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**Determination of Channeling
Perspectives for Complex
Crystal Structures**

W. R. Allen

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Metals and Ceramics Division

**DETERMINATION OF CHANNELING PERSPECTIVES
FOR COMPLEX CRYSTAL STRUCTURES**

W. R. Allen

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NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

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DETERMINATION OF CHANNELING PERSPECTIVES FOR COMPLEX CRYSTAL STRUCTURES*

W. R. Allen

ABSTRACT

Specification of the atomic arrangement for axes and planes of high symmetry is essential for crystal alignment using Rutherford backscattering and for studies of the lattice location of impurities in single crystals. By rotation of an inscribed orthogonal coordinate system, a visual image for a given perspective of a crystal structure can be specified. Knowledge of the atomic arrangement permits qualitative channeling perspectives to be visualized and calculation of continuum potentials for channeling. Channeling angular-yield profiles can then be analytically modeled and, subsequently, shadowing by host atoms of positions within the unit cell predicted. Software to calculate transformed atom positions for a channeling perspective in a single crystal will be described and illustrated for the spinel crystal structure.

1. INTRODUCTION

The interpretation of the angular dependence of ion channeling relies upon accurate identification of crystalline axes and planes. Converging at an axis of high symmetry are several low-index planes. Among other factors, axis identification in a channeling experiment depends upon the number and relative scattering yield of intersecting planes. A specific plane is identified with the assistance of stereographic projections and knowledge of interplanar spacings. Details of channeling in simple cubic and hexagonal crystal structures are given in ref. 1.

Theoretical modeling of ion channeling depends upon accurate knowledge of geometrical (i.e., visual) perspectives for axes and planes. For axes, the spacing between axial strings and linear atomic density and, for planes, the interplanar spacing and areal atomic density, can be calculated with the aid of a simple algorithm. From this information, lattice continuum potentials can be calculated that permit analytical calculations of channeling angular yield profiles. One important application is the qualitative and quantitative identification of a lattice site for an impurity species within the unit cell.

Although the process is almost trivial for simple cubic crystals, visualization of channeling perspectives for crystals with complex unit cells is, at best, difficult. The calculation of geometrical perspectives for axial and planar ion channeling in a complicated crystal structure will be illustrated with magnesium aluminate spinel (MgAl_2O_4). One unit cell in the spinel

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crystal structure of MgAl_2O_4 contains 56 atoms. A computer code will be presented that can be used to calculate atomic positions following rotation(s) of an inscribed Cartesian coordinate system.

2. COORDINATE SYSTEM MANIPULATION

A perspective parallel to a specific crystallographic axis can be obtained by an orthogonal transformation of the Cartesian coordinates of atomic positions within the unit cell. A simple rotation of the coordinate system can make the transformed x-axis coincide with the axial direction. The familiar elements of the 3 x 3 proper, orthogonal transformation matrix **A** described in terms of the Euler angles α , β , and γ are:²

$$\begin{aligned}
 A_{11} &= \cos \gamma \cos \beta \cos \alpha - \sin \gamma \sin \alpha, \\
 A_{12} &= \cos \gamma \cos \beta \sin \alpha + \sin \gamma \cos \alpha, \\
 A_{13} &= -\cos \gamma \sin \beta, \\
 A_{21} &= -\sin \gamma \cos \beta \cos \alpha - \cos \gamma \sin \alpha, \\
 A_{22} &= -\sin \gamma \cos \beta \sin \alpha + \cos \gamma \cos \alpha, \\
 A_{23} &= \sin \gamma \sin \beta, \\
 A_{31} &= \sin \beta \cos \alpha, \\
 A_{32} &= \sin \beta \sin \alpha, \text{ and} \\
 A_{33} &= \cos \beta.
 \end{aligned} \tag{1}$$

References 2 and 3 can be consulted for further details and figures defining the transformation employing the set of Euler angles. This definition of the axes and sequence of rotation for specifying the Euler angles is known as the *y-convention*.³ Figure 1 illustrates the definition of the set of Euler angles and the associated axis of rotation for each.

A computer program has been coded in Microsoft QuickBASIC version 4.5 to perform the orthogonal transformation to produce a channeling perspective for a given crystallographic direction. A listing of the program is presented in Appendices A, B, and C. The transformation matrix **A** is applied to the vectors defined by the coordinate system origin and the Cartesian coordinates of each atom within a unit cell. Transformed atomic positions are projected onto the Y-Z plane normal to the crystallographic direction to produce a channeling perspective for the crystal axis. In other words, the crystallographic axis is rotated such that it coincides with the X'-coordinate axis. Atom positions are sorted to eliminate duplicity in coordinates. Atomic spacing within each individual atomic string can also be obtained from the calculated X-positions normal to the Y-Z plane. An accurate determination for a complex unit cell requires that atom positions in neighboring unit cells be included so that the atom sequencing in each string is correct and complete. Such a process was required in the program listed in Appendix B. Transformed Cartesian coordinates are written to an ASCII file and subsequently loaded into a technical graphics package (SigmaPlot 5.0 by Jandel Scientific) for display. Any commercial graphics package capable of importing ASCII text files or link graphics subroutines directly to the program could be optionally employed. Another enhancement would be to perform the transformation interactively and display the channeling perspective in live time on the computer video display. Although illustrated only for cubic lattice structures, the code can be simply modified to calculate channeling perspectives for any crystal structure.

