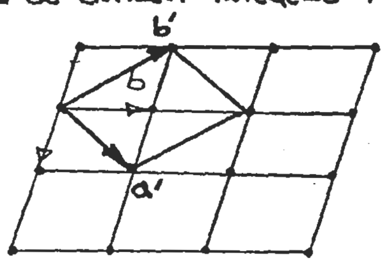
3.60 Symmetry, Structure and Tensor Properties of Materials

LATTICE TRANSFORMATIONS

Suppose we have defined a lattice in terms of the usual three non-coplanar translational periodicities $\vec{a}, \vec{b}, \vec{c}$ (conjugate translations) and now choose instead to define the lattice in terms of a new set $\vec{a}', \vec{b}', \vec{c}'$. As we use the three translations, the cell edges, as the basis vectors of the coordinate system with respect to which features of the lattice are referred — coordinates of points, directions, planes — the indices used to define these features clearly must change as well. The reciprocal lattice translations will also change. We here consider the problem of obtaining these indices in terms of the original values and the matrix which relates the new lattice vectors to the original choice.

① Relation between lattices

As lattice points represent rational (integer) coordinates, and the new translation vectors also extend between lattice points, the new translations may be expressed as a linear combination of the original vectors, and the coefficients in the vector sum will be entirely integers if two primitive cells are involved in the transformation.



In the example to the left (in two dimensions) for example:

$$\begin{cases} \vec{a}' = \vec{a} + \vec{b} \\ \vec{b}' = -\vec{a} + \vec{b} \end{cases}$$

In general

$$\begin{cases} \vec{a}' = S_{11}\vec{a} + S_{12}\vec{b} + S_{13}\vec{c} \\ \vec{b}' = S_{21}\vec{a} + S_{22}\vec{b} + S_{23}\vec{c} \\ \vec{c}' = S_{31}\vec{a} + S_{32}\vec{b} + S_{33}\vec{c} \end{cases}$$

or, more compactly,

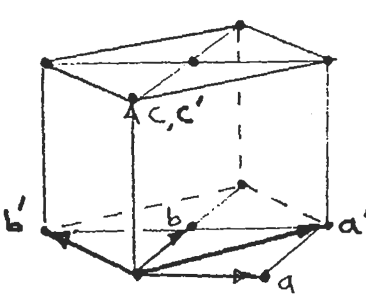
$$\boxed{[a_i'] = [S_{ij}][a_j]}$$

where $a_1 \equiv a$, $a_2 \equiv b$, $a_3 \equiv c$, etc.

$[S_{ij}]$ is called the matrix of the transformation

Examples:

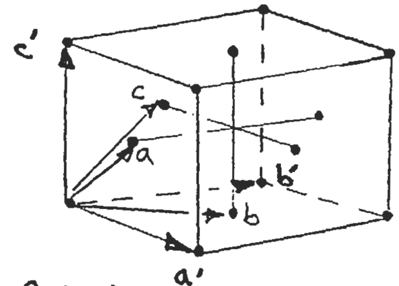
C-centered lattice in terms of primitive cell with diamond base



$$\begin{cases} \vec{a}' = \underbrace{\vec{a} + \vec{b}}_{\text{primitive}} \\ \vec{b}' = -\vec{a} + \vec{b} \\ \underbrace{\vec{c}'}_{\text{C-cent}} = \vec{c} \end{cases}$$

$$[S_{ij}] = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Face-centered cubic in terms of primitive rhombohedral



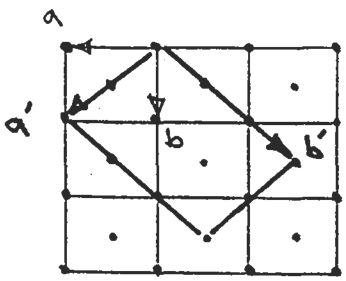
$$\begin{cases} a' = \vec{a} + \vec{b} - \vec{c} \\ b' = -\vec{a} + \vec{b} + \vec{c} \\ c' = \vec{a} - \vec{b} + \vec{c} \end{cases}$$

$$[S_{ij}] = \begin{bmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{bmatrix}$$

Fractional matrix elements S_{ij} may be involved in transformation matrices which express a non-primitive cell in terms of another, or a primitive cell in terms of the translations which define a multiple cell.

