

MAIN PROGRAM OUTPUT

THIS RUN WAS DONE ON 20/10/78 AT 20/49/47

ENTER N AND M >

N WAS 3 M WAS 3

ENTER XSIZE(N-DIR) AND YSIZE(M-DIR) IN MM

XSIZE(N-DIR) WAS 3.0000 MM YSIZE(M-DIR) WAS 3.0000 MM

ENTER NUMBER OF INCLUSIONS

THE NUMBER OF INCLUSIONS WAS 1

ENTER THERMAL CONDUCTIVITY OF THE MESH >

THE THERMAL CONDUCTIVITY OF THE MESH WAS 0.1000

+++++

*** INFORMATION ABOUT INSERT NUMBER 1 ***

ENTER THERMAL CONDUCTIVITY OF THE INCLUSION(S) >

THE THERMAL CONDUCTIVITY OF THE INCLUSION(S) WAS 1.0000

ENTER SHAPE CODE:1=SQUARE OR RECTANGLE,2=CIRCLE

SHAPE CODE WAS 2

ENTER CENTRE POSITION (N/X,M/Y)

CENTRE POSITION IN "N/X" DIRECTION WAS 3.000000

CENTRE POSITION IN "M/Y" DIRECTION WAS 0.000000

+++++ALL SIZES MUST BE REAL.+++++

ENTER RADIUS IN MM >

RADIUS WAS 2.500000

MAIN PROGRAM OUTPUT

+++++

THE MATRIX IS NOW SET UP, TIME WAS 20/49/49

FOR CALL TO F03AJF, IFAIL WAS 0

FOR CALL TO F04APF, IFAIL WAS 0

NAG ROUTINE FINISHED, TIME WAS 20/49/50

POSITIONS OF 0.1 U INCREMENTS ACROSS THE SAMPLE.

0.1325	0.2649	0.3974	0.5298	0.6623	0.7948	0.9272	1.3506	2.1421
0.1317	0.2634	0.3951	0.5268	0.6585	0.7902	0.9219	1.3126	2.0958
0.1577	0.3154	0.4731	0.6308	0.7886	0.9463	1.2348	1.5909	1.9471
0.1887	0.3775	0.5662	0.7550	0.9437	1.2183	1.5295	1.8407	2.3280

KEFFECTIVE = 0.261443

JOB FINISHED AT 20/49/50

GRID TEMPERATURES

1			
3	3	1	
3.0000	3.0000	0.1000	
1.0000			
2			
3.0000	0.0000	2.5000	
0.2614			
0.0000	0.0000	0.0000	0.0000
0.7550	0.7593	0.6341	0.5298
0.8834	0.8894	0.9149	0.8512
1.0000	1.0000	1.0000	1.0000

GRAPHICS PROGRAM INPUT FILE

```
1
3      3      1
3.0000 3.0000 0.1000
1.0000
2
3.0000 0.0000 2.5000
0.2614
0.1325 0.2649 0.3974 0.5298 0.6623 0.7948 0.9272 1.3506 2.1421
0.1317 0.2634 0.3951 0.5268 0.6585 0.7902 0.9219 1.3126 2.0958
0.1577 0.3154 0.4731 0.6308 0.7886 0.9463 1.2348 1.5909 1.9471
0.1887 0.3775 0.5662 0.7550 0.9437 1.2183 1.5295 1.8407 2.3280
-1
```

A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

```

MASTER CONTOURMAP
C
C   A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP.
C
COMMON/GFCURV/CB,SB,CF,SF,XB,YB,XF,YF
DIMENSION U(9,101),D(2,20),UX(101),YY(101)
DIMENSION POS(2,20),G(20),IC(20),B(20)
C
C   THE PROGRAM PRODUCES AN ISOTHERM CONTOUR MAP
C   FOR A COMPOSITE MATERIAL FROM DATA CALCULATED
C   BY THE MAIN ANALYSIS PROGRAM.
C   THIS PROGRAM USES SUBROUTINES FROM THE GINO-F
C   GRAPHICS PACKAGE.
C
CALL PLOTNA(7)
CALL DEVPA(270.,270.,IT)
CALL WINDOW(2)
C
CALL SCALE(0.75)
CALL SHIFT2(46.0,46.0)
C
C   READ DATA IN.
C
14 READ(5,110)ICON
110 FORMAT(1I0)
IF(ICON.EQ.-1) GO TO 25
READ(5,101)M,N,IP
101 FORMAT(3I0)
READ(5,102)XS,YS,A
102 FORMAT(3F0.0)
DO 1 I=1,IP
READ(5,107) B(I)
107 FORMAT(F0.0)
READ(5,105) IC(I)
105 FORMAT(I0)
IF(IC(I).EQ.1) READ(5,103) D(1,I),D(2,I),POS(1,I),POS(2,I)
103 FORMAT(4F0.0)
IF(IC(I).EQ.2) READ(5,106) D(1,I),D(2,I),G(I)
106 FORMAT(3F0.0)
1 CONTINUE
READ(5,108) SI
108 FORMAT(F0.0)
K=M+1
DO 2 I=1,K
2 READ(5,104)(U(J,I),J=1,9)
104 FORMAT(9F0.0)
C
C   CALCULATE SCALING FACTOR FOR MESH.
C
IF(YS-XS) 15,15,16
15 FAC=200.0/XS
GO TO 17
16 FAC=200.0/YS
17 CALL SCALE(FAC)
CALL PENSEL(1,0.1,2)
C

