DETERMINATION OF CONTAINED FUNCTIONS IN THE MODIFIED-PLANE-WAVE METHOD OF BAND STRUCTURE CALCULATION

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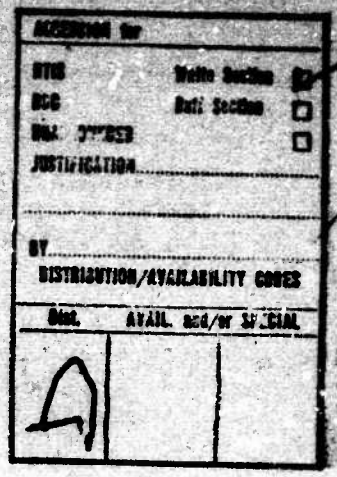

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The Modified Plane Wave (MPW) method of calculating electronic band structures is a variational procedure in which the eigenfunctions are linear expansions of atomic-like functions (a.l.f.'s) and plane waves. In this I we show how one uses ℓ character tables in conjunction with the ordinary point group character tables to determine what types of a.l.f.'s are contained in a particular group representation. Examples are given using the Cu_3Au and CsCl structures. Particular attention is given to the "non-central" atoms in such

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structures. Determination of the contained plane waves is also discussed. In Part II we introduce a perturbation involving a change in lattice symmetry. Using an example in which the lattice changes from face-centered cubic (fcc) to simple tetragonal, we show how to obtain the contained functions for the new lattice.

Examples are given using the direct approach of Part I and also using the contained functions of the unperturbed lattice to determine those for the perturbed lattice.

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DETERMINATION OF CONTAINED FUNCTIONS IN THE MODIFIED-PLANE-WAVE METHOD OF BAND STRUCTURE CALCULATION

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TABLE OF CONTENTS

FIGURES

Page

TABLES

Part II

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INTRODUCTION

The reader is expected to be generally familiar with the application of group theory to electronic band structure, including representation theory, symmetrization, and compatibility. We outline a standard procedure for determining the "contained" trial expansion functions (the ϕ_i) used in a Modified-Plane Wave (MPW) Method[1-4] band structure calculation. The MPW method is a variational method in which the eigenfunctions are represented as

$$\psi_n^{\vec{k},\lambda}(\vec{r}) = \sum_i c_i^{\vec{k},\lambda,n} \phi_i^{\vec{k},\lambda}(\vec{r}) \qquad (1)$$

In eqn (1), $\vec{k}$ labels a symmetry point in reciprocal space ($\vec{k}$-space), λ labels the irreducible representation, the ϕ_i are atomic-like functions (a.l.f.'s) or plane waves, and the coefficients c_i are determined by the Variational Procedure. The ϕ_i are symmetrized according to the $\vec{k}_\lambda$ representation. The "contained" ϕ's for a particular representation are those a.l.f.'s or plane waves which symmetrize to non-zero values for that representation.

---

1. E. Brown and J.A. Krumhansl, Phys. Rev. 109, 30 (1958).

2. D. Gray and E. Brown, Phys. Rev. 160, 567 (1967).

3. D. Gray, Watervliet Arsenal Technical Report WVT-7005 (1970). In comparing the present report with ref. 3, statements in ref. 3 such as "P_R takes $\vec{s}_g$ to $\vec{s}_a$" should be replaced with "P_R takes a function centered at $\vec{s}_a$ into a similar function centered at $\vec{s}_g$".

4. D. Gray, Watervliet Arsenal Technical Report WVT-7163 (1971). Eqn (22) of ref. 4 should be $R^{-1} s_\mu = s_\nu + \vec{\tau}$.

In Part I we outline both how one determines, a priori, what types of Φ's will be contained in a particular representation and how one works out the explicit functions. Examples are given utilizing the simple cubic system (Cu_3Au and CsCl structures).

In Part II a perturbation application is involved in which the perturbed lattice has a different symmetry from the original lattice. Using an fcc to simple tetragonal change as an example, we show how the contained functions for the perturbed lattice may be readily obtained from those of the original lattice.

Throughout this report the discussion is restricted to symmorphic groups.

NOTATION

The labeling of all group operators follows Bouckaert, Smoluchowski, and Wigner[5] (BSW). For the cubic system, the symmetry points and irreducible representations are labeled as per BSW. In the "reduced scheme" used in Part II the representation labels are quite arbitrary; we have tried to follow Koster's[6] labeling system as far as possible. Throughout this report, the number of members in a group is given by g and the dimensionality of an irreducible representation by h.

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5. L.P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).

6. G.F. Koster in "Solid State Physics, Vol 5" (Academic Press, 1957); page 173.

Atomic sites are labeled by vectors from the origin of the chosen coordinate system to the center of the atomic "sphere" in question. Two atomic sites, $\vec{s}_\mu$ and $\vec{s}_\nu$ are "equivalent" if they are separated by a primitive lattice vector, i.e., if $\vec{s}_\nu = \vec{s}_\mu + \vec{t}$.

PART I: THE STANDARD PROCEDURE

CHARACTER TABLES AND D MATRICES.