Thus far we have talked about matrices which involve going from one description to another of the <u>same</u> lattice. The formalism is also useful, however, in describing substructure — supercell relations (as the translation group of the supercell is a subgroup of the translation group of the ideal structure)

Example: $PbAgAsS_3$ — a superstructure which we studied a few years ago in which the three metal species order among the cation positions in the rocksalt structure type to give a monoclinic pseudo-orthorhombic supercell.



$$\begin{cases} \vec{a}' = \vec{a} + \vec{b} \\ \vec{b}' = -\frac{3}{2}\vec{a} + \frac{3}{2}\vec{b} \\ \vec{c}' = \qquad\qquad \vec{c} \end{cases} \qquad [S_{ij}] = \begin{bmatrix} 1 & 1 & 0 \\ -\frac{3}{2} & \frac{3}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(Note the appearance of non-integers as the original cell was non-primitive

<u>The Reverse Transformation</u>

If $[a_i'] = [S_{ij}][a_j]$

we can write, in terms of matrix algebra:

$[a_i] = [S_{ij}]^{-1}[a_j']$ where $[S_{ij}]^{-1}$ is the inverse of the matrix of the transformation, $[S_{ij}]$.

Let us evaluate $[S_{ij}]^{-1}$ in order to review a few definitions and the method for evaluation of determinants

$$\text{If} \quad \begin{cases} a' = S_{11}a + S_{12}b + S_{13}c \\ b' = S_{21}a + S_{22}b + S_{23}c \\ c' = S_{31}a + S_{32}b + S_{33}c \end{cases}$$

Then <u>Kramer's Rule</u> states that each of the original variables (a, b, c) may be written as the ratio of two 3×3 determinants: the denominator is the determinant $|S_{ij}|$, the numerator is the determinant of the array S_{ij} <u>but</u> in which the column in which the desired variable appears is replaced by a', b' c'

Example:

$$a = \frac{\begin{vmatrix} a' & S_{12} & S_{13} \\ b' & S_{22} & S_{23} \\ c' & S_{32} & S_{33} \end{vmatrix}}{\begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{vmatrix}}$$

The rule for expanding a determinant is that $|S_{ij}|$ is the product of the three elements in any row or column times the 2×2 determinant which remains upon deleting the row and column in which the corresponding element is situated, times $(-1)^{i+j}$ [equivalent to starting with + in any corner of the array and changing sign +, −, +, − etc upon skipping along any row or column — ie, $\begin{vmatrix} + & - & + \\ - & + & - \\ + & - & + \end{vmatrix}$]

EXPANDING $|S_{ij}|$ AS AN EXAMPLE:

$$|S_{ij}| = (-1)^2 S_{11}\begin{vmatrix} S_{22} & S_{23} \\ S_{32} & S_{33}\end{vmatrix} + (-1)^3 S_{21}\begin{vmatrix} S_{12} & S_{13} \\ S_{32} & S_{33}\end{vmatrix} + (-1)^{3+1} S_{31}\begin{vmatrix} S_{12} & S_{13} \\ S_{22} & S_{23}\end{vmatrix}$$

EXPANDING THE 2X2 DETERMINANTS ACCORDING TO THE SAME RULE GIVES

$$|S_{ij}| = S_{11}(S_{22}S_{33} - S_{32}S_{23}) - S_{21}(S_{12}S_{33} - S_{32}S_{13}) + S_{31}(S_{12}S_{23} - S_{22}S_{13})$$

THE <u>COFACTOR</u> OF AN ELEMENT S_{ij} IS DEFINED AS $(-1)^{i+j}$ TIMES THE 2X2 DETERMINANT WHICH REMAINS UPON DELETING THE ROW AND COLUMN IN WHICH THE ELEMENT APPEARS. THUS, THE FIRST EQUATION FOR THE EXPANSION MAY BE WRITTEN

$$|S_{ij}| \equiv S_{11}\,\mathrm{Cof}\,S_{11} + S_{21}\,\mathrm{Cof}\,S_{21} + S_{31}\,\mathrm{Cof}\,S_{31} \quad (= S_{11}\,\mathrm{Cof}\,S_{11} + S_{12}\,\mathrm{Cof}\,S_{12} + S_{13}\,\mathrm{Cof}$$

ETC.