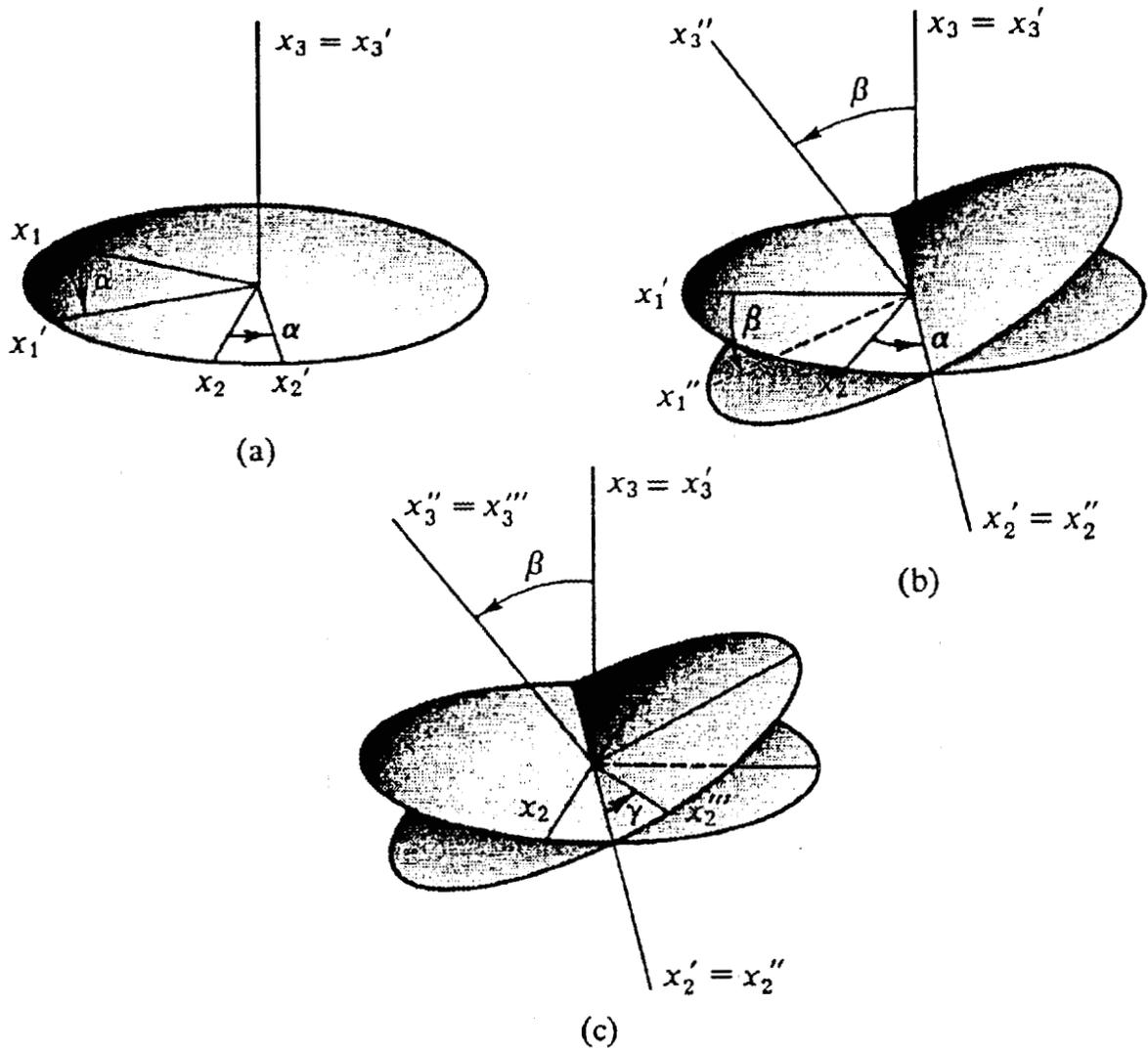


Fig. 1. Schematic diagrams defining the three Euler angles as described by the *y-convention*.

The rotation(s) necessary to obtain the atomic configuration for a given geometrical perspective are easily calculated. The angle ϕ between two crystal planes (h_1, k_1, l_1) and (h_2, k_2, l_2) for a cubic space lattice is given by the following equation:

$$\cos \phi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}} \quad (2)$$

Equations to determine angular separation between planes in other crystal structures can be found in ref. 4. Spherical geometry is used to determine the individual rotation angles required to create a given channeling perspective. For example, a 45° rotation about the vertical Z-axis transforms a (100) perspective for spinel (or any cubic crystal structure) into a (110) perspective. An additional 35.26° rotation of the Z-axis about the rotated X-axis will transform a (110) perspective for spinel into a (111) perspective. Appendix A contains a simple code that calculates atom positions following rotation for a face-centered-cubic (fcc) lattice structure. This is provided as a check of the validity of the algorithm. Determination of channeling perspectives for the spinel crystal structure (as coded in Appendices B and C) will be illustrated for MgAl_2O_4 in Sect. 3.

3. SPINEL: CRYSTAL STRUCTURE AND CHANNELING PERSPECTIVES

The spinel structure (space group Fd3m) of MgAl_2O_4 has a framework of oxygen anions in nearly perfect fcc close-packing.^{5,6} (The slight displacement of anions will be ignored in ensuing discussions.) Anion layers are stacked in an A,B,C,A fashion with cations lying in the interstices. Each Al cation is octahedrally surrounded by six anions and each Mg cation by four tetrahedrally distributed anions. A single unit cell of natural MgAl_2O_4 ($a_0 = 0.808$ nm) contains 32 anions, 16 Al cations, and 8 Mg cations. The 16 octahedral and 56 tetrahedral interstices that are intrinsically unfilled will be described in this study by the term "vacant". The unit cell can be sectioned into eight subcells of two equiprobable, distinct varieties—Types I and II. These are ordered such that the six nearest-neighbor subcells adjoining the cube faces of a subcell are of the opposite type (see ref. 5 for further details).

A channeling perspective for the $\langle 100 \rangle$ axis of MgAl_2O_4 is displayed in Fig. 2. Axial strings of anions and Al cations shield all vacant octahedral interstices. Axial strings of Mg cations incorporate three out of seven vacant tetrahedral interstices. The remaining vacant tetrahedral interstices are unshielded by host atoms, and resident impurity atoms would be visible to channeled analysis ions. Four distinct varieties of axial strings are present for a $\langle 110 \rangle$ axial channeling perspective of MgAl_2O_4 , shown in Fig. 3. Anions exclusively populate one type of axial string. Aluminum cations constitute two axial string types, one in which alternating octahedral interstices are vacant. Magnesium cations alternate with vacant tetrahedral interstices in the fourth type of axial string. Six out of seven vacant tetrahedral interstices and one-half of the vacant octahedral interstices are unshielded by host atoms. A channeling perspective for the $\langle 111 \rangle$ axis of MgAl_2O_4 is shown in Fig. 4. All axial strings contain Al cations and anions with a minority fraction incorporating Mg cations. Since all vacant octahedral and tetrahedral