It is first necessary to set up (or obtain from standard references[5-9]) the pertinent character tables. For representations of dimension higher than one it is necessary to obtain the actual D matrices as well; this may also be done by recourse to references or by working out the individual cases. If the latter procedure is used, one generally uses a trial and error method to first determine "basis functions", i.e., functions which satisfy

$$P_R f_\mu^{(j)} = \sum_{\lambda=1}^{h_j} D^{(j)}(R)_{\lambda\mu} f_\lambda^{(j)} \qquad (2)$$

A function $f_\chi^{(j)}$ is said to belong to the χth row of the irreducible representation $D^{(j)}(R)$ if there exist "partner" functions $f_1^{(j)}$, $f_2^{(j)}, \cdots f_{\chi-1}^{(j)}, f_{\chi+1}^{(j)}, \cdots f_{h_j}^{(j)}$ such that all the $f_\lambda^{(j)}$ satisfy (2). It should be noted that (2) implies (for a 2-dimensional representation)

$$\begin{pmatrix} P_R f_1 \\ P_R f_2 \end{pmatrix} = \begin{pmatrix} D_{11} & D_{21} \\ D_{12} & D_{22} \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \qquad (3)$$

as a matrix equation, i.e., that

$$\vec{P_R f} = \tilde{D}\,\vec{f}\,. \qquad (4)$$

---

7. "Group Theory", E. Wigner (Academic Press, 1959).
8. "Group Theory and Quantum Mechanics", M. Tinkham (McGraw-Hill, 1964).
9. "Quantum Theory of Molecules and Solids, Vol. 2 - Symmetry and Energy Bands in Crystals", J.C. Slater (McGraw-Hill, 1965).

Note that the matrix in (4) is D-transpose ($\tilde{D}$) and not D itself. This trial and error procedure must give D's which satisfy

$$\Sigma_R D^{(i)}(R)^*_{\mu\nu} D^{(j)}(R)_{\mu'\nu'} = \frac{g}{h} \delta_{ij} \delta_{\mu\mu'} \delta_{\nu\nu'} \tag{5}$$

where g is the order of the group and h is the dimensionality of the representation; i and j label irreducible representations. The D matrices must also satisfy

$$D(S)D(T) = D(ST) \tag{6}$$

(The set of D's which satisfies eq. (2) will automatically satisfy eq. (6); see pgs 108-9 of ref. 7.)

The operation "triads" for the cubic system are given in Table A-I of Appendix A. Character tables for selected symmetry points of the simple cubic $\vec{k}$-space zone are given in Appendix B.

ATOMIC-LIKE FUNCTIONS

A. Inclusion of Non-Central Atoms, i.e., More Than One Atom per Primitive Cell.

In real space we indicate the location of all non-central atoms in the primitive cell by $\vec{s}$ vectors. The Cu_3Au crystal, for example, has a simple cubic lattice with Au atoms at the cube corners and Cu atoms at the face centers as shown in Fig. 1. One may take the origin at an Au atom, use the cubic axes to define $\hat{i}$, $\hat{j}$, $\hat{k}$ directions, and define