```

A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

```

C
C   DRAW CELL BOUNDS IN A SOLID LINE.
C
      X=XS
      Y=YS
      CALL MOUTO2(0.0,0.0)
      CALL LINBY2(X,0.0)
      CALL LINBY2(0.0,Y)
      X=-X
      Y=-Y
      CALL LINBY2(X,0.0)
      CALL LINBY2(0.0,Y)
C
C
C   DRAW IN HORIZONTAL MESH LINES.
C
      CALL DASHED(1,4.0,2.0,0.0)
C
C
      DY=YS/M
      X=XS
      CALL MOUTO2(0.,DY)
      DO 3 I=2,M
      CALL LINBY2(X,0.0)
      X=-X
3 CALL MOUBY2(0.0,DY)
C
C   DRAW IN VERTICAL LINES.
C
      DX=XS/N
      CALL MOUTO2(DX,0.0)
      Y=YS
      L=N+1
      DO 4 I=2,N
      CALL LINBY2(0.0,Y)
      Y=-Y
4 CALL MOUBY2(DX,0.0)
C
      CALL DASHED(0,1.0,1.0,0.0)
C
C
C   RESET WINDOW TO ACTUAL SIZE OF MESH.
C
      XW=184.5
      YW=184.5
      CALL WINDO2(10.,XW,10.,YW)
      FACT=1.0/FAC
      XWT=200.0
      YWT=200.0
      XWTT=186.5
      YWTT=186.5
C
C   DRAW IN INSERT OUTLINES.
C
      DO 5 I=1,IP

```

A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

```

      GG=2*G(I)
      CX=D(1,I)
      CY=D(2,I)
      CALL MOUTO2(CX,CY)
      CALL WINDO2(32.5,XWT,32.5,YWT)
      CALL DOT(0.5)
      CALL WINDO2(34.5,XW,34.5,YW)
      IF(IC(I).EQ.1) GO TO 13
C
C   CIRCULAR INSERTS.
C
      CALL MOUBY2(-G(I),0.0)
      CALL ARCBY2(G(I),0.0,-GG,0.0,1)
      GOTO 35
C
C   SQUARE/RECTANGULAR INSERTS.
C
13  CALL MOUBY2(-POS(1,I),-POS(2,I))
      XT=2.0*POS(1,I)
      YT=2.0*POS(2,I)
      CALL LINBY2(0.0,YT)
      CALL LINBY2(XT,0.0)
      CALL LINBY2(0.0,-YT)
      CALL LINBY2(-XT,0.0)
C
C   CHECK IF INSERT IS COMPLETELY WITHIN MESH BOUNDS.
C
35  IF(CX.LT.XS.AND.
      CCX.GT.0.0.AND.
      CCY.LT.YS.AND.
      CCY.GT.0.0) GO TO 34
      GO TO 32
C
C   SECTION TO PUT INSERT NUMBER BY CENTRE POINT
C   AS INSERT DOES NOT CROSS MESH BOUNDARIES.
C
34  CALL MOUTO2(CX,CY)
      CALL SCALE(FACT)
      CALL MOUBY2(1.0,1.0)
      CALL CHAINT(I,-2)
      CALL SCALE(FAC)
      GO TO 5
C
C   SECTION TO PUT THE NUMBER OF THE INSERT BY THE MESH
C   SIDE NEAREST TO THE INSERT CENTRE.
C
32  XCENT=XS/2.0
      YCENT=YS/2.0
      XL=CX-XCENT
      YL=CY-YCENT
      AHT=YCENT/XCENT*ABS(XL)
      Y1=AHT+YCENT
      Y2=AHT-YCENT
C
      IF(CX.LE.XCENT.AND.CY.LE.Y1.AND.CY.GE.-Y2) GO TO 41
C