< 100 > AXIS

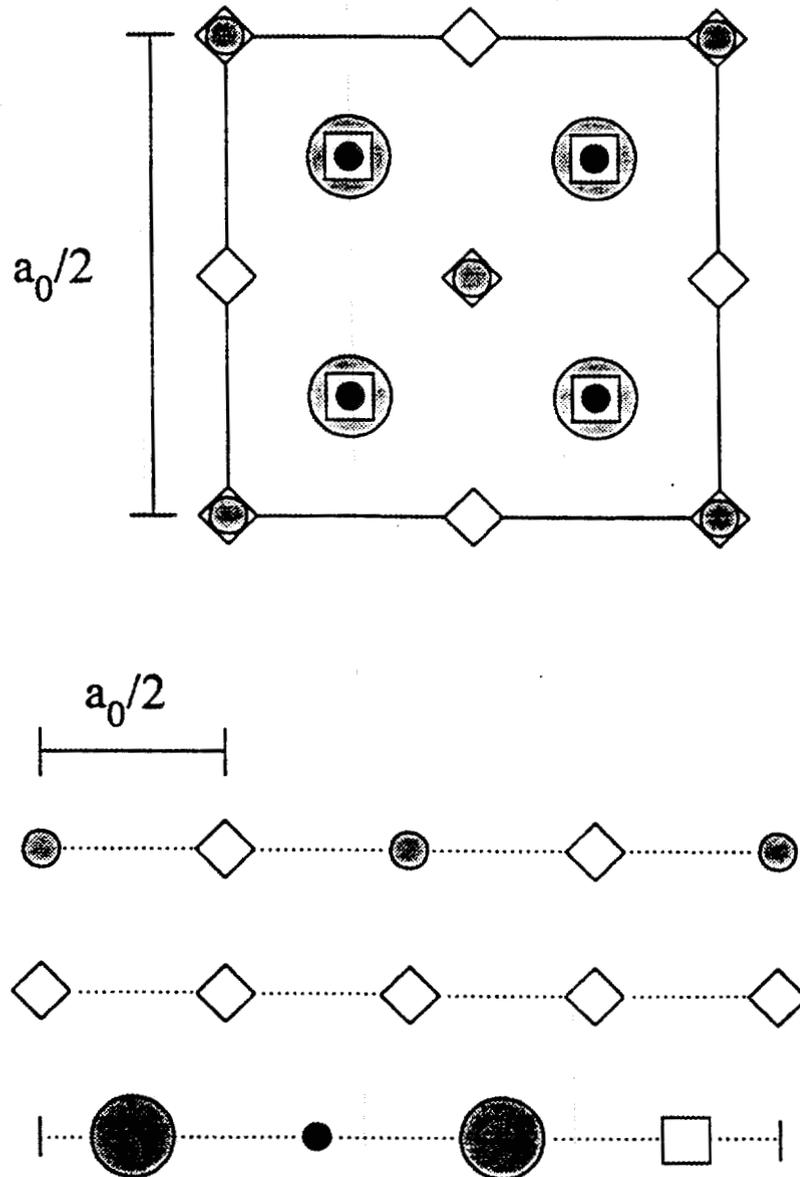


Fig. 2. Atomic arrangement for MgAl_2O_4 from a perspective parallel to the $\langle 100 \rangle$ axis (upper) and end-views indicating the interatomic spacing for each constituent string type. Oxygen anions, Al cations, and Mg cations are represented by large shaded circles, small solid circles, and small shaded circles, respectively. Vacant octahedral and tetrahedral interstices are denoted by open squares and diamonds, respectively.

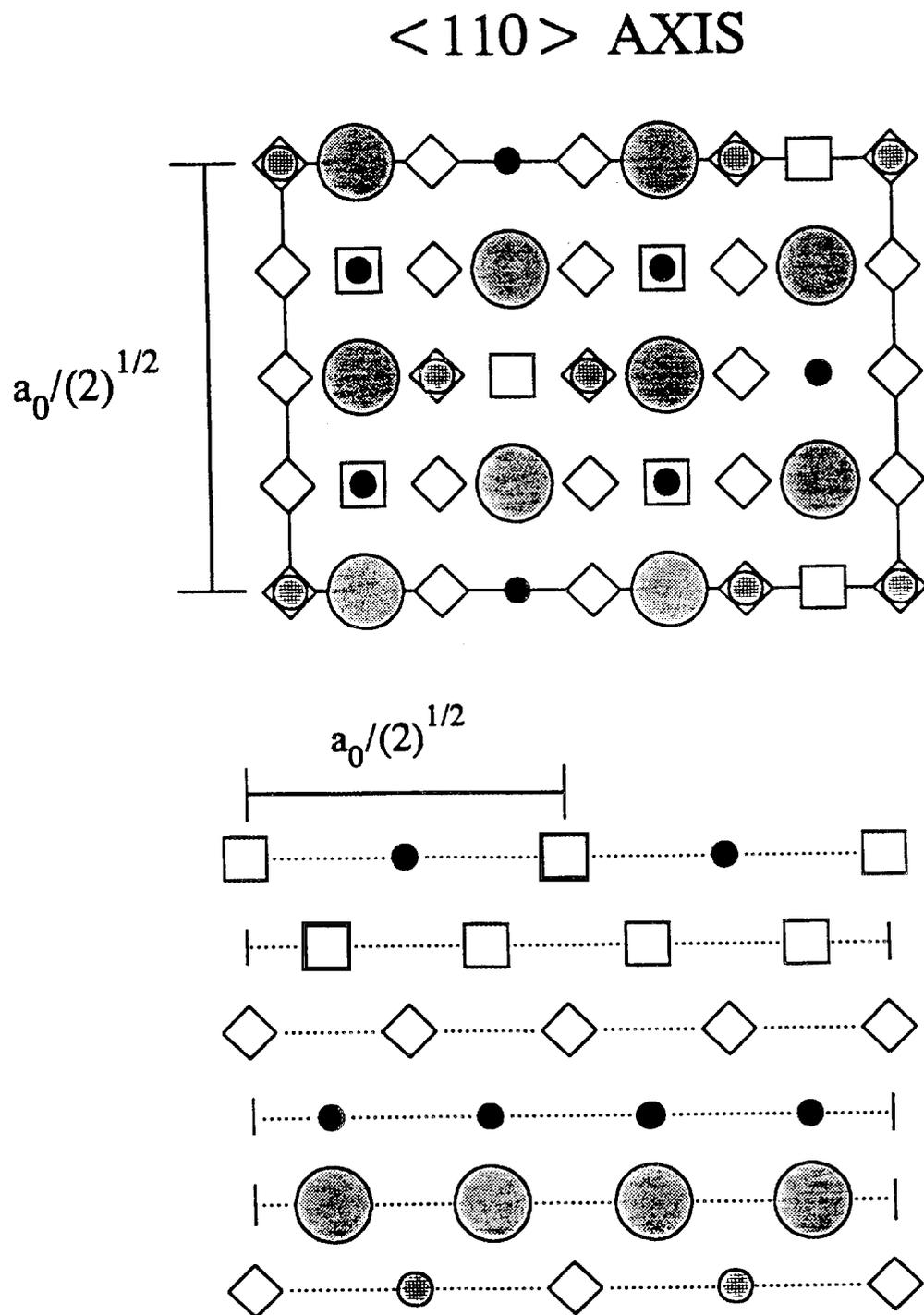


Fig. 3. Atomic arrangement for MgAl_2O_4 from a perspective parallel to the $\langle 110 \rangle$ axis (upper) and end-views indicating the interatomic spacing for each constituent string type (symbolism as in Fig. 1).

