICAL MATRIX, OF DIMENSION NXN, W2 IS THE ARRAY
C      OF EIGENVALUES (THE SQUARES OF THE NORMAL MODE FREQUENCIES),
C      WKSPC IS AN ARRAY OF DIMENSION N PROVIDED FOR WORKING SPACE
C      AND IFAIL IS AN INTEGER DETERMINING THE MODE OF ACTION IN
C      THE EVENT OF FAILURE OF THE SUBROUTINE. THE VALUE 0 CAUSES
C      TERMINATION OF THE PROGRAM   WHENEVER AN ERROR IS DETECTED.
C
       DO 501 I=1,3,1
          IF(ABS(W2(I)).LT.0.00001) W2(I)=0.0
C
C      ROUNDING ERRORS MAY PRODUCE SMALL NEGATIVE VALUES IN
C      THE EIGENVALUES WHEN THE CORRECT VALUES ARE ZERO
C
          IF(W2(I).LT.0.0) GOTO 502
          W(DIR,I,K)=SQRT(W2(I))
   501 CONTINUE
       RETURN
   502 WRITE(2,5001)
  5001 FORMAT(42H SUBROUTINE D1 PRODUCES NEGATIVE FREQUENCY)
       IFAIL=1
       RETURN
       END


       SUBROUTINE D2(DIR,K,QX,QY,QZ,R,RO,W,IFAIL)
       INTEGER DIR,K,I,J,IFAIL
       REAL QX,QY,QZ,R,RO,ROOTRO,W(3,6,200),D(6,6),S(3),C(3),
      1      W2(6),WKSPC(6)
C
C      THIS SUBROUTINE IS SIMILAR TO D1, EXCEPT THAT IT SOLVES THE 6*6
C      MATRIX FOR THE TWO ATOM UNIT CELL.
C
       C(1)=COS(QX)
       C(2)=COS(QY)
       C(3)=COS(QZ)
       S(1)=SIN(QX)
       S(2)=SIN(QY)
       S(3)=SIN(QZ)
       ROOTRO=SQRT(RO)
       DO 801 I=1,6,1
          DO 801 J=1,6,1
             D(I,J)=0.0
   801 CONTINUE
```

LATTICE DYNAMICS PROGRAM

```
      D(1,1)=ROOTRO*(1.0+0.75*R-0.75*R*COS(2.0*QX))
      D(2,2)=ROOTRO*(1.0+0.75*R-0.75*R*COS(2.0*QY))
      D(3,3)=ROOTRO*(1.0+0.75*R-0.75*R*COS(2.0*QZ))
      D(4,4)=(1.0+0.75*R-0.75*R*COS(2.0*QX))/ROOTRO
      D(5,5)=(1.0+0.75*R-0.75*R*COS(2.0*QY))/ROOTRO
      D(6,6)=(1.0+0.75*R-0.75*R*COS(2.0*QZ))/ROOTRO
      DO 802 I=1,3,1
         D(I,I+3)=-C(1)*C(2)*C(3)
         D(I+3,I)=D(I,I+3)
  802 CONTINUE
      D(1,5)=S(1)*S(2)*C(3)
      D(1,6)=S(1)*C(2)*S(3)
      D(2,6)=C(1)*S(2)*S(3)
      D(5,1)=D(1,5)
      D(2,4)=D(1,5)
      D(4,2)=D(1,5)
      D(6,1)=D(1,6)
      D(3,4)=D(1,6)
      D(4,3)=D(1,6)
      D(6,2)=D(2,6)
      D(3,5)=D(2,6)
      D(5,3)=D(2,6)
      CALL F02AAF(D,6,6,W2,WKSPC,0)
      DO 803 I=1,6,1
         IF (ABS(W2(I)).LT.0.00001) W2(I)=0.0
C
C     ROUNDING ERRORS MAY PRODUCE SMALL NEGATIVE VALUES IN
C     THE EIGENVALUES WHEN THE CORRECT VALUES ARE ZERO
C
         IF (W2(I).LT.0.0) GOTO 804
         W(DIR,I,K)=SQRT(W2(I))
  803 CONTINUE
      RETURN
  804 WRITE(2,8001)
 8001 FORMAT(42H SUBROUTINE D2 PRODUCES NEGATIVE FREQUENCY)
      IFAIL=1
      RETURN
      END


      SUBROUTINE PRDC(INT,DIR,J,DCYSC,W,WMAX)
      INTEGER INT,DIR,J,I,K,L,M,KMAX,XAXIS,YAXIS,SPACE,CROSS,SUB,
     1          DCYSC,STAR,PT(6),CH(120),NOUGHT,ONE,TWO,THREE,
     2          FOUR,FIVE,SIX,SEVEN,EIGHT,NINE,DCYSC2,SCALE
      REAL WMAX,W(3,6,200)
      COMMON CH
      DATA XAXIS,YAXIS,SPACE,CROSS,STAR/1HI,1H-,1H ,1H+,1H*/
      DATA NOUGHT,ONE,TWO,THREE,FOUR/1H0,1H1,1H2,1H3,1H4/
      DATA FIVE,SIX,SEVEN,EIGHT,NINE/1H5,1H6,1H7,1H8,1H9/
C
C     THIS SUBROUTINE PRODUCES A GRAPH OF THE DISPERSION CURVES ON
C     THE LINEPRINTER.
C
```

LATTICE DYNAMICS PROGRAM

```
        DCYSC2=DCYSC+2
        DO 601 L=1,DCYSC2,1
601        CH(L)=SPACE
        CH(2)=NOUGHT
        CH(12)=ONE
        CH(22)=TWO
        CH(32)=THREE
        CH(42)=FOUR
        CH(52)=FIVE
        CH(62)=SIX
        CH(72)=SEVEN
        CH(82)=EIGHT
        CH(92)=NINE
        CH(102)=NOUGHT
        CH(112)=ONE
        WRITE(2,1601) (CH(K),K=1,DCYSC2)
        DO 602 L=2,DCYSC2,1
602        CH(L)=YAXIS
        CH(1)=NOUGHT
        WRITE(2,1601) (CH(K),K=1,DCYSC2)
1601 FORMAT(1H ,120A1)
        DO 603 I=1,INT,1
           DO 604 L=1,DCYSC2,1
              CH(L)=SPACE
              IF(DIR.EQ.3.AND.J.EQ.3.AND.I.EQ.INT/2
     1           .AND.L.EQ.(L/2)*2) CH(L)=YAXIS
604        CONTINUE
           CH(1)=XAXIS
           DO 605 L=1,J,1
              PT(L)=IFIX(W(DIR,L,I)*FLOAT(DCYSC-1)/WMAX+1.5)
              SUB=PT(L)
              IF (CH(SUB).EQ.CROSS.OR.CH(SUB).EQ.STAR) GOTO 606
              CH(SUB)=CROSS
              GOTO 605
606           CH(SUB)=STAR
605        CONTINUE
           SCALE=I/10
           IF(SCALE*10.EQ.I) GOTO 607
           WRITE(2,1602) (CH(K),K=1,DCYSC2)
1602       FORMAT(2H ,120A1)
           GOTO 603
607        IF(SCALE.LT.10) GOTO 608
           SCALE=SCALE-10
           GOTO 607
608        WRITE(2,1603)SCALE, (CH(K),K=1,DCYSC2)
1603       FORMAT(1H ,I1,120A1)
603 CONTINUE
        RETURN
        END
```