```

A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

```

      IF(CX.LE.XCENT.AND.CY.GT.Y1) GO TO 42
C
      IF(CX.LE.XCENT.AND.CY.LT.-Y2) GO TO 44
C
      IF(CX.GT.XCENT.AND.CY.LE.Y1.AND.CY.GE.-Y2) GO TO 43
C
      IF(CX.GT.XCENT.AND.CY.GT.Y1) GO TO 42
C
      IF(CX.GT.XCENT.AND.CY.LT.-Y2) GO TO 44
C
C
      WRITE(6,400)
400 FORMAT(' NUMBERING EXERCISE FAILED'//)
      GO TO 5
C
41 AMULT=ABS(XCENT/XL)
   YL=YL*AMULT
   YCENT=YCENT+YL
   CALL MOUTO2(-5.0/FAC,YCENT)
   GO TO 33
C
42 AMULT=ABS(YCENT/YL)
   XL=XL*AMULT
   XCENT=XCENT+XL
   CALL MOUTO2(XCENT,YS+2.0/FAC)
   GO TO 33
C
43 AMULT=ABS(XCENT/XL)
   YL=YL*AMULT
   YCENT=YCENT+YL
   CALL MOUTO2(XS+2.0/FAC,YCENT)
   GO TO 33
C
44 AMULT=ABS(YCENT/YL)
   XL=XL*AMULT
   XCENT=XCENT+XL
   CALL MOUTO2(XCENT,-7.0/FAC)
C
33 CALL WINDO2(0.0,XWT,0.0,YWT)
   CALL SCALE(FACT)
   CALL CHAINT(I,-2)
   CALL SCALE(FAC)
   CALL WINDO2(34.5,XW,34.5,YW)
5 CONTINUE
C
C   SET UP CONTOUR VERTICAL STEPS.
C
      S=0.0
      DO 6 I=1,K
      YY(I)=S
6 S=S+DY
      CB=0.0
      SB=1.0
      CF=0.0
      SF=1.0
C

```


A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

C DRAW IN CONTOURS.

C

DO 7 I=1,9

DO 8 J=1,K

8 UX(J)=UX(I,J)

CALL MOUTO2(UX(1),0.0)

7 CALL CURTO2(UX,YY,K,1,1)

C

C RESET SCALE TO UNITY.

C

CALL WINDOW(2)

FAC=1.0/FAC

CALL SCALE(FAC)

NUMLINE=3+IP

C

C OUTPUT ALL TITLES.

C

FAC=1.0

YPOS=220.0+FLOAT(NUMLINE)*6.0

IF(IP.GT.3) YPOS=256.0

CALL MOUTO2(0.0,YPOS)

CALL CHASWI(1)

IF(IP.LE.3) GO TO 31

IHT=IP-3

FAC=9.0/(9.0+FLOAT(IHT))

CALL SCALE(FAC)

31 CALL CHAHOL('THERMAL CONDUCTIVITY OF A COMPOSITE*')

YPOS=(YPOS-6.0)*FAC

CALL MOUTO2(0.0,YPOS/FAC)

CALL CHAHOL('THERMAL CONDUCTIVITY OF MATRIX *')

CALL CHAFIX(A,8,3)

CALL CHAHOL('WATT/METRE/DEGREE KELVIN*')

YPOS=(YPOS-6.0)*FAC

CALL MOUTO2(0.0,YPOS/FAC)

CALL CHAHOL('THERMAL CONDUCTIVITY OF INSERTS *')

DO 30 I=1,IP

YPOS=(YPOS-6.0)*FAC

J=I+2

CALL MOUTO2(0.0,YPOS/FAC)

CALL CHAHOL('CONDUCTIVITY OF INSERT *UN*LOS *')

CALL CHAINT(I,-3)

CALL CHAHOL('WAS *')

CALL CHAFIX(B(I),10,3)

30 CALL CHAHOL('WATT/METRE/DEGREE KELVIN*')

YPOS=(YPOS-6.0)*FAC

CALL MOUTO2(0.0,YPOS/FAC)

CALL CHAHOL('EFFECTIVE THERMAL CONDUCTIVITY *')

CALL CHAFIX(SI,8,3)

CALL CHAHOL('WATT/METRE/DEGREE KELVIN*')

YPOS=(YPOS-6.0)*FAC

CALL MOUTO2(0.0,YPOS/FAC)

CALL CHAHOL('SAMPLE DIMENSIONS X =*')

CALL CHAFIX(XS,10,3)

CALL CHAHOL('MM Y =*')

CALL CHAFIX(YS,10,3)

CALL CHAHOL('MM*')

A PROGRAM TO PLOT AN ISOTHERM CONTOUR MAP

```

IP=M*N
YPOS=(YPOS-6.0#FAC)
CALL MOUTO2(0.0,YPOS/FAC)
CALL CHAHOL('THE UNIT CELL IS DIVIDED INTO #.')
CALL CHAINT(M,-5)
CALL CHAHOL('#L ROWS BY #.')
CALL CHAINT(N,-5)
CALL CHAHOL('#L COLUMNS#.')
CALL PICCLE
GOTO 14
25 CALL DEVFIN
STOP
END
FINISH

```

C
C
C

CHAPTER 13

Computational Study of Diffraction by Microcrystalline and Amorphous Bodies

P. J. GRUNDY

1. INTRODUCTION

One of the areas in science that has benefited greatly from the development of the large computers is concerned with the study of atomic and molecular structural arrangements. The successful unravelling of the atomic arrangements in DNA, proteins, and other large biological molecules and crystals by X-ray diffraction is perhaps the most well-known example of what is, essentially, a multidisciplinary field of study. Whilst some progress can be made by a combination of experience, intuition, and skill in such investigations, it is the ability of the large computer to perform many calculation steps in a reasonable time that has made complete characterization possible. This chapter is not concerned with biophysical subjects as such, but with the application of essentially similar, and simpler, techniques to crystalline and non-crystalline atomic arrangements found in metals and alloys. The examples used here to illustrate the computational exercises have been developed in connection with electron diffraction studies of thin metal films; however, the principles, theories, and subject matter apply equally well, with minor modifications, to X-ray and neutron diffraction.