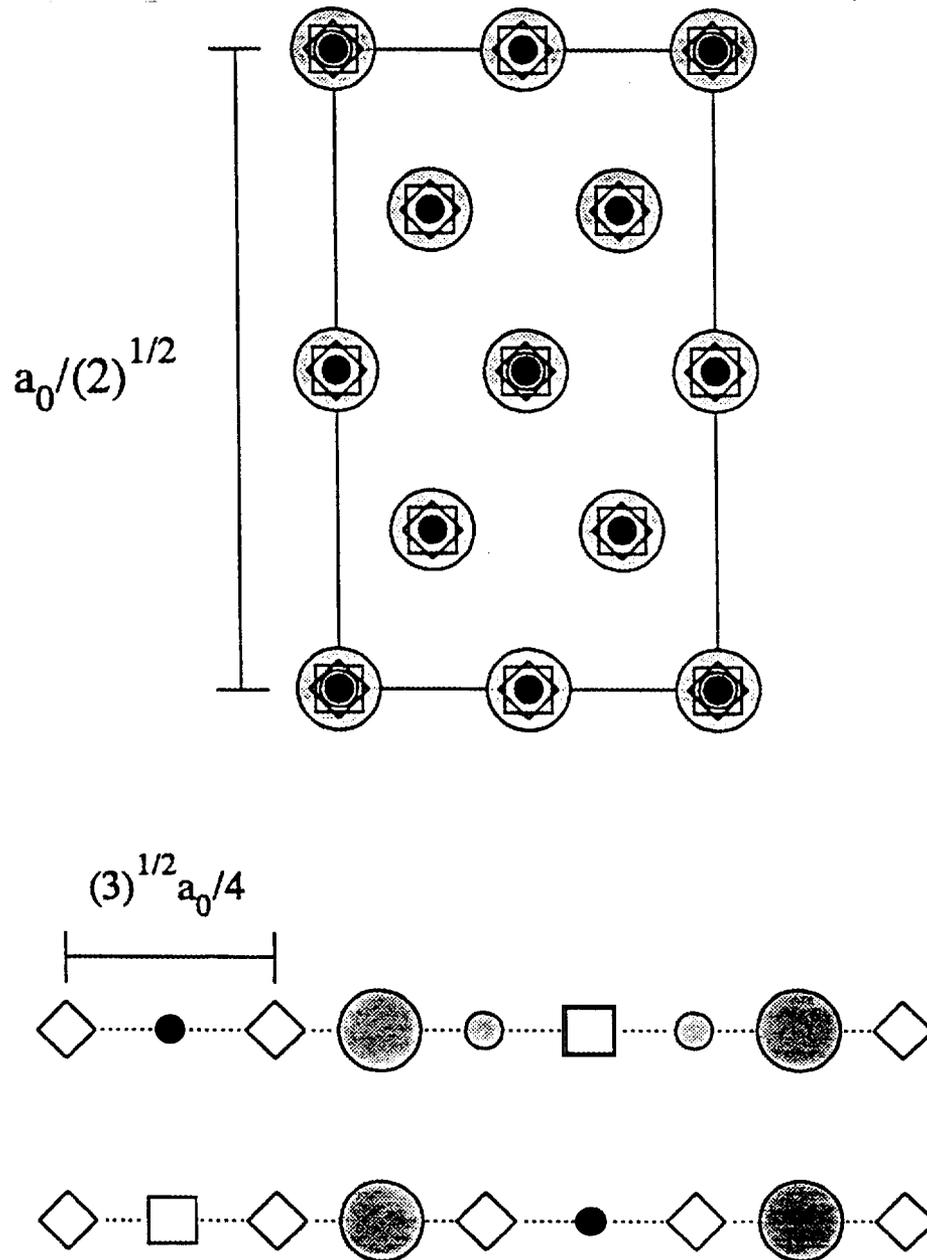
< 111 > AXIS

Fig. 4. Atomic arrangement for MgAl_2O_4 from a perspective parallel to the $\langle 111 \rangle$ axis (upper) and end-views indicating the interatomic spacing for each constituent string type (symbolism as in Fig. 1).

interstices are collinear with the axial strings, impurity atoms in these positions would be shielded for $\langle 111 \rangle$ axial channeling.

Figure 5 schematically displays the atomic configurations and populations of vacant interstices for the major high-symmetry planes of MgAl_2O_4 . Mixed atomic sheets of anions and Al cations that alternately incorporate Mg cations constitute the (110) plane. Mixed atomic sheets of anions and Al cations alternate with pure atomic sheets of Mg cations to form the (100) plane. All atomic sheets of the (211) plane contain anions and Al cations. Alternating atomic sheets incorporate Mg cations. For these three planes, all vacant octahedral and tetrahedral interstices are coplanar with the atomic sheets and are shielded by host atoms. Atomic sheets of the (111) plane contain a single element. All vacant octahedral interstices and three out of seven vacant tetrahedral interstices are shielded for (111) planar channeling.

Above 1100 K in natural MgAl_2O_4 , or at any temperature in synthetic MgAl_2O_4 , cations randomly populate the permitted (i.e., stoichiometrically correct) interstices.⁷ In this inverse spinel structure, up to one-half of the Al cations occupy tetrahedrally coordinated interstices, and the remainder share the octahedrally coordinated interstices with Mg cations. Although cations are shuffled in the interstices, the crystal structure remains intact.

4. SUMMARY

A computer program has been developed herein to aid in the determination of geometrical perspectives of use in ion channeling. For a complex crystal structure such as spinel, computer assistance is required to obtain accurate channeling perspectives.

5. ACKNOWLEDGMENTS

The author would like to thank M. W. Terrell and M. L. Hodges for report preparation final make-up and composition, respectively, and K. Spence for editing.