RETURNING TO OUR EXPRESSION FOR a AS A FUNCTION OF THE RATIO OF TWO DETERMINANTS, AND EXPANDING THE NUMERATOR GIVES

$$a = \left\{ a'\,\mathrm{cof}\,S_{11} + b'\,\mathrm{cof}\,S_{21} + c'\,\mathrm{cof}\,S_{31} \right\}\frac{1}{|S_{ij}|}$$

AS THE COEFFICIENT MODIFYING THE TERMS a', b' & c' ARE, BY DEFINITION, THE DESIRED ELEMENTS OF THE INVERSE MATRIX, WE HAVE SHOWN THAT

$$S_{11}^{-1} = \frac{\mathrm{Cof}\,S_{11}}{|S_{ij}|} \qquad S_{12}^{-1} = \frac{\mathrm{Cof}\,S_{21}}{|S_{ij}|} \qquad S_{13}^{-1} = \frac{\mathrm{Cof}\,S_{31}}{|S_{ij}|}$$

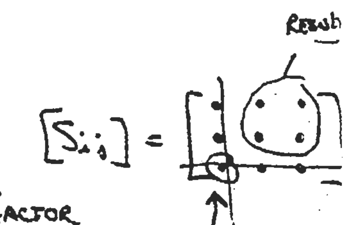
OR, IN GENERAL,

$$\boxed{S_{ij}^{-1} = \frac{\mathrm{Cof}\,S_{ji}}{|S_{ij}|}}$$

WHICH IS TO SAY THAT IF YOU WANT THE ELEMENT OF THE INVERSE MATRIX WHICH SITS HERE

$$[S_{ij}^{-1}] = \begin{bmatrix} \cdot & \cdot & \odot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}$$

THEN YOU GO AFTER THE COFACTOR OF THE TERM IN THE MATRIX $[S_{ij}]$ WHICH SITS HERE



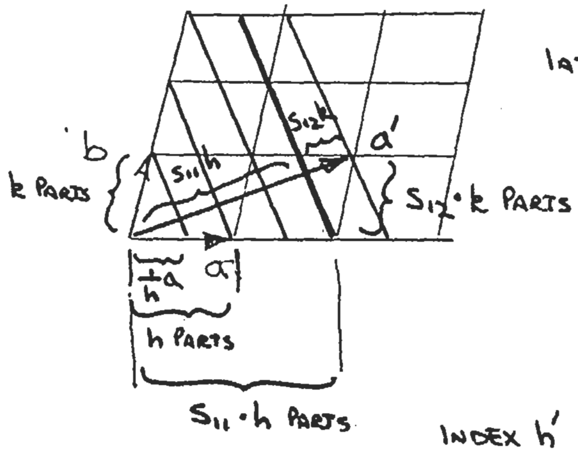
<u>RELATION BETWEEN VOLUME OF TWO CELLS</u>

If $[a_i'] = [S_{ij}][a_j]$

then $\boxed{V' = |S_{ij}|\,V}$ WHERE V' AND V ARE THE VOLUMES OF THE NEW AND OLD UNIT CELLS, RESPECTIVELY

WE WILL NOT BOTHER TO PROVE THIS RELATION. THE RESULT MAY BE DEMONSTRATED STRAIGHTFORWARDLY BY WRITING $V' = \vec{a}' \times \vec{b}' \cdot \vec{c}'$, EXPRESSING a', b' & c' IN TERMS OF a, b & c USING THE MATRIX OF THE TRANSFORMATION, AND SHOWING THAT THE RESULTING COLLECTION OF ELEMENTS S_{ij} IS EQUIVALENT TO $|S| \cdot \vec{a} \times \vec{b} \cdot \vec{c}$