The results of a diffraction experiment are usually obtained in the form of a diffraction 'pattern' in analogue or digital form. This information, often in a subsequently refined and corrected form, is determined by the time-averaged atomic arrangement in the test specimen and it can be 'inverted' mathematically to obtain the detail of these arrangements. However, this procedure is only approximate in many cases (particularly for non-crystalline structures and small crystals and atomic clusters) and an alternative procedure is to calculate a diffraction pattern from a model for comparison with the experimental pattern. This last exercise is found to be very useful, not

only in diffraction applications but in any experimental technique, such as electron microscopy, that is concerned with information recorded as intensity variations in two dimensions as in a micrograph. The excellent graphical facilities available with modern computers are obviously of great benefit here.

Below we give a computer program designed to carry out these operations for simple systems. However, before doing this it is helpful to outline a simple theory of diffraction^{1,2} that leads to the concepts and equations we shall use in this program.

2. DIFFRACTION THEORY

In a diffraction experiment the angular distribution of scattered intensity is given in terms of a differential scattering cross-section, $D(\theta)$, for the sample. In a convenient approximation for electrons, due to Born, where the scattering is assumed to be weak and dynamic events, such as multiple scattering, do not occur, $D(\theta)$ can be factorized into two terms:

$$D(\theta) = P(\mathbf{S}) \cdot F(\mathbf{S}, \omega).$$

Here 2θ is the scattering angle, S is the scattering parameter ($4\pi \sin \theta/\lambda$, often called k or q) corresponding to a change in momentum on scattering, and ω is a frequency dependence corresponding to a change in energy, $\hbar\omega$, on scattering. $P(\mathbf{S})$ depends on the type of interaction between the incident radiation (e.g. electron, X-ray, neutron) and the scattering centres and is calculable and fairly well known.

For elastic scattering F depends only on \mathbf{S} , i.e. only a spatial dependence exists, and $D(\theta)$ is essentially a function of $F(\mathbf{S})$. $F(|\mathbf{S}|)$ is isotropic for scattering from a single atom or from a randomly related set of scatterers. However, if some spatial correlation exists between the scattering centres $F(\mathbf{S})$ will vary with \mathbf{S} . These are, of course, the two extreme cases of a truly amorphous atomic arrangement and an ordered crystal.

$F(\mathbf{S})$ is variously called the interference function, the structure-sensitive intensity, or the structure factor for the system and, notwithstanding this confusion, is a very useful function in defining the structure and, through this, in deducing some physical properties of the system. In general $F(\mathbf{S})$ is related to the distribution of atoms in the system through a Fourier transform of a radial distribution function $G(\mathbf{r})$ which defines the deviation from an average atomic density ρ_0 , $\rho(\mathbf{r}) - \rho_0$, at some point \mathbf{r} . Clearly, by use of the Fourier transform in an inverse sense it is possible to obtain structural information from experimental diffraction patterns, as pointed out above. In inverse relation to $F(\omega)$, G in general has a time dependence $G(\tau)$ but here we are only concerned with a time average distribution or stationary distribution of scattering centres.

To outline a calculation of $F(S)$, consider a plane electron wave of unit amplitude and wave vector \mathbf{K}_0 ($K_0 = 2\pi/\lambda$) incident on a distribution of N scattering centres or atoms at positions \mathbf{r}_n from some origin atom (Figure 1). The total amplitude A_d diffracted into some angle 2θ is the sum of all the individual contributions from each atom modified by the phase factor ϕ which is determined by the relative positions of the atoms. Hence A_d is given by

$$A_d(2\theta) = \sum_n^N f_n(2\theta) \exp(i\phi_n).$$

Here $f_n(2\theta)$ is the scattering factor of the n th atom and is the fraction of the amplitude incident on that atom that is elastically scattered at 2θ . The phase difference for the two atoms at O and P is given by

$$\begin{aligned} \phi &= \frac{2\pi}{\lambda} \cdot (\text{the path difference, } OA - PB) \\ &= \frac{2\pi}{\lambda} \cdot \frac{\mathbf{r}_1 \cdot \mathbf{K}_d - \mathbf{r}_1 \cdot \mathbf{K}_0}{|\mathbf{K}_d|} = \mathbf{r}_1 \cdot (\mathbf{K}_d - \mathbf{K}_0) \\ &= \mathbf{r}_1 \cdot \mathbf{S}_1, \end{aligned}$$