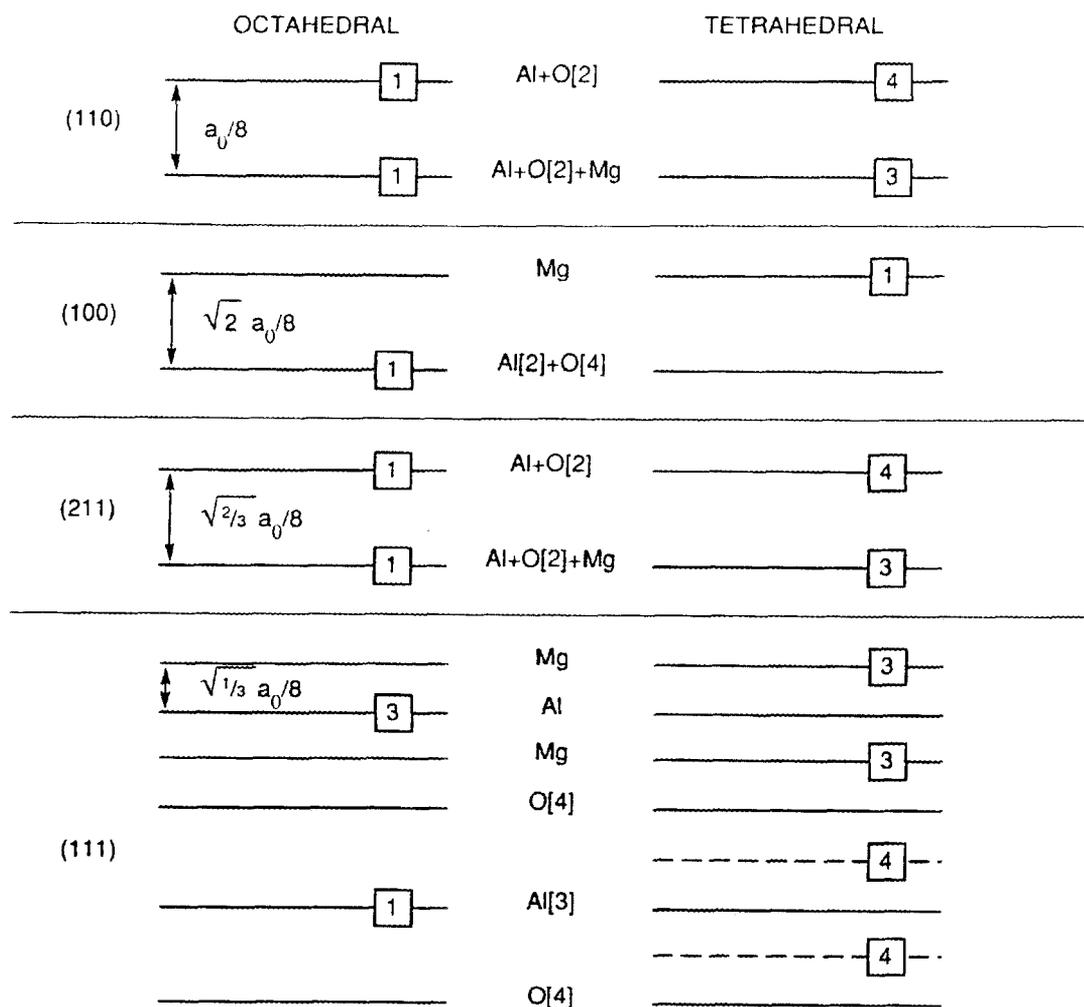


Fig. 5. Schematic of major crystal planes for $MgAl_2O_4$. The numbers in the squares indicate the relative probability of occurrence for vacant octahedral and tetrahedral interstices in the atomic sheet. For example, one out of two vacant octahedral interstices are shielded by each type of atomic sheet for the (110) plane. The relative atomic population of each atomic sheet is bracketed beside each constituent element (a weight of unity if no number is listed). For example, the (110) plane consists of atomic sheets of two types. One type contains Al and O in a 1:2 ratio, and the second contains Al, O, and Mg in a 1:2:1 ratio. Interplanar spacings are given as a fraction of the lattice constant a_0 .

6. REFERENCES

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4. P. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whalen, *Electron Microscopy of Thin Crystals*, Appendix 9, Robert E. Kreiger, Malabar, Fla., 1977.
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6. R. W. G. Wyckoff, pp. 75-76 in *Crystal Structures*, 2nd ed., Vol. 3, John Wiley, New York, 1965.
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APPENDIX A

COMPUTER PROGRAM FOR FCC STRUCTURE

APPENDIX A

COMPUTER PROGRAM FOR FCC STRUCTURE

```

*****
'      Name:      FCCPerspective
'      Type:      Module
'      Language:  MS QuickBASIC Version 4.5
'
'      Calculation of atomic positions within a single unit cell
'      of the general fcc structure following a rotation of 45°
'      about the vertical axis. Employs orthogonal transformation
'      and matrix algebra to transform from a (100) perspective
'      to a (110) perspective.
'
'  VARIABLES:
'      x(I)      Array of X cartesian coordinates for atoms
'      y(I)      Array of Y cartesian coordinates for atoms
'      z(I)      Array of Z cartesian coordinates for atoms
'      A(I,J)    Rotation matrix
'      alpha     One of three Euler angles
'      beta      One of three Euler angles
'      gamma     One of three Euler angles
'      xprime    Array of transformed X cartesian coordinates for atoms
'      yprime    Array of transformed Y cartesian coordinates for atoms
'      zprime    Array of transformed Z cartesian coordinates for atoms
*****

```

```

DIM x(14), y(14), z(14), A(3, 3)
CONSTANT pi = 3.14159263539#

```

```

' -- Cartesian coordinates of atoms within the unit cell of an fcc crystal.

```

```

x(1) = 0:  y(1) = 0:  z(1) = 0
x(2) = 1:  y(2) = 0:  z(2) = 0
x(3) = 0:  y(3) = 1:  z(3) = 0
x(4) = 0:  y(4) = 0:  z(4) = 1
x(5) = 1:  y(5) = 1:  z(5) = 0
x(6) = 1:  y(6) = 0:  z(6) = 1
x(7) = 0:  y(7) = 1:  z(7) = 1
x(8) = 1:  y(8) = 1:  z(8) = 1
x(9) = .5: y(9) = .5: z(9) = 0
x(10) = .5: y(10) = 0: z(10) = .5
x(11) = .5: y(11) = .5: z(11) = 1
x(12) = .5: y(12) = 1: z(12) = .5
x(13) = 0: y(13) = .5: z(13) = .5
x(14) = 1: y(14) = .5: z(14) = .5

```

```

alpha = 45! * pi / 180          ' -- Set of Euler angles to transform
beta = 0!                      ' -- from a (100) to a (110)
gamma = 0!                     ' -- perspective in cubic crystal.

' -- Define the elements of the rotation matrix.

A(1, 1) = COS(gamma) * COS(beta) * COS(alpha) - SIN(gamma) * SIN(alpha)
A(1, 2) = COS(gamma) * COS(beta) * SIN(alpha) + SIN(gamma) * COS(alpha)
A(1, 3) = -COS(gamma) * SIN(beta)
A(2, 1) = -SIN(gamma) * COS(beta) * COS(alpha) - COS(gamma) * SIN(alpha)
A(2, 2) = -SIN(gamma) * COS(beta) * SIN(alpha) + COS(gamma) * COS(alpha)
A(2, 3) = SIN(gamma) * SIN(beta)
A(3, 1) = SIN(beta) * COS(alpha)
A(3, 2) = SIN(beta) * SIN(alpha)
A(3, 3) = COS(beta)

' -- Define an ASCII text file (Plot41$) to receive the transformed
' -- Cartesian coordinates of the atom positions.

Plot41$ = "E:ATOMS.1"
OPEN Plot41$ FOR OUTPUT AS #4 LEN = 8

' -- Perform rotation and indiscriminately output transformed coordinates
' -- to the ASCII file.

FOR I = 1 TO 14
  xprime = A(1, 1) * x(I) + A(1, 2) * y(I) + A(1, 3) * z(I)
  yprime = A(2, 1) * x(I) + A(2, 2) * y(I) + A(2, 3) * z(I)
  zprime = A(3, 1) * x(I) + A(3, 2) * y(I) + A(3, 3) * z(I)
  WRITE #4, yprime, zprime
NEXT I

CLOSE #4
END