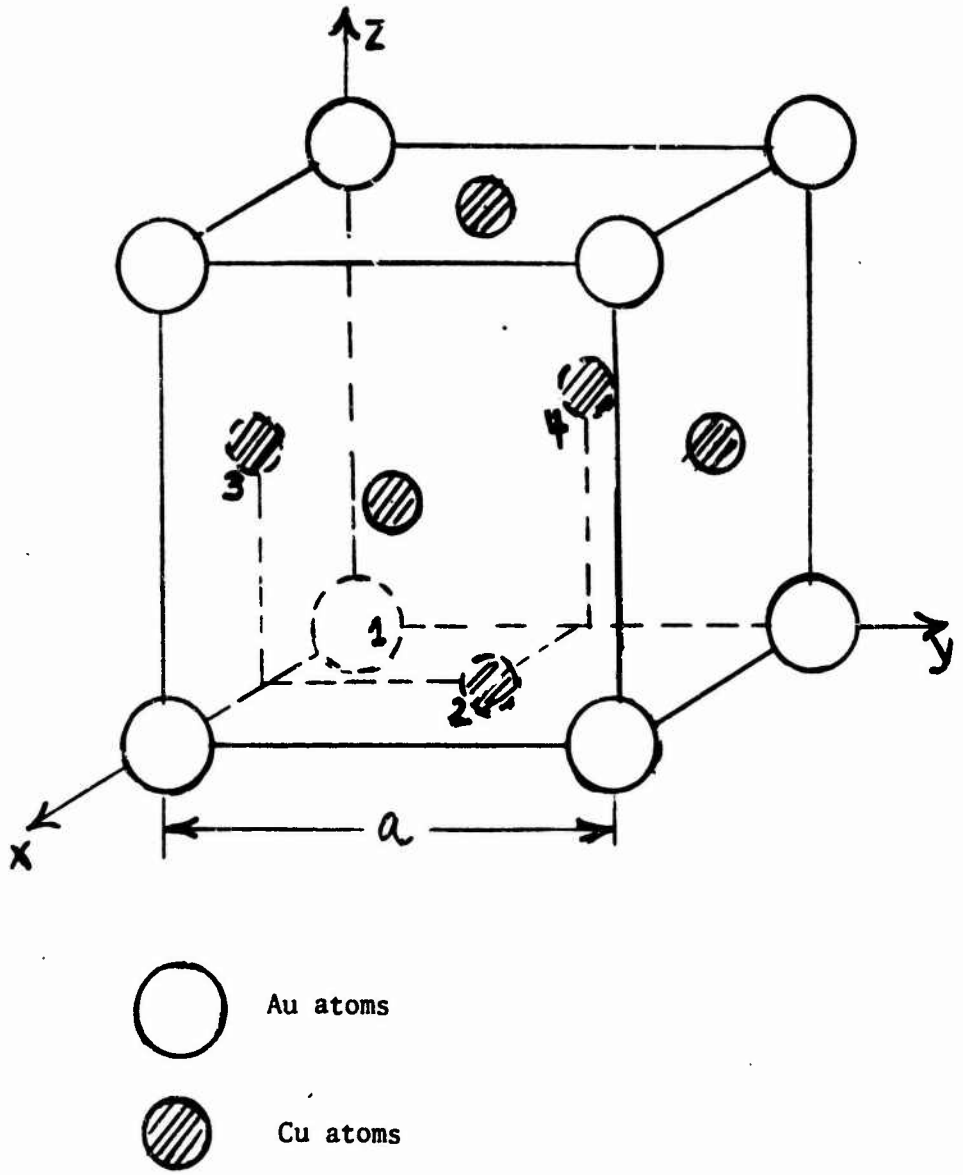


Figure 1. A unit cell in real space for the Cu_3Au structure. The numbering of atomic sites in the primitive cell is consistent with eqs. (7a) and (7b) of the text.

$$\vec{s}_1 = (a/2)\ (000) \tag{7a}$$

for the central (Au) atom, and

$$\vec{s}_2 = (a/2)\ (110)$$
$$\vec{s}_3 = (a/2)\ (101) \tag{7b}$$
$$\vec{s}_4 = (a/2)\ (011)$$

to describe the location of the three Cu atoms in the primitive cell.

For cubic systems, the unsymmetrized atomic-like functions (a.l.f.'s) used in a band structure calculation may conveniently be taken to be of the form

$$[u_{n\ell}(\rho)/\rho]\, X_q(\hat{\rho}/\rho)$$

where $u_{n\ell}$ is the ordinary radial atomic function and X_q is chosen from the set of cubic harmonics given in Table B-II of Appendix B. These functions will be centered on particular atomic sites; i.e., for an a.l.f. centered on site 2, for example, $\vec{\rho} = \vec{r} - \vec{s}_2$.

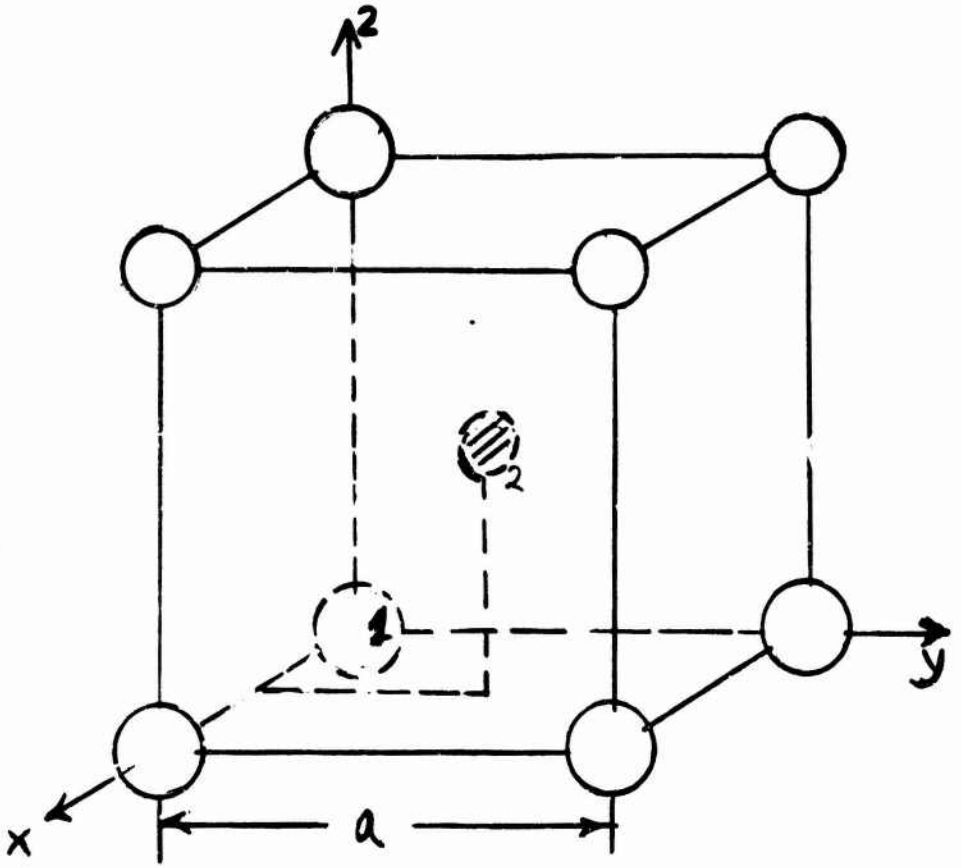
As a second example consider a simple cubic lattice with two atoms per primitive cell, A type atoms at the cube corners and B type atoms at the cube center (eg, CsCl). Taking the origin at an A type atom and using the cubic axes to define $\hat{i}$, $\hat{j}$, $\hat{k}$, one has

$$\vec{s}_1 = (a/2)\ (000) \tag{8a}$$

for the central (A type) atom, and

$$\vec{s}_2 = (a/2)\ (111) \tag{8b}$$

for the non-central (B type) atom. The real space unit cell for the CsCl type lattice is shown in Fig. 2. The simple cubic reciprocal



Cs (A type atoms)

Cl (B type atoms)

Figure 2. A unit cell in real space for the CsCl structure. The numbering of atomic sites in the primitive cell is consistent with eqs. (8a) and (8b) of the text.

space ($\vec{k}$-space) Brillouin zone is shown in Fig. 3; this is the first Brillouin zone for any simple cubic lattice and is thus valid for both Cu_3Au and CsCl type structures.