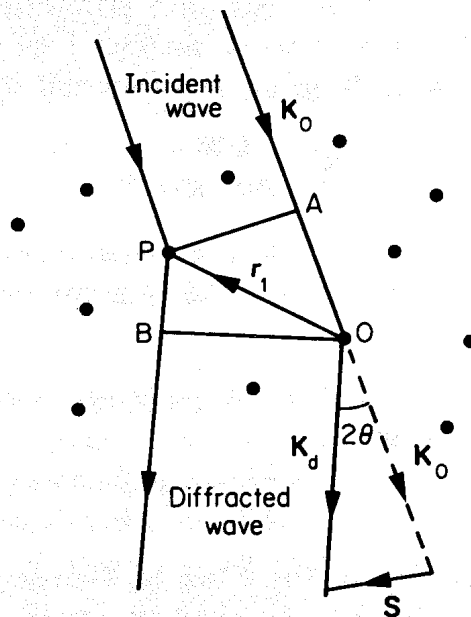


Figure 1. A schematic diagram illustrating the scattering of electrons by a group of atoms. \mathbf{K}_0 is the incident wave, \mathbf{K}_d is the wave diffracted through 2θ , and \mathbf{S} is the scattering vector

where \mathbf{K}_d is the diffracted wave. For this elastic scattering $|\mathbf{K}_d| = |\mathbf{K}_0|$, and $\mathbf{S} = \mathbf{K}_d - \mathbf{K}_0$ and has the modulus $4\pi \sin \theta/\lambda$. Hence, replacing 2θ by \mathbf{S} and summing for all the phase terms,

$$A_d(\mathbf{S}) = \sum_n^N f_n(S) \exp i(\mathbf{r}_n \cdot \mathbf{S}). \quad (1)$$

The diffracted intensity is given by the real part of $A_d(\mathbf{S}) \cdot A_d^*(\mathbf{S})$ and is written as

$$I(\mathbf{S}) = \sum_m^N \sum_n^N f_n(S) f_m(S) \cos(\mathbf{r}_{nm} \cdot \mathbf{S}), \quad (2)$$

where $\mathbf{r}_{nm} = \mathbf{r}_n - \mathbf{r}_m$ is the separation of the n th and m th atoms and each atom is considered as an origin in turn. This equation gives the diffraction pattern in the Fraunhofer approximation and is applicable to all atomic arrangements, ordered or disordered. For a single component specimen, i.e. one composed of like atoms, equation (2) reduces to

$$\begin{aligned} I(\mathbf{S}) &= Nf^2(S) + f^2(S) \sum_{m \neq n}^n \cos(\mathbf{r}_{nm} \cdot \mathbf{S}) \\ &= Nf^2(S)[1 + F(\mathbf{S})] \end{aligned} \quad (3)$$

for $f_n(S) = f_m(S) = f(S)$, say. Here $F(\mathbf{S})$, the Debye function, is the part of $I(\mathbf{S})$ that is dependent only on the particular arrangement of the atoms and not their identity. Clearly, if we wish to abstract $F(\mathbf{S})$ from an experimental diffraction pattern and hence from an experimental trace of $I(\mathbf{S})$, then

$$F(\mathbf{S}) = \frac{I(\mathbf{S})}{Nf^2(S)} - 1 \quad (4)$$

and to a good approximation for a multicomponent arrangement with n atomic species of atomic concentration C_i (e.g. for $i = 1$ $C_1 = (\text{no. of atoms of species 1})/N$)

$$F(\mathbf{S}) = \frac{I(\mathbf{S}) - N \sum_i^n C_i f_i^2(\mathbf{S})}{N \left[\sum_i^n C_i f_i(\mathbf{S}) \right]^2}. \quad (4a)$$

In systems containing many atoms it can be assumed that any particular \mathbf{r} lies at all azimuthal angles to the incident wave and $\cos(\mathbf{r} \cdot \mathbf{S})$ can be replaced by an average value $\sin(Sr)/Sr$. This average is obtained as

$$\overline{\cos(\mathbf{r}_{nm} \cdot \mathbf{S})} = \int_{\alpha=0}^{\pi} \int_{\phi=0}^{2\pi} \cos(Sr_{nm} \cos \alpha) 2\pi \sin \alpha \, d\alpha \, \frac{d\phi}{2\pi},$$

where α is the angle between the moduli of \mathbf{r} and \mathbf{S} and ϕ is here the azimuthal angle formed by the plane containing \mathbf{r} and \mathbf{S} with an arbitrary plane. This simplification can also be applied to large assemblies of uncorrelated small crystals or atomic clusters if the above assumption is valid. Clearly, any intercrystalline interference effects are neglected and the interference function is then

$$F(S) = \frac{1}{N} \sum_{m \neq n} \sum_{NN} \frac{\sin(Sr_{nm})}{Sr_{nm}}, \quad (5)$$

and can be further written as

$$F(S) = \frac{2}{N} \sum_n B_n \frac{\sin(Sr_n)}{Sr_n} \quad (6)$$

if the particular interatomic spacing r_n occurs B_n times but is summed over once in view of the factor 2. Here, of course, $F(S)$ is isotropic in S and a calculated $I(S)$ via equation (3) would have circular symmetry in the Fraunhofer diffraction plane, as would the experimental $I(S)$ from a specimen composed of many small crystals or a disordered 'glassy' atomic arrangement.