```

APPENDIX B

COMPUTER PROGRAM FOR SPINEL STRUCTURE

APPENDIX B

COMPUTER PROGRAM FOR SPINEL STRUCTURE

```

*****
'   Name:      SpinelPer
'   Type:      Module
'   Language:  MS QuickBASIC Version 4.5
'
'   Calculation of atomic positions within a single unit cell
'   of the spinel structure. The user can select a transform
'   from a (100) perspective to either a (110) or a (111) perspective.
'   Employs orthogonal transformation and matrix algebra.
'
'   VARIABLES:
'       x(I)      Array of X cartesian coordinates for atoms
'       y(I)      Array of Y cartesian coordinates for atoms
'       z(I)      Array of Z cartesian coordinates for atoms
'       A(I,J)    Rotation matrix
'       alpha     One of three Euler angles
'       beta      One of three Euler angles
'       gamma     One of three Euler angles
'       xprime    Array of transformed X cartesian coordinates for atoms
'       yprime    Array of transformed Y cartesian coordinates for atoms
'       zprime    Array of transformed Z cartesian coordinates for atoms
*****

DIM x0(1700), y0(1700), z0(1700), A(3, 3)
DIM xinc(30), yinc(30), zinc(30)
CONSTANT pi=3.14159265359#

' -- Copy the block of Cartesian coordinates for each atom or interstice
' -- from the master list in Appendix C to the appropriate location below.
' -- Values are given as a multiple of the lattice spacing  $a_0$ .

' -- Magnesium cation positions - Type I sub-cell - chosen from master list

First(1) = 1: Last(1) = 4          ' -- (X0, Y0, Z0) array subscript range

x0(1) = 0   : y0(1) = 0   : z0(1) = 0
x0(2) = 0   : y0(2) = 1 / 2 : z0(2) = 1 / 2
x0(3) = 1 / 2 : y0(3) = 1 / 2 : z0(3) = 0
x0(4) = 1 / 2 : y0(4) = 0   : z0(4) = 1 / 2

' -- Magnesium cation positions - Type II subcell - chosen from master list

First(2) = 36: Last(2) = 40       ' -- (X0, Y0, Z0) array subscript range

```

$x0(36) = 3 / 4 : y0(36) = 1 / 4 : z0(36) = 1 / 4$
 $x0(37) = 1 / 2 : y0(37) = 1 / 2 : z0(37) = 0$
 $x0(38) = 1 / 2 : y0(38) = 0 : z0(38) = 1 / 2$
 $x0(39) = 1 : y0(39) = 1 / 2 : z0(39) = 1 / 2$
 $x0(40) = 1 : y0(40) = 0 : z0(40) = 0$

' -- Array of increments for atomic positions (x0, y0, z0) to translate
 ' -- the initial unit cell to other relative locations without having to enter
 ' -- the coordinates of each separately. This enables the accurate
 ' -- determination of relative positions of atoms within the atomic strings
 ' -- without omitting any pertinent information. Values are given as a multiple
 ' -- of the lattice spacing a_0 . For example, $xinc(2) = 0 : yinc(2) = 1 : zinc(2) = 0$
 ' -- will result in the calculation of transformed atom positions in the unit cell
 ' -- displaced by a_0 along the Y-axis.

$xinc(1) = 0 : yinc(1) = 0 : zinc(1) = 0$
 $xinc(2) = 0 : yinc(2) = 1 : zinc(2) = 0$
 $xinc(3) = 0 : yinc(3) = -1 : zinc(3) = 0$
 $xinc(4) = -1 : yinc(4) = 0 : zinc(4) = 0$
 $xinc(5) = 1 : yinc(5) = 0 : zinc(5) = 0$
 $xinc(6) = 1 : yinc(6) = 1 : zinc(6) = 0$
 $xinc(7) = -1 : yinc(7) = -1 : zinc(7) = 0$
 $xinc(8) = 1 : yinc(8) = -1 : zinc(8) = 0$
 $xinc(9) = -1 : yinc(9) = 1 : zinc(9) = 0$
 $xinc(10) = 0 : yinc(10) = 0 : zinc(10) = 1$
 $xinc(11) = 1 : yinc(11) = 1 : zinc(11) = 1$
 $xinc(12) = 0 : yinc(12) = 1 : zinc(12) = 1$
 $xinc(13) = 1 : yinc(13) = 0 : zinc(13) = 1$
 $xinc(14) = -1 : yinc(14) = 0 : zinc(14) = 1$
 $xinc(15) = 0 : yinc(15) = -1 : zinc(15) = 1$
 $xinc(16) = 0 : yinc(16) = 0 : zinc(16) = -1$
 $xinc(17) = 1 : yinc(17) = -1 : zinc(17) = -1$
 $xinc(18) = 0 : yinc(18) = 1 : zinc(18) = -1$
 $xinc(19) = 1 : yinc(19) = 0 : zinc(19) = -1$
 $xinc(20) = -1 : yinc(20) = 0 : zinc(20) = -1$
 $xinc(21) = 0 : yinc(21) = -1 : zinc(21) = -1$
 $xinc(22) = -1 : yinc(22) = -1 : zinc(22) = 1$
 $xinc(23) = 1 : yinc(23) = -1 : zinc(23) = 1$
 $xinc(24) = -1 : yinc(24) = 1 : zinc(24) = 1$
 $xinc(25) = -1 : yinc(25) = -1 : zinc(25) = -1$
 $xinc(26) = 1 : yinc(26) = -1 : zinc(26) = -1$
 $xinc(27) = -1 : yinc(27) = 1 : zinc(27) = -1$

' -- Define the magnitudes of the Eulerian angles for a given rotation.
 ' -- Choose one of the sets of angles and enter on the line below.
 ' *** To produce a (111) perspective, choose
 ' alpha = 45. * pi / 180.: beta = 35.2644 * Pi / 180.: gamma = 0

```

' *** To produce a (110) perspective, choose
' alpha = 45. * pi / 180.: beta = 0: gamma = 0

alpha = 45! * pi / 180!: beta = 0: gamma = 0

' -- Define the elements of the rotation matrix.

A(1, 1) = COS(gamma) * COS(beta) * COS(alpha) - SIN(gamma) * SIN(alpha)
A(1, 2) = COS(gamma) * COS(beta) * SIN(alpha) + SIN(gamma) * COS(alpha)
A(1, 3) = -COS(gamma) * SIN(beta)
A(2, 1) = -SIN(gamma) * COS(beta) * COS(alpha) - COS(gamma) * SIN(alpha)
A(2, 2) = -SIN(gamma) * COS(beta) * SIN(alpha) + COS(gamma) * COS(alpha)
A(2, 3) = SIN(gamma) * SIN(beta)
A(3, 1) = SIN(beta) * COS(alpha)
A(3, 2) = SIN(beta) * SIN(alpha)
A(3, 3) = COS(beta)

' -- Define an ASCII text file (Plot41$) to receive the transformed
' -- Cartesian coordinates of the atom positions.

Plot41$ = "E:ATOMS.1"
OPEN Plot41$ FOR OUTPUT AS #4 LEN = 8

' -- 27 total translations of the initial unit cell given by the
' -- array xinc(), yinc(), zinc()

FOR K = 1 TO 27

' -- Calculations are done for 4 translations of the individual Type I subcell
' -- locations within the unit cell.

FOR I = First(1) TO Last(1)          ' -- Subcell Type I
  xp = x0(I) + xinc(K): yp = y0(I) + yinc(K): zp = z0(I) + zinc(K)

  ' Box I
  xprime = A(1, 1) * xp + A(1, 2) * yp + A(1, 3) * zp
  yprime = A(2, 1) * xp + A(2, 2) * yp + A(2, 3) * zp
  zprime = A(3, 1) * xp + A(3, 2) * yp + A(3, 3) * zp
  WRITE #4, xprime, yprime, zprime

  ' Box Ia
  xprime = A(1, 1) * (xp + 1 / 2) + A(1, 2) * yp + A(1, 3) * (zp + 1 / 2)
  yprime = A(2, 1) * (xp + 1 / 2) + A(2, 2) * yp + A(2, 3) * (zp + 1 / 2)
  zprime = A(3, 1) * (xp + 1 / 2) + A(3, 2) * yp + A(3, 3) * (zp + 1 / 2)
  WRITE #4, xprime, yprime, zprime

  ' Box Ib
  xprime = A(1, 1) * xp + A(1, 2) * (yp + 1 / 2) + A(1, 3) * (zp + 1 / 2)