For the non-central atoms the rotation of one site into another must be considered in determining symmetrized functions. The basic symmetrization formula (see ref. 7) is

$$\Phi_i^{\lambda\nu}(\vec{r}) = h/g \sum_R D^{\lambda}_{\mu\nu}(R)^* P_R f_\mu(\vec{r}) \tag{9}$$

where Φ_i is the "symmetrized" function generated from the "unsymmetrized" function f_i ; λ labels the irreducible representation. Consider, for example, a function defined on a particular site,

$$F(\vec{r}) = \sum_j e^{i\vec{k}\cdot(\vec{\tau}_j+\vec{s}_\nu)} \delta(\vec{r}-\vec{\tau}_j-\vec{s}_\nu) \tag{10}$$

with the lattice translation vectors $\vec{\tau}_j$ running over all the primitive cells of the crystal and

$$\delta(\vec{\rho}) = 0 \quad \text{for} \quad \rho \geq d \tag{11}$$

with d equal to the radius of an "atomic sphere" at site $\vec{s}_\nu$. When $F(\vec{r})$ of eq. (10) is substituted into the symmetrization formula (9) one must consider the rotation of $\vec{r}$ from one site to another. (It should be understood that $P_R \delta(\vec{r}-\vec{\tau}_j-\vec{s}_\nu) = \delta(R^{-1}\vec{r}-\vec{\tau}_j-\vec{s}_\nu)$, i.e., the operator P_R affects only $\vec{r}$ and not $\vec{\tau}_j$ or $\vec{s}_\nu$; this point is discussed in detail below.) For the CsCl structure <u>every</u> group operation takes the non-central site into itself or into an

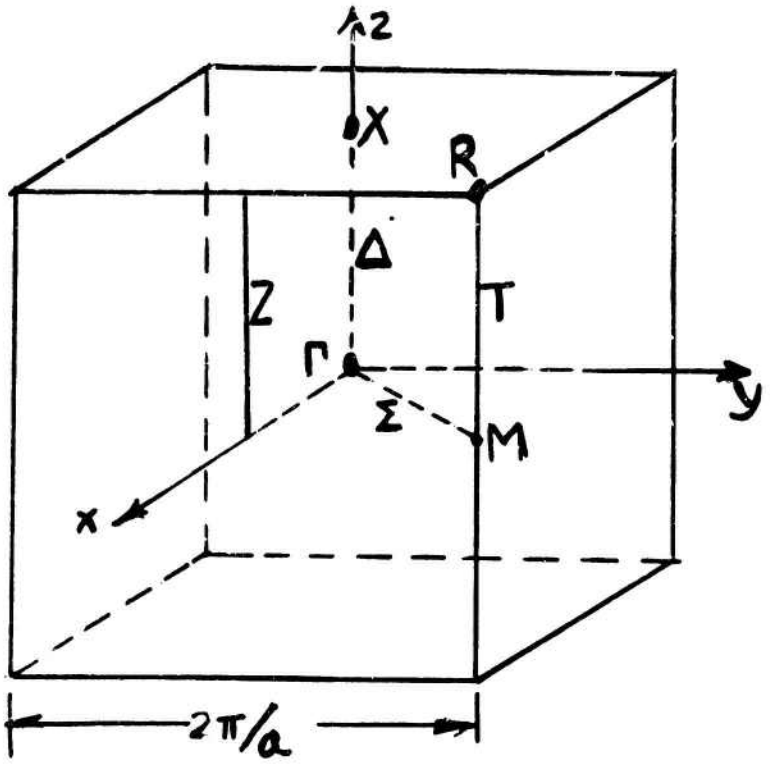


Figure 3. The first Brillouin zone for the simple cubic lattice. Valid for both the Cu_3Au and CsCl structures. Selected symmetry points are labeled in the BSW notation.

"equivalent" site, i.e., a site reachable by a $\vec{\tau}$ vector from the original site; this makes symmetrization simpler than in the Cu_3Au case where there are three non-equivalent non-central sites. Prediction and construction of the contained functions for both cases are discussed below.

B. ℓ Character Tables.

The ℓ character tables may be used to determine n_ℓ^λ . i.e., how many times functions of a given ℓ value will "show up" in a given irreducible representation. The pertinent equation is

$$n_\ell^\lambda = (1/g)\Sigma_R \chi^\lambda(R)\chi^\ell(R)^* \qquad (12)$$

where $\chi^\lambda(R)$ is the character for operator R in the λ th representation and $\chi^\ell(R)$ is taken from the ℓ character table. Eq. (12) follows from the orthogonality equation (eq. (5), above) and the fact that, for the various $\vec{k}$ points, the ℓ representations are, in general, reducible. (See sections 3-2 through 3-6 of ref. 8.)

1. For the central atom, a single ℓ character table suffices for <u>all</u> symmetry points. $\chi^\ell(R)$ may be obtained from

$$\chi^\ell(R \text{ of angle } \theta) = 1 + 2\cos\theta + 2\cos 2\theta + \cdots + 2\cos\ell\theta \qquad (13)$$

(See pg 155 of ref. 7; in particular, eq. (15.7) and the associated discussion.) For even ℓ , $\chi^\ell(JR)$, where J is the inversion operator, has the same sign as $\chi^\ell(R)$; for odd ℓ , $\chi^\ell(JR) = -\chi^\ell(R)$. In this way one obtains the ℓ character tables C-I (cubic system)

and F-I ("reduced" simple tetragonal) given in Appendices C and F respectively. For $\ell > 0$ these characters can be "broken down" into the appropriate "Γ" representations as indicated in Tables C-I and F-I.