The radial distribution function of an arrangement of identical atoms describes the average number of atoms at distances between r and $r+dr$ from some chosen atom as origin, further averaged by taking each atom in turn as the origin. The average number of atoms is given by $4\pi r^2 \rho(r)$ and the radial distribution function $R(r)$ is just $4\pi r^2 \rho(r)$ or in a 'reduced' form $G(r) = 4\pi r \rho(r)$. Here $\rho(r)$ is equal to the density of atoms at r and for fluctuations about a mean density ρ_0 , i.e. for local atomic arrangements, $G(r)$ can be written in an integral form as

$$G(r) = 4\pi r(\rho(r) - \rho_0) = \frac{2}{\pi} \int_0^{S_{\max}, \infty} SF(S) \sin(Sr) dS \quad (7)$$

with limits for an interference function obtained in principle out to $S = \infty$ or, as more practically possible, to some cut-off value S_{\max} . Maxima in $G(r)$ represent the most commonly occurring values of r in any atomic arrangement. The Fourier transformation of known spatial detail in a structure can be used in principle, of course, to calculate a spatial frequency spectrum or diffraction pattern, $I(S)$, in the Fraunhofer diffraction plane via

$$SF(S) = \int_0^{r_{\max}, \infty} 4\pi r(\rho(r) - \rho_0) \sin(Sr) dr \quad (8)$$

and then equation (3).

Computation of $G(r)$ via equation (7), and indeed $R(r)$, from experimentally obtained values of $I(S)$ and then $F(S)$ are often used to obtain structural information on a specimen. However, the accuracy of the calculation can suffer from the fact that experimental measurements are usually limited to some maximum value of S and certainly the use of the 'reverse' procedure of equation (8) to calculate a diffraction pattern from a known model is unwise. Recourse to the Debye equation followed by equation (3), or its equivalent for a multicomponent structure, is advised. For such systems separate interference and radial distribution functions can, of course, be calculated for the separate correlations, e.g. for an alloy AB the values of r_{A-A} , r_{A-B} , and r_{B-B} .

Calculation of these functions for systems of significant size involves many repeated steps, i.e. N atoms involve $N(N-1)/2$ interatomic distances, and rapid and automatic computation is clearly essential. For polycrystalline assemblies of larger crystals, and for single crystals, it is obviously more convenient to take advantage of the periodicity and symmetry properties of the atomic arrangement and to calculate the structure factor and the diffracted intensity² via the reciprocal lattice concept.

3. STRUCTURES AND MODELS

As examples of the calculation of $F(S)$, and $I(S)$ if required, we consider particular models that have been used in investigations^{3,4} of the atomic arrangements in thin metal films formed by deposition from the vapour phase on to substrates usually cooled to low temperatures. Figure 2 shows the $F(S)$ and $G(r)$ functions determined for nickel films, using equations (4) and (7), from *experimentally* determined $I(S)$ functions. These are interpreted as typical of those obtained from non-crystalline atomic arrangements, the broad maxima and 'split' nature of the second peak (at $S = 5.4$ and 5.9 \AA^{-1}) being characteristic of these structures.⁵

To corroborate such conclusions interference functions are often calculated for a variety of microcrystalline models to compare with the experimental function. Table 1 gives typical information for small FCC (face centred cubic) and HCP (hexagonal close packed) microcrystals of single elements and for a hexagonal microcrystal of one particular compound. Changes in 'packing' caused by the presence of crystal defects and the presence of strains³ can easily be incorporated in such lists.

As an example that could be used in the program at the end of this chapter consider the case of strain. The complexity of calculating the effect of an anisotropic distribution of strains on a crystal is prohibitive and here only a Gaussian distribution is considered. If, in the unstrained crystal, there are B_n atoms separated by a distance r_n then in the strained crystal there will be B_n atoms in a Gaussian distribution about r_n , and the number of