```

```

yprime = A(2, 1) * xp + A(2, 2) * (yp + 1 / 2) + A(2, 3) * (zp + 1 / 2)
zprime = A(3, 1) * xp + A(3, 2) * (yp + 1 / 2) + A(3, 3) * (zp + 1 / 2)
WRITE #4, xprime, yprime, zprime

```

```

' Box Ic

```

```

xprime = A(1, 1) * (xp + 1 / 2) + A(1, 2) * (yp + 1 / 2) + A(1, 3) * zp
yprime = A(2, 1) * (xp + 1 / 2) + A(2, 2) * (yp + 1 / 2) + A(2, 3) * zp
zprime = A(3, 1) * (xp + 1 / 2) + A(3, 2) * (yp + 1 / 2) + A(3, 3) * zp
WRITE #4, xprime, yprime, zprime

```

```

NEXT I

```

```

' -- Calculations are done for 4 translations of the individual Type II subcell
' -- locations within the unit cell.

```

```

FOR I = First(2) TO Last(2)          ' -- SubCell type II
  xp = x0(I) + xinc(K): yp = y0(I) + yinc(K): zp = z0(I) + zinc(K)

```

```

' Box II

```

```

xprime = A(1, 1) * xp + A(1, 2) * yp + A(1, 3) * zp
yprime = A(2, 1) * xp + A(2, 2) * yp + A(2, 3) * zp
zprime = A(3, 1) * xp + A(3, 2) * yp + A(3, 3) * zp
WRITE #4, xprime, yprime, zprime

```

```

' Box IIa

```

```

xprime = A(1, 1) * (xp - 1 / 2) + A(1, 2) * yp + A(1, 3) * (zp + 1 / 2)
yprime = A(2, 1) * (xp - 1 / 2) + A(2, 2) * yp + A(2, 3) * (zp + 1 / 2)
zprime = A(3, 1) * (xp - 1 / 2) + A(3, 2) * yp + A(3, 3) * (zp + 1 / 2)
WRITE #4, xprime, yprime, zprime

```

```

' Box IIb

```

```

xprime = A(1, 1) * xp + A(1, 2) * (yp + 1 / 2) + A(1, 3) * (zp + 1 / 2)
yprime = A(2, 1) * xp + A(2, 2) * (yp + 1 / 2) + A(2, 3) * (zp + 1 / 2)
zprime = A(3, 1) * xp + A(3, 2) * (yp + 1 / 2) + A(3, 3) * (zp + 1 / 2)
WRITE #4, xprime, yprime, zprime

```

```

' Box IIc

```

```

xprime = A(1, 1) * (xp - 1 / 2) + A(1, 2) * (yp + 1 / 2) + A(1, 3) * zp
yprime = A(2, 1) * (xp - 1 / 2) + A(2, 2) * (yp + 1 / 2) + A(2, 3) * zp
zprime = A(3, 1) * (xp - 1 / 2) + A(3, 2) * (yp + 1 / 2) + A(3, 3) * zp
WRITE #4, xprime, yprime, zprime

```

```

NEXT I

```

```

NEXT K

```

```

CLOSE #4

```

```

' -- Read the transformed coordinates from the ASCII file into an array.

```

```

Plot41$ = "E:ATOMS.1"
OPEN Plot41$ FOR INPUT AS #4 LEN = 8
Index = 1
DO UNTIL EOF(4)
  INPUT #4, x0(Index), y0(Index), z0(Index)
  Index = Index + 1
LOOP
CLOSE #4

```

```

' -- Select unique transformed coordinates and output to the ASCII file.
' -- Prevents atoms with the same Y-Z coordinates from being output.

```

```

Plot41$ = "E:ATOMS.1"
OPEN Plot41$ FOR OUTPUT AS #4 LEN = 8
WRITE #4, y0(1), z0(1)
FOR I = 2 TO Index
  FOR J = 1 TO I - 1
    IF ABS(y0(J) - y0(I)) < .00001 THEN
      IF ABS(z0(J) - z0(I)) < .00001 THEN
        flag = 1
      END IF
    END IF
  NEXT J
  IF flag = 0 THEN
    WRITE #4, y0(I), z0(I)
  END IF
  flag = 0
NEXT I
CLOSE #4
END

```

```

' -- Routine to check if a point is within y-z limits specified within
' -- the y-z plane normal to the x-axis (i.e., the axial direction).
' -- To enable this option, enter limits below and replace starred section
' -- of code immediately above. Y and Z are the two axes of the Cartesian
' -- coordinate system normal to the crystal axis. Values are given as a
' -- multiple of the lattice spacing  $a_0$ .

```

```

YLimit = .708
ZLimit = 1.01
IF flag = 0 THEN
  IF ABS(y0(I)) < YLimit THEN
    IF z0(I) < ZLimit THEN
      IF z0(I) > -.01 THEN
        WRITE #4, y0(I), z0(I)
      END IF
    END IF
  END IF
END IF