2. For the non-central atoms, obtaining the ℓ character tables is somewhat more involved.

(a) Review of manipulations involved in operating on a function: Following ref. 7,

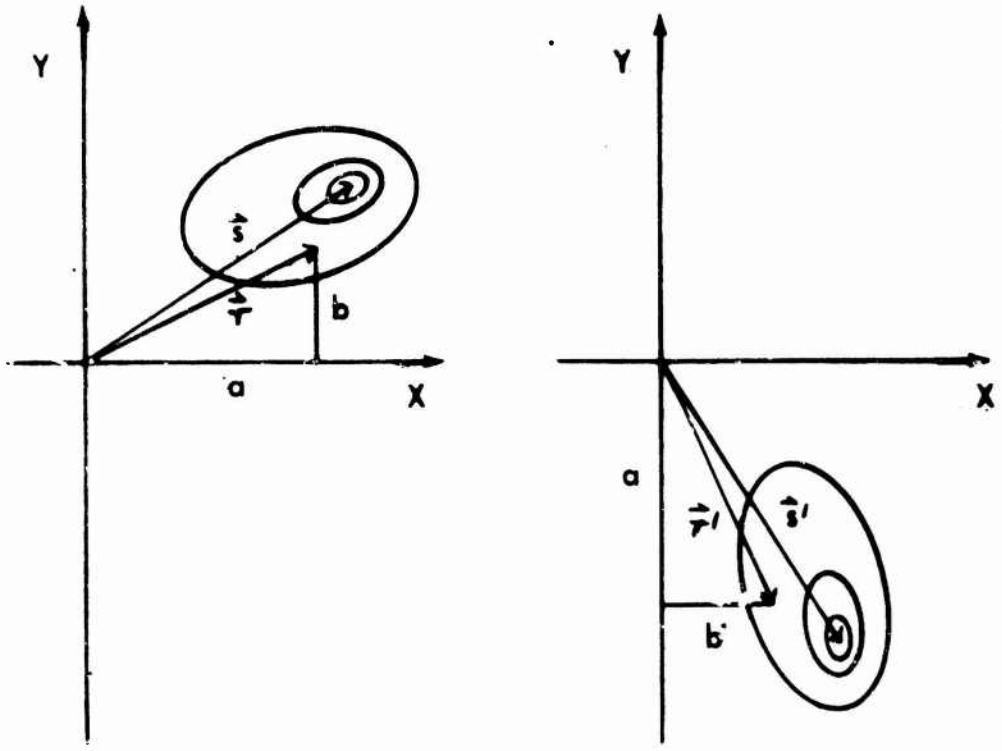
$$P_R f(\vec{r}') = f(\vec{r}) \tag{14}$$

means that the function $P_R f$ has the same value at $\vec{r}'$ as f has at $\vec{r}$ with

$$\vec{r}' = \bar{\bar{R}}\vec{r}. \tag{15}$$

Suppose we have a function f represented by the contour lines in Fig. 4a. Consider an R such that $P_R f$ is the function shown in Fig. 4b. Suppose that $f(\vec{r})$ in Fig. 4a has the value 6 when $x = a$, $y = b$, $z = 0$; then we want $P_R f(\vec{r}')$ in Fig. 4b to have the value 6 when $x' = b$, $y' = -a$, $z' = 0$. Thus

$$\bar{\bar{R}} = \begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{16}$$



(a) The function f (b) The rotated function $P_R f$

Figure 4. Rotation of a function.

so that eq. (15) becomes

$$\begin{pmatrix} b \\ -a \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ 0 \end{pmatrix}$$

and in Fig. 4b, $\vec{r}' = \overline{\overline{R}}\vec{r}$ and $\vec{s}' = \overline{\overline{R}}\vec{s}$.

Let us see what this means in terms of our "triad" system, i.e., P_R associated with $(x', y', z') \rightarrow (\bar{y}', x', z')$, say. (A list of the cubic triads is given in Appendix A.) For this triad, to find $P_R f$, we keep the same functional form f, but replace x' with $-y'$, y' with x', and z' with z' . To be consistent with eqs. (14) and (15)

$$\begin{aligned} x &= R_{11}x' + R_{21}y' + R_{31}z' \\ y &= R_{12}x' + R_{22}y' + R_{32}z' \\ z &= R_{13}x' + R_{23}y' + R_{33}z' \end{aligned} \qquad (15a)$$

(From (15), $\vec{r} = \overline{\overline{R}}^{-1}\vec{r}'$, and, since the R's are real, orthogonal matrices, $\overline{\overline{R}}^{-1} = \overline{\overline{R}}$ transpose.) To be consistent with the triad chosen, $x = -y'$, $y = x'$, $z = z'$; we must have $R_{21} = -1$, $R_{12} = 1$, $R_{33} = 1$ so that the $\overline{\overline{R}}$ obtained here is identical to the $\overline{\overline{R}}$ in (16); thus the triad $(\bar{y}', x', z')$ is associated with the P_R used in Fig. 4.

Further, let $f(x = a, y = b, z = 0) = 6$ as before; then, using the triad notation, and the triad $(\bar{y}', x', z')$ as above;

$$P_R f(x', y', z') = f(\bar{y}', x', z'),$$

so that

$$P_R f(b, \bar{a}, 0) = f(a, b, 0) = 6,$$

as desired.