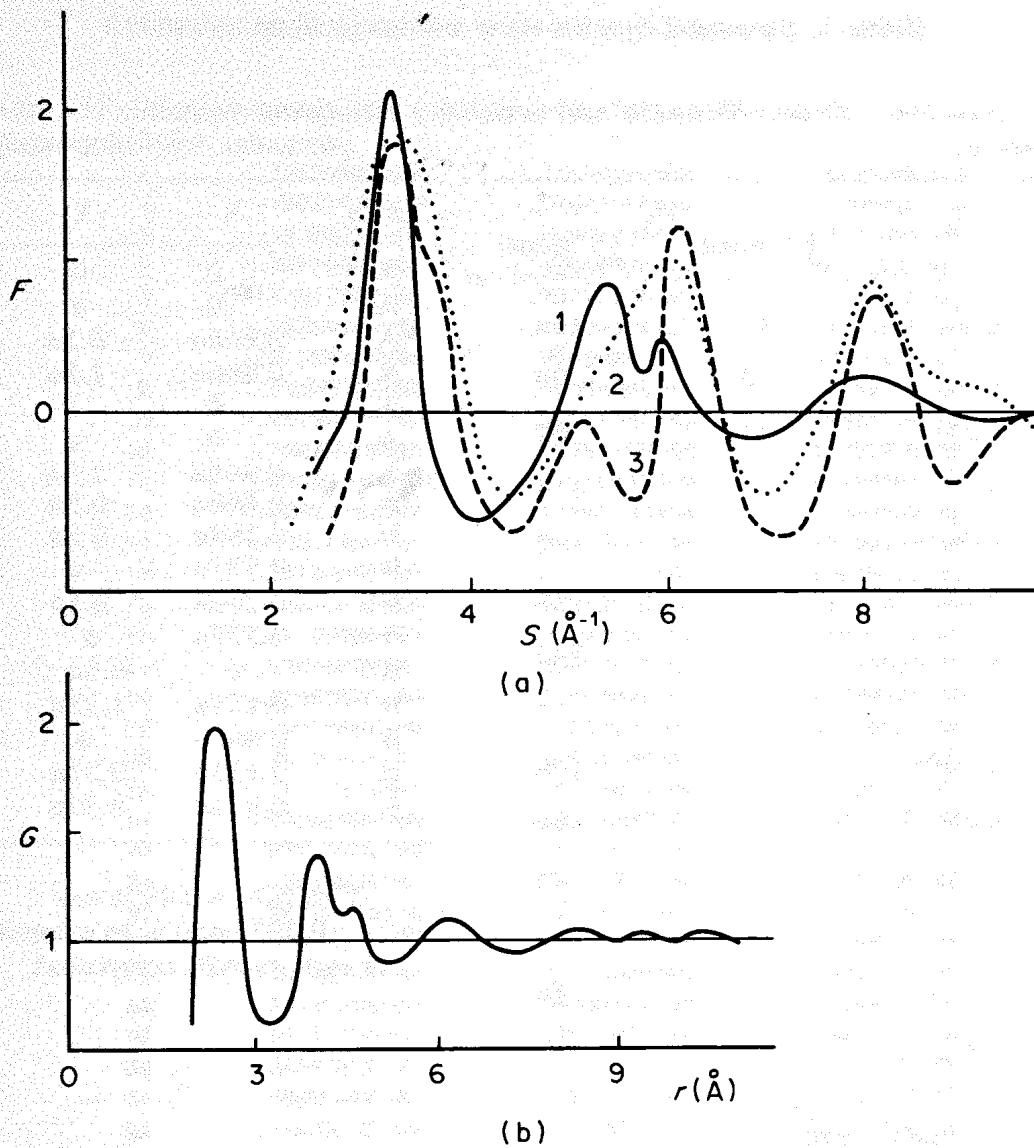


Figure 2. (a) Interference functions from: (1) a diffraction experiment on thin film (~ 100 nm thick) nickel evaporated on to a cold (77 K) substrate; (2) a calculation for a random assembly of 13 atom FCC nickel microcrystallites; and (3) a calculation for a similar assembly of 55-atom microcrystallites. (b)

The radial distribution junction G derived from the data of curve (1)

atoms separated by r is Y_n where

$$Y_n = B_n [2\pi\sigma^2 r_n^2]^{-\frac{1}{2}} \exp[-(r - r_n)^2 / 2\sigma^2 r_n^2] \quad (9)$$

and σ is the rms strain. The interference function is then calculated by substituting Y_n into equation (6) and integrating over r from, say, $r_{\min} = r_n - 4\sigma r_n$ to $r_{\max} = r_n + 4\sigma r_n$ for each value of r_n and B_n encountered in the unstrained crystal as

$$F(S) = \frac{2}{N} \sum_{n=1}^{r_{\max}} \int_{r_{\min}}^{r_{\max}} Y_n \frac{\sin(Sr)}{Sr} dr. \quad (10)$$

Table 1. Structural data for some microcrystalline assemblies

(a) FCC crystallite (13 and 55 atoms and lattice parameter a) (c) Hexagonal crystallite (17 atoms for a particular AB_5 compound)