```


APPENDIX C

COMPUTER PROGRAM SECTION LISTING ATOM POSITIONS IN SPINEL

APPENDIX C

COMPUTER PROGRAM SECTION LISTING ATOM POSITIONS IN SPINEL

```

' *****
'   Master List of Atomic Cartesian Coordinates for the Spinel Structure
'   of MgAl2O4.
' *****

' -- Values are given as a multiple of the lattice spacing  $a_0$ .

' -- Magnesium positions - Type I SubCell

First(1) = 1: Last(1) = 4           ' (X0, Y0, Z0) array subscript range
x0(1) = 0   : y0(1) = 0   : z0(1) = 0
x0(2) = 0   : y0(2) = 1 / 2 : z0(2) = 1 / 2
x0(3) = 1 / 2 : y0(3) = 1 / 2 : z0(3) = 0
x0(4) = 1 / 2 : y0(4) = 0   : z0(4) = 1 / 2

' -- Aluminum positions - Type I SubCell

First(1) = 5: Last(1) = 8           ' (X0, Y0, Z0) array subscript range
x0(5) = 3 / 8 : y0(5) = 1 / 8 : z0(5) = 1 / 8
x0(6) = 1 / 8 : y0(6) = 3 / 8 : z0(6) = 1 / 8
x0(7) = 1 / 8 : y0(7) = 1 / 8 : z0(7) = 3 / 8
x0(8) = 3 / 8 : y0(8) = 3 / 8 : z0(8) = 3 / 8

' -- Oxygen positions - Type I SubCell

First(1) = 9: Last(1) = 12          ' (X0, Y0, Z0) array subscript range
x0(9) = 1 / 8 : y0(9) = 1 / 8 : z0(9) = 1 / 8
x0(10) = 3 / 8 : y0(10) = 3 / 8 : z0(10) = 1 / 8
x0(11) = 3 / 8 : y0(11) = 1 / 8 : z0(11) = 3 / 8
x0(12) = 1 / 8 : y0(12) = 3 / 8 : z0(12) = 3 / 8

' -- Tetrahedral interstices - Type I SubCell

First(1) = 13: Last(1) = 35         ' (X0, Y0, Z0) array subscript range
x0(13) = 0   : y0(13) = 0   : z0(13) = 1 / 4
x0(14) = 0   : y0(14) = 0   : z0(14) = 1 / 2
x0(15) = 0   : y0(15) = 1 / 4 : z0(15) = 0
x0(16) = 0   : y0(16) = 1 / 4 : z0(16) = 1 / 4
x0(17) = 0   : y0(17) = 1 / 4 : z0(17) = 1 / 4

```

$x_0(18) = 0 : y_0(18) = 1/2 : z_0(18) = 0$
 $x_0(19) = 0 : y_0(19) = 1/2 : z_0(19) = 1/4$
 $x_0(20) = 1/4 : y_0(20) = 0 : z_0(20) = 0$
 $x_0(21) = 1/4 : y_0(21) = 0 : z_0(21) = 1/4$
 $x_0(22) = 1/4 : y_0(22) = 0 : z_0(22) = 1/2$
 $x_0(23) = 1/4 : y_0(23) = 1/4 : z_0(23) = 0$
 $x_0(24) = 1/4 : y_0(24) = 1/4 : z_0(24) = 1/4$
 $x_0(25) = 1/4 : y_0(25) = 1/4 : z_0(25) = 1/2$
 $x_0(26) = 1/4 : y_0(26) = 1/2 : z_0(26) = 0$
 $x_0(27) = 1/4 : y_0(27) = 1/2 : z_0(27) = 1/4$
 $x_0(28) = 1/4 : y_0(28) = 1/2 : z_0(28) = 1/2$
 $x_0(29) = 1/2 : y_0(29) = 0 : z_0(29) = 0$
 $x_0(30) = 1/2 : y_0(30) = 0 : z_0(30) = 1/4$
 $x_0(31) = 1/2 : y_0(31) = 1/4 : z_0(31) = 0$
 $x_0(32) = 1/2 : y_0(32) = 1/4 : z_0(32) = 1/4$
 $x_0(33) = 1/2 : y_0(33) = 1/4 : z_0(33) = 1/2$
 $x_0(34) = 1/2 : y_0(34) = 1/2 : z_0(34) = 1/4$
 $x_0(35) = 1/2 : y_0(35) = 1/2 : z_0(35) = 1/2$

' -- Magnesium positions - Type II SubCell

First(2) = 36: Last(2) = 40 ' (X0, Y0, Z0) array subscript range
 $x_0(36) = 3/4 : y_0(36) = 1/4 : z_0(36) = 1/4$
 $x_0(37) = 1/2 : y_0(37) = 1/2 : z_0(37) = 0$
 $x_0(38) = 1/2 : y_0(38) = 0 : z_0(38) = 1/2$
 $x_0(39) = 1 : y_0(39) = 1/2 : z_0(39) = 1/2$
 $x_0(40) = 1 : y_0(40) = 0 : z_0(40) = 0$

' -- Oxygen positions - Type II SubCell

First(2) = 41: Last(2) = 44 ' (X0, Y0, Z0) array subscript range
 $x_0(41) = 5/8 : y_0(41) = 1/8 : z_0(41) = 1/8$
 $x_0(42) = 7/8 : y_0(42) = 3/8 : z_0(42) = 1/8$
 $x_0(43) = 5/8 : y_0(43) = 3/8 : z_0(43) = 3/8$
 $x_0(44) = 7/8 : y_0(44) = 1/8 : z_0(44) = 3/8$

' -- Octahedral interstices - Type II SubCell

First(2) = 45: Last(2) = 48 ' (X0, Y0, Z0) array subscript range
 $x_0(45) = 7/8 : y_0(45) = 1/8 : z_0(45) = 1/8$
 $x_0(46) = 7/8 : y_0(46) = 3/8 : z_0(46) = 3/8$
 $x_0(47) = 5/8 : y_0(47) = 3/8 : z_0(47) = 1/8$
 $x_0(48) = 5/8 : y_0(48) = 1/8 : z_0(48) = 3/8$

' -- Tetrahedral interstices - Type II SubCell

First(2) = 49: Last(2) = 70 ' (X0, Y0, Z0) array subscript range

$x0(49) = 1/2 : y0(49) = 0 : z0(49) = 0$
 $x0(50) = 1/2 : y0(50) = 0 : z0(50) = 1/4$
 $x0(51) = 1/2 : y0(51) = 1/4 : z0(51) = 0$
 $x0(52) = 1/2 : y0(52) = 1/4 : z0(52) = 1/4$
 $x0(53) = 1/2 : y0(53) = 1/4 : z0(53) = 1/2$
 $x0(54) = 1/2 : y0(54) = 1/2 : z0(54) = 1/4$
 $x0(55) = 1/2 : y0(55) = 1/2 : z0(55) = 1/2$
 $x0(56) = 3/4 : y0(56) = 0 : z0(56) = 0$
 $x0(57) = 3/4 : y0(57) = 0 : z0(57) = 1/4$
 $x0(58) = 3/4 : y0(58) = 0 : z0(58) = 1/2$
 $x0(59) = 3/4 : y0(59) = 1/4 : z0(59) = 0$
 $x0(60) = 3/4 : y0(60) = 1/4 : z0(60) = 1/2$
 $x0(61) = 3/4 : y0(61) = 1/2 : z0(61) = 0$
 $x0(62) = 3/4 : y0(62) = 1/2 : z0(62) = 1/4$
 $x0(63) = 3/4 : y0(63) = 1/2 : z0(63) = 1/2$
 $x0(64) = 1 : y0(64) = 1/4 : z0(64) = 0$
 $x0(65) = 1 : y0(65) = 1/2 : z0(65) = 0$
 $x0(66) = 1 : y0(66) = 0 : z0(66) = 1/4$
 $x0(67) = 1 : y0(67) = 1/4 : z0(67) = 1/4$
 $x0(68) = 1 : y0(68) = 1/2 : z0(68) = 1/4$
 $x0(69) = 1 : y0(69) = 0 : z0(69) = 1/2$
 $x0(70) = 1 : y0(70) = 1/4 : z0(70) = 1/22$

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