We now consider

$$P_R f(\vec{r}' - \vec{s}')$$

with $\vec{s}'$ a fixed vector. The matrix $\bar{\bar{R}}$ transforms $\vec{r}'$ <u>not</u> $\vec{r}' - \vec{s}'$; this is equivalent to the statement that, for proper rotations, P_R represents a rotation about an axis through $\vec{r}' = 0$, <u>not</u> through $\vec{r}' - \vec{s}' = 0$. We now show that

$$P_R f(\vec{r}' - \vec{s}') = f(\bar{\bar{R}}^{-1}\vec{r}' - \vec{s}') \tag{17}$$

(and <u>not</u> $f(\bar{\bar{R}}^{-1}[\vec{r}' - \vec{s}'])$):

Define $h(\vec{r}') = f(\vec{r}' - \vec{s}')$

Then $P_R f(\vec{r}' - \vec{s}') = P_R h(\vec{r}')$

$$= h(\bar{\bar{R}}^{-1}\vec{r}') \quad \text{using (14) and (15),}$$
$$= f(\bar{\bar{R}}^{-1}\vec{r}' - \vec{s}')$$

Referring to Fig. 4, if $f(\vec{r} - \vec{s}) = 12$, say, at $\vec{r} = \vec{s}$, we want $P_R f(\vec{r}' - \vec{s}) = 12$ at $\vec{r}' = \bar{\bar{R}}\vec{r} = \bar{\bar{R}}\vec{s}$; using (17),

$P_R f(\vec{r}' - \vec{s}) = f(\bar{\bar{R}}^{-1}(\bar{\bar{R}}\vec{s}) - \vec{s}) = f(0) = 12$, as desired.

We now consider writing a rotation (about $\vec{r} = 0$) of a function centered at $\vec{s}$ of Fig. 4a as a rotation about an axis through $\vec{r} = \vec{s}$ followed by a translation.

Let

$$P_R f(\vec{p}) = f(\bar{R}^{-1}\vec{p}) = g(\vec{p}), \tag{18}$$

i.e., g represents the rotated function (rotated about an axis through $\vec{p} = 0$). Using (17) and (18)

$$P_R f(\vec{r}-\vec{s}) = f(\bar{R}^{-1}\vec{r}-\vec{s}) = f(\bar{R}^{-1}[\vec{r}-\bar{R}\vec{s}]) = g(\vec{r}-\bar{R}\vec{s}). \tag{19}$$

All our functions are Bloch functions, so we may write

$$g(\vec{r}-\bar{R}\vec{s}+\vec{\tau}) = e^{i\vec{k}\cdot\vec{\tau}} g(\vec{r}-\bar{R}\vec{s}).$$

Substituting this into eq. (19) we have

$$P_R f(\vec{r}-\vec{s}) = g(\vec{r}-\bar{R}\vec{s}+\vec{\tau}) e^{-i\vec{k}\cdot\vec{\tau}} \tag{20}$$

where $\vec{\tau}$ is any primitive translation in real space.

Now let

$$\bar{R}\vec{s} = \vec{s} + \vec{\tau}, \tag{21}$$

i.e., for a given $\vec{s}$ we allow only those $\bar{R}$ which satisfy (21); thus if $\vec{s}$ is a vector defining a non-central atomic site, $\bar{R}\vec{s}$ is a vector to an equivalent site. Substituting (21) into (20)

$$P_R f(\vec{r}-\vec{s}) = g(\vec{r}-\vec{s}) e^{-i\vec{k}\cdot(\bar{R}\vec{s}-\vec{s})}. \tag{22}$$

Referring to eq. (18), g $(\vec{r} - \vec{s})$ represents the function f after rotation about an axis through $\vec{r} = \vec{s}$; thus, <u>for Bloch functions</u>, a rotation about $\vec{r} = 0$ is equal to a rotation about $\vec{r} = \vec{s}$, times a factor exp $[-i\vec{k}\cdot(\bar{R}\vec{s} - \vec{s})]$ with the restriction on $\bar{R}$ implied by (21). An alternative derivation of this "parallel axis" theorem is given in Appendix D.

(b) It is now easy to see how to extend the predictive

equation (eq. (12)) to the non-central atoms: Centering a given ℓ-type function at $\vec{r} = \vec{s}$ and rotating about $\vec{r} = 0$ is equivalent to rotation of this function about $\vec{r} = \vec{s}$ (represented by $g(\vec{r} - \vec{s})$ in (22)) multiplied by a phase factor. If $\chi_c^{\ell}(R)$ is the trace for the central atom, then we will have this same trace associated with $g(\vec{r} - \vec{s})$. Thus

$$\chi^{\ell}_{nc,\vec{s}}(R) = \chi^{\ell}_{c}(R)\, e^{-i\vec{k}\cdot(\bar{R}\vec{s}-\vec{s})} \tag{23}$$

Using $\bar{R}^{-1}\vec{k} = \vec{k} + \vec{K}$ and the fact that $\bar{R}\vec{s} - \vec{s}$ is a $\vec{\tau}$ vector, we may write (23) as

$$\chi^{\ell}_{nc,\vec{s}}(R) = \chi^{\ell}_{c}(R)\, e^{i\vec{k}\cdot(\bar{R}^{-1}\vec{s}-\vec{s})} \tag{23a}$$

Thus, combining eqs. (12) and (23),

$$n^{\lambda}_{\ell}(\text{non-central}) = (1/g)\sum_R \chi^{\lambda}(R)\chi^{\ell}_{c}(R)^{*}\sum'_{\nu} e^{i\vec{k}\cdot(\bar{R}\vec{s}_{\nu}-\vec{s}_{\nu})} \tag{24}$$

or, using (23a),

$$n^{\lambda}_{\ell}(\text{non-central}) = (1/g)\sum_R \chi^{\lambda}(R)\chi^{\ell}_{c}(R)^{*}\sum'_{\nu} e^{-i\vec{k}\cdot(\bar{R}^{-1}\vec{s}_{\nu}-\vec{s}_{\nu})}. \tag{24a}$$