② TRANSFORMATION of INDICES



RECALL THAT, IN A STACK of TRANSLATION-EQUIVALENT LATTICE PLANES WITH MILLER INDICES $(hk\ell)$, THE FIRST PLANE FROM THE ORIGIN INTERCEPTS $\vec{a}$, $\vec{b}$ AND $\vec{c}$ AT $1/h$, $\frac{1}{k}$ & $\frac{1}{\ell}$ RESPECTIVELY.

STATED IN A DIFFERENT WAY, SINCE ALL PLANES ARE EQUIDISTANT FROM EACH OTHER, A STACK of PLANES WITH INDICES $(hk\ell)$ DIVIDES THE TRANSLATION $\vec{a}$ INTO h INTERVALS, $\vec{b}$ INTO k AND $\vec{c}$ INTO ℓ. WE MAY THUS DETERMINE THE NEW INDEX h' APPROPRIATE TO THE NEW AXIS a' BY ENUMERATING THE NUMBER of INTERVALS INTO WHICH OUR STACK of PLANES DIVIDES a'

SUPPOSE $\vec{a}'$ IS DEFINED BY A STEP $S_{11}\vec{a}$ ALONG $\vec{a}$, A STEP $S_{12}\vec{b}$ ALONG $\vec{b}$ AND $S_{13}\vec{c}$ ALONG $\vec{c}$.

IF THE PLANES DIVIDE a INTO h PARTS THEY DIVIDE $S_{11}\vec{a}$ TRANSLATIONS INTO $S_{11}\cdot h$ PARTS AND ALSO INTERCEPT a' AS $S_{11}h$ INTERVALS TO THIS POINT (SEE DIAGRAM) SIMILARLY THE PLANES DIVIDE THE LEG $S_{12}\vec{b}$ INTO $S_{12}\cdot k$ PARTS AND ALSO INTERCEPT a' IN S_{12} INTERVALS. USING A SIMILAR ARGUMENT FOR A STEP of $S_{13}\vec{c}$ ALONG $\vec{c}$, ONE FINDS THAT $\vec{a}'$ IS CUT INTO $S_{11}h + S_{12}k + S_{13}\ell$ PARTS AND THUS

$$\left.\begin{aligned} h' &= S_{11}h + S_{12}k + S_{13}\ell \\ \text{SIMILARLY}\quad k' &= S_{21}h + S_{22}k + S_{23}\ell \\ \text{AND}\quad \ell' &= S_{31}h + S_{32}k + S_{33}\ell \end{aligned}\right\} \quad \text{OR} \quad \boxed{[h_i'] = [S_{ij}][h_j]}$$

WHERE $h_1 \equiv h$, $h_2 \equiv k$ $h_3 \equiv \ell$ etc

THAT IS, <u>MILLER INDICES of PLANES $(hk\ell)$ TRANSFORM ACCORDING TO THE SAME RELATIONS AS DO LATTICE TRANSLATIONS!</u>

③ TRANSFORMATION of RECIPROCAL AXES

THE RECIPROCAL LATTICE TRANSLATION $\vec{a}^*$ IS DEFINED BY

$$\vec{a}^* = \frac{\vec{b}\times\vec{c}}{V}$$

SO

$$\vec{a}^{*\prime} = \frac{\vec{b}'\times\vec{c}'}{V'} = \frac{\vec{b}'\times\vec{c}'}{|S_{ij}|\,V}$$

$$= \frac{1}{|S_{ij}|V}\left[(S_{21}\vec{a} + S_{22}\vec{b} + S_{23}\vec{c}) \times (S_{31}\vec{a} + S_{32}\vec{b} + S_{33}\vec{c})\right]$$