n	r_n	B_n		Atom	X	Y	Z
		13 atoms	55 atoms				
1	$a/\sqrt{2}$	36	216	A	0	0	0
2	a	12	90	A	0	a	0
3	$a\sqrt{3}/2$	24	264	A	$0.866a$	$0.5a$	0
4	$a\sqrt{2}$	6	114	A	$0.866a$	$1.5a$	0
5	$a\sqrt{5}/2$		192	A	0	0	0
6	$a\sqrt{3}$		48	A	0	a	c
7	$a\sqrt{7}/2$		240	A	$0.866a$	$1.5a$	c
8	$2a$		27	A	$0.866a$	$0.5a$	c
9	$a\sqrt{9}/2$		108	B	$0.289a$	$0.5a$	0
10	$a\sqrt{5}$		48	B	$0.577a$	a	0
11	$a\sqrt{11}/2$		48	B	$0.289a$	$0.5a$	c
12	$a\sqrt{6}$		36	B	$0.577a$	a	c
13	$a\sqrt{13}/2$		48	B	0	$0.5a$	$0.5c$
14	$a\sqrt{8}$		6	B	$0.433a$	$1.25a$	$0.5c$
				B	$0.866a$	a	$0.5c$
				B	$0.433a$	$0.25a$	$0.5c$
				B	$0.433a$	$0.75a$	$0.5c$

GdCo₅ ($a = 0.4976$ nm and $c = 0.3973$ nm) is an example of such an AB_5 compound.

(b) HCP crystallite (with 9 atoms and lattice parameters c and a)

n	r_n	B_n
1	a	16
2	$a\sqrt{2}$	2
3	$(a\sqrt{8/3})c$	4
4	$a\sqrt{3}$	2
5	$a\sqrt{11/3}$	10
6	$a\sqrt{17/3}$	2

Table 2. Coordinates for a 66-atom polytetrahedral model

COORDINATES FOR A 66 ATOM POLYTETRAHEDRAL MODEL			
ATOM	X	Y	Z
1	-.4863886E+00	-.2953945E+00	-.1922949E+00
2	.4906244E+00	-.2953474E+00	-.1990868E+00
3	-.1810224E-01	.4804142E+00	-.1818506E+00
4	-.3077860E-01	-.4364057E-01	.6651296E+00
5	-.1707290E-01	.3927625E-01	-.1013845E+01
6	-.1325838E-01	-.1029454E+01	.1871708E+00
7	-.8125635E+00	.4543660E+00	.3479783E+00
8	.7429578E+00	.4805490E+00	.3714333E+00
9	-.6418542E-02	-.8680445E+00	-.7689570E+00
10	.7867370E+00	.4776615E+00	-.6765297E+00
11	-.8519302E+00	.4572374E+00	-.6614606E+00
12	-.8202376E+00	-.6429253E+00	.6133292E+00
13	-.4281090E-01	.9934240E+00	.5788397E+00
14	.7676529E+00	-.6121813E+00	.6405042E+00
15	-.8404372E+00	-.4399824E+00	-.1081307E+01
16	.8118558E+00	-.4280836E+00	-.1108470E+01
17	-.4384662E-01	.9861227E+00	-.9754062E+00
18	-.8246563E+00	-.1144300E+01	-.3679007E+00
19	.7941500E+00	-.1183392E+01	-.3620953E+00
20	-.2423443E-01	-.1073528E+01	.1121757E+01
21	-.1411787E+01	-.1564587E+00	-.8360812E-01
22	-.5362258E+00	.1255099E+01	-.1896423E+00
23	-.5561840E+00	.6312257E+00	.1274361E+01
24	.1397363E+01	-.1015376E+00	.1769679E-01
25	.4677623E+00	.1277841E+01	-.1839424E+00
26	.4584101E+00	.6472854E+00	.1290835E+01
27	-.4313629E-01	-.6519132E+00	-.1699498E+01
28	.5415432E+00	.5603805E+00	-.1620441E+01
29	-.6312472E+00	.4897407E+00	-.1604143E+01
30	-.3894207E-01	-.1772164E+01	-.4349459E+00
31	-.7865489E+00	-.1607124E+01	.4596921E+00
32	.7303235E+00	-.1573403E+01	.5219583E+00
33	-.1474769E+01	.9814941E+00	-.1378851E+00
34	-.1348411E+01	.5837886E-01	.1042099E+01
35	-.9207767E+00	.1386698E+01	.6899666E+00
36	.1428550E+01	.9393049E+00	-.1382706E+00
37	.8190813E+00	.1413906E+01	.7087494E+00
38	.1271128E+01	.9794284E-01	.1078886E+01
39	.5236714E+00	-.1434411E+01	-.1300074E+01
40	-.5891278E+00	-.1421382E+01	-.1278153E+01
41	.1666675E+01	.1756494E+00	-.8879475E+00
42	.8683543E+00	.1380016E+01	-.1048241E+01
43	-.1683674E+01	.7033924E-01	-.9951138E+00
44	-.9411843E+00	.1363316E+01	-.1053054E+01
45	-.1614555E+01	-.1062371E+01	.2200583E+00
46	-.5294313E+00	-.3193201E+00	.1478330E+01
47	-.6843712E-01	.1924308E+01	.3454938E+00
48	-.6616315E-01	.1527842E+01	.1351138E+01
49	.1553146E+01	-.1045730E+01	.2503108E+00
50	.4487337E+00	-.3046936E+00	.1496514E+01
51	-.1656540E+01	-.8929604E+00	-.7631010E+00