We sum on ν since we must consider functions on all the non-central sites; the prime on the ν sum in (24) and (24a) indicates that, for a given $\bar{R}$, only those $\vec{s}_{\nu}$ are allowed for which $\bar{R}\vec{s}_{\nu} = \vec{s}_{\nu} + \vec{\tau}$. For a given $\vec{k}$ we may perform the ν sum for each $\bar{R}$ and write

$$n^{\lambda}_{\ell}(\text{non-central}) = (1/g)\sum_R \chi^{\lambda}(R)\,\chi^{\ell,\vec{k}}_{nc}(R)^{*} \tag{25}$$

with

$$\chi^{\ell,k}_{nc}(R)^* = \chi^{\ell}_{c}(R)^* \sum_\nu' e^{i\vec{k}\cdot(R\vec{s}_\nu - \vec{s}_\nu)} \tag{26}$$

$$= \chi^{\ell}_{c}(R)^* \sum_\nu' e^{-i\vec{k}\cdot(R^{-1}\vec{s}_\nu - \vec{s}_\nu)} \tag{26a}$$

$$= \chi^{\ell}_{c}(R)^* \sum_\nu' e^{i(\vec{k} - R\vec{k})\cdot\vec{s}_\nu} \tag{26b}$$

Consider Cu_3Au as an example. The primitive cell may be taken as in Figure 1 with the three Cu sites labeled 2, 3, 4 and $\vec{s}_\nu$ given by (7b). We now illustrate how to find $\chi^{\ell,k}_{nc}(R)$ for $\ell = 1$ for the T point located at $\vec{k} = (2\pi/a)(\frac{1}{2}\,\frac{1}{2}\,b)$, $0 < b < \frac{1}{2}$ in Figure 3. Under the identity operation E all three non-central sites go into themselves so $R\vec{s}_\nu - \vec{s}_\nu = 0$ for all three $\vec{s}_\nu$; thus all three phase factors in eq. (26) are +1 and $\sum_\nu' = +3$; then, since eq. (13) gives $\chi^{\ell=1}_{c}(E) = 3$, we have $\chi^{1,T}_{nc}(E) = 3\times3 = 9$. The operation $C_4^2(z)$, i.e., 180° about the z axis, takes all three Cu sites to corresponding equivalent sites. Using eq. (26b), $\vec{k} - R\vec{k} = (2\pi/a)(110)$. This gives 2π when dot multiplied with $\vec{s}_2$, π when dot multiplied with $\vec{s}_3$ or $\vec{s}_4$; $\sum_\nu'$ is then 1-1-1 = -1 and, since eq. (13) gives $\chi^{1}_{c}(180°) = -1$, we have

$$\chi^{1,T}_{nc}(C_4^2(z)) = -1 \times -1 = 1.$$

For the $C_4(z)$ operation (90° about z) represented by the $\overline{R}$ of eq. (16) (i.e., operation number 5 in our triad list of App. A) only site 2 goes into an equivalent site. For this R, $\vec{k} - R\vec{k} = (2\pi/a)(010)$; this

gives π when dot multiplied with $\vec{s}_2$ so $\Sigma'_\nu = -1$. Eq. (13) gives $\chi^1_c(90^\circ) = 1$ so

$$\chi^{l,T}_{nc}(C_4(\#5)) = 1 \times -1 = -1.$$

In similar fashion one finds $\chi^{l,T}_{nc}(JC_4^2(x)) = -1$ and $\chi^{l,T}_{nc}(JC_2(\#35)) = 1$. ($JC_4^2(x)$ takes all three $\vec{s}_\nu$ into equivalent sites, $JC_2(\#35)$ takes only $\vec{s}_2$ into an equivalent site. Both C_4^2 and C_2 are 180° operations; eq. (13) gives $\chi^1_c(180^\circ) = -1$ but, since l is odd, $\chi^1_c(JC_4^2)$ and $\chi^1_c(JC_2) = -1 \times \chi^1_c(180^\circ) = -1 \times -1 = 1$.) Since it is only necessary to work out one operator in each class, we have thus obtained the $l=1$ trace table for the T point for the non-central atoms of Cu_3Au type structures.

class	E	$C_4^2(z)$	$2C_4$	$2JC_4^2$	$2JC_2$
$\chi_{nc}(l=1)$	9	1	-1	-1	1

(The number in front of the BSW class label simply gives the number of members in the class.) In Appendix C we give Σ'_ν for all eight operators of T (Table C-IV) and the complete ($l = 0,1,2$) character table (Table C-III).

For interior $\vec{k}$ points eq. (26b) reduces to

$$\chi^{l,\vec{k}}_{nc}(R)^* = \chi^l_c(R)^* \sum_\nu \delta(R\vec{s}_\nu - \vec{s}_\nu - \vec{t}), \qquad \text{(interior-}\vec{k}\text{)} \qquad (27)$$

since, for interior $\vec{k}$, $R\vec{k} = \vec{k}$ for all R in the point group of $\vec{k}$ so that one need only ascertain how many sites go to equivalent sites under each operation R. Since, for a given R, the delta function in (27) is independent of $\vec{k}$, the <u>same</u> l-character table will suffice for <u>all</u> interior-$\vec{k}$ points for the non-central atoms (for a given crystal

structure). More precisely, one may make a single "master table" listing $\chi^{\ell}_{nc}(R)$ for each R of the full point group, then immediately write down the ℓ-character table for a given interior-$\vec{k}$ point by simply selecting those R belonging to the point group of $\vec{k}$. An interior-$\vec{k}$ master table for Cu_3Au type structures is given in Appendix C (Table C-II).