$$\begin{aligned} = \frac{1}{|S|V}\Big[& S_{21}S_{31}\cancel{\vec{a}\times\vec{a}} + S_{21}S_{32}\,\vec{a}\times\vec{b} + S_{21}S_{33}\,\vec{a}\times\vec{c} \\ & + S_{22}S_{31}\,\vec{b}\times\vec{a} + S_{22}S_{32}\,\cancel{\vec{b}\times\vec{b}} + S_{22}S_{33}\,\vec{b}\times\vec{c} \\ & + S_{23}S_{31}\,\vec{c}\times\vec{a} + S_{23}S_{32}\,\vec{c}\times\vec{b} + S_{23}S_{33}\,\cancel{\vec{c}\times\vec{c}}\ \Big] \end{aligned}$$

REARRANGING, AND NOTING $\vec{u}_1\times\vec{u}_2 = -\vec{u}_2\times\vec{u}_1$,

$$= \frac{1}{|S_{ij}|}\left\{(S_{22}S_{33} - S_{23}S_{32})\frac{\vec{b}\times\vec{c}}{V} + (S_{23}S_{31} - S_{21}S_{33})\frac{\vec{c}\times\vec{a}}{V} + (S_{21}S_{32} - S_{22}S_{3}\ldots)\frac{\vec{a}\times\vec{b}}{}\right.$$

$$\text{so } \vec{a}^{*\prime} = \underbrace{\frac{(S_{22}S_{33} - S_{23}S_{32})}{|S_{ij}|}}_{\substack{\text{This combination}\\ \text{of elements is Cof } S_{11}}} \vec{a}^* - \underbrace{\frac{(S_{21}S_{33} - S_{23}S_{31})}{|S_{ij}|}}_{\substack{\text{this combination of}\\ \text{elements is Cof } S_{12}}} \vec{b}^* + \underbrace{\frac{(S_{21}S_{32} - S_{23}S_{32})}{|S_{ij}|}}_{\substack{\text{This combination}\\ \text{is Cof } S_{13}}} \vec{c}^*$$

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix} \qquad \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix} \qquad \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix}$$

Thus $$\vec{a}^{*\prime} = \frac{\text{Cof } S_{11}}{|S_{ij}|}\vec{a}^* + \frac{\text{Cof } S_{12}}{|S_{ij}|}\vec{b}^* + \frac{\text{Cof } S_{13}}{|S_{ij}|}\vec{c}^*$$

or, in general $$\boxed{[a_i^{*\prime}] = \left[\frac{\text{Cof } S_{ij}}{|S_{ij}|}\right][a_j^*]}$$

This looks suspiciously like the INVERSE of the matrix $[S_{ij}]$, but it's NOT! — the subscripts are in the wrong order [that is, to find the element S_{ij}^{-1} we evaluate the cofactor of S_{ji}. Here we put the cofactor ij directly in the ij slot] The matrix relating $[a_i^{*\prime}]$ to $[a_j^*]$ is thus the inverse matrix $[S_{ij}]^{-1}$ with rows & columns interchanged. A matrix so transformed is said to be the TRANSPOSE and is written $[\tilde{a}_{ij}]$.

$$\text{ie} \quad [\tilde{a}_{ij}] \equiv [a_{ji}]$$

thus $$\boxed{[a_i^{*\prime}] = [\tilde{S}_{ij}]^{-1}[a_j^*]}$$

that is, Reciprocal lattice translations transform as the transpose of the inverse of the matrix of the transformation

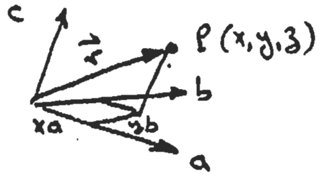
Practical notes:

(a) is the order important? that is, is the transpose of the inverse the same as the inverse of the transpose? Sure. Doesn't matter whether we transpose first and the evaluate the cofactor of the transposed element OR evaluate the cofactor of the transposed element and then transpose the result

(b) If one can write the new axes as a vector sum of the original axes according to $[a_i'] = [S_{ij}][a_j]$ to initiate the whole business, one could just as easily write the OLD axes in terms of the new — that is, $[a_i] \equiv [T_{ij}][a_j']$ — by inspection. Clearly then, $[T_{ij}]$ is $[S_{ij}]^{-1}$ directly, and $[\tilde{T}_{ij}]$ gives directly the relation between $a_i^{*\prime}$ and a_j^* without the bother of evaluating the inverse of $[S_{ij}]$.

(clearly, to inverse is worse than transpose, one knows)

(4) Transformation of Coordinates



Coordinates of a point within the unit cell $x y z$ may be considered as the components $x\vec{a}$, $y\vec{b}$, $z\vec{c}$ of a vector from the origin to the location:

$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$

In the new coordinate system one must write:

$$\vec{r} = x'\vec{a}' + y'\vec{b}' + z'\vec{c}'$$

If $\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$

And
$$\begin{cases} \vec{a} = S_{11}^{-1}\vec{a}' + S_{12}^{-1}\vec{b}' + S_{13}^{-1}\vec{c}' \\ \vec{b} = S_{21}^{-1}\vec{a}' + S_{22}^{-1}\vec{b}' + S_{23}^{-1}\vec{c}' \\ \vec{c} = S_{31}^{-1}\vec{a}' + S_{32}^{-1}\vec{b}' + S_{33}^{-1}\vec{c}' \end{cases}$$

where S_{ij}^{-1} is the element ij in the inverse of the matrix of the transformation

Substituting,
$$\begin{aligned} \vec{r} &= x\left(S_{11}^{-1}\vec{a}' + S_{12}^{-1}\vec{b}' + S_{13}^{-1}\vec{c}'\right) \\ &\quad + y\left(S_{21}^{-1}\vec{a}' + S_{22}^{-1}\vec{b}' + S_{23}^{-1}\vec{c}'\right) \\ &\quad + z\left(S_{31}^{-1}\vec{a}' + S_{32}^{-1}\vec{b}' + S_{33}^{-1}\vec{c}'\right) \\ &= \left(S_{11}^{-1}x + S_{21}^{-1}y + S_{31}^{-1}z\right)\vec{a}' + \left(S_{12}^{-1}x + S_{22}^{-1}y + S_{32}^{-1}z\right)\vec{b}' \\ &\quad + \left(S_{13}^{-1}x + S_{23}^{-1}y + S_{33}^{-1}z\right)\vec{c}' \end{aligned}$$

But $\vec{r} = x'\vec{a}' + y'\vec{b}' + z'\vec{c}'$

from which, comparing terms,

$$\begin{cases} x' = S_{11}^{-1}x + S_{21}^{-1}y + S_{31}^{-1}z \\ y' = S_{12}^{-1}x + S_{22}^{-1}y + S_{32}^{-1}z \\ z' = S_{13}^{-1}x + S_{23}^{-1}y + S_{33}^{-1}z \end{cases}$$

or $[x_i'] = [S_{ji}^{-1}][x_j]$

$$\boxed{[x_i'] = [\tilde{S}_{ij}^{-1}]\, x_j}$$

Atomic coordinates transform according to the same relation as do reciprocal lattice translations — i.e., the transpose of the inverse of the matrix of the transformation.

Summary

$$\begin{aligned} [a_i'] &= [S_{ij}][a_j] \\ [h_i'] &= [S_{ij}][h_j] \\ [a_i^{*\prime}] &= [\tilde{S}_{ij}]^{-1}[a_j^*] \\ [x_i'] &= [\tilde{S}_{ij}]^{-1}[x_j] \end{aligned}$$

or if one writes directly

$$[a_i] = [T_{ij}][a_j'] \qquad [T_{ij}] \equiv [S_{ij}]^{-1}$$
$$[h_i] = [T_{ij}][h_j']$$

then

$$[a_i^{*\prime}] = [\tilde{T}_{ij}][a_j^*]$$
$$[x_i'] = [\tilde{T}_{ij}][x_j]$$