For points on the zone boundary the "master table" idea above is not of much use and a different ℓ character table is (in general) required for each $\vec{k}$ point for the non-central atoms. Table C-III of Appendix C (T point of simple cubic Cu_3Au structure) is an example of such a table. The phase factors used in constructing Table C-III are given in Table C-IV. Because of these phase factors, the entries in Table C-III are not (in general) equal to the entries for corresponding R, ℓ in Table C-II (interior-$\vec{k}$ points).

(c) Systems with only one non-central site. In such a system this non-central site must go into itself (or equivalent) under every operation of the group. The CsCl structure with two atoms per primitive cell, an A type atom at the corners and a B type atom at the body-center position (see Fig. 2) is an example of such a system.

For the <u>interior</u>-k points of such a system, eq. (26) reduces to

$$\chi^{\ell,\vec{k}}_{nc}(R)^* = \chi^{\ell}_{c}(R)^*. \qquad \text{(one non-central atom; interior-}\vec{k}\text{)} \quad (28)$$

For these cases eq. (25) reduces to eq. (12) so that the central atom ℓ character table also suffices for the non-central atom. (See Table C-I, Appendix C.)

For $\vec{k}$ points on the zone boundary different ℓ character tables will (in general) be needed for each $\vec{k}$ point and the factor

$$e^{i\vec{k}\cdot(R\vec{s}_2-\vec{s}_2)}$$

must be evaluated for each $\vec{k}$, each R. For CsCl type structures $\vec{s}_2$ is given by eq. (8b). As an example, the ℓ character table for the symmetry point T of the CsCl structure is given as Table C-VI (App. C); phase factors used in constructing Table C-VI are given in Table C-VII.

C. Using the ℓ character tables to predict the pattern of contained functions: We give three examples; an interior point of Cu_3Au, an exterior point of Cu_3Au, and an exterior point of CsCl.

1. Simple cubic Cu_3Au; $\Delta(z)$ i.e., an interior point on the z axis. $\vec{k} = (2\pi/a)\ (00b)$, $0 < b < \frac{1}{2}$.

(a) Central atom: Using the Δ character table (B-III), the appropriate ℓ character table (C-I), and eq. (12) one finds that:

Δ_1 contains $\ell = 0$

$\ell = 1$

$\ell = 2\ (\Gamma_{12})$

Δ_2 contains $\ell = 2\ (\Gamma_{12})$

Δ_1' contains no a.l.f.'s

Δ_2' contains $\ell = 2\ (\Gamma_{25'})$

Δ_5 contains $\ell = 1$

$\ell = 2\ (\Gamma_{25'})$

Once all the irreducible representations for a given symmetry point have been listed as above, there is an important consistency check that may be used:

$$\Sigma_\lambda n_\ell^\lambda h_\lambda = p(2\ell+1) \qquad (29)$$

where the sum is over all the irreducible representations of the symmetry point, n_ℓ^λ is the number of times an a.l.f. function of type ℓ shows up on representation λ, and h_λ is the dimensionality of the λ representation. (p is the number of atoms involved; for the central atom case p = 1.) Eq. (29) simply reflects the fact that, when a reducible ℓ representation is decomposed into the irreducible representations of a given symmetry point, the total dimensionality of the decomposition must equal the original dimensionality. In the case above we see that this sum is:

1x1 = 1 for $\ell = 0$;

1x1 + 1x2 = 3 for $\ell = 1$;

1x1 + 1x1 + 1x1 + 1x2 = 5 for $\ell = 2$;

all agreeing with eq. (29). (Δ_5 is 2-dimensional; the other Δ representations are 1-dimensional.) Eq. (29) can be extended to check the individual "Γ" breakdown as expressed here by Γ_{12} and $\Gamma_{25'}$. The right hand side of (29) is just the dimensionality of the representation for ℓ; thus, when ℓ is decomposed into different (Γ) representations,

$$\Sigma_\lambda n_{\ell(\Gamma_a)}^\lambda h_\lambda = p(\text{dimensionality of } \ell(\Gamma_a)) \qquad (30)$$

Checking this for the case above:

$1x1 + 1x1 = 2$ for $\ell = 2$, Γ_{12} type;

$1x1 + 1x2 = 3$ for $\ell = 2$, $\Gamma_{25'}$ type;

both agreeing with eq. (30). (Γ_{12} is 2-dimensional; $\Gamma_{25'}$ is 3-dimensional.)

(b) Non-central atoms: Since Δ is an interior $-\vec{k}$ point we use the Cu_3Au interior-$\vec{k}$ "master table" (C-II) and the Δ character table (B-III) with eq. (25). We find:

Δ_1 contains $\ell = 0$ (twice)

$\ell = 1$ (twice)

$\ell = 2$ (Γ_{12}) (three times)

Δ_2 contains $\ell = 0$

$\ell = 1$

$\ell = 2$ (Γ_{12}) (three times)

Δ_1' contains $\ell = 2$ ($\Gamma_{25'}$)

Δ_2' contains $\ell = 2$ ($\Gamma_{25'}$) (twice)

Δ_5 contains $\ell = 1$ (three times)

$\ell = 2$ ($\Gamma_{25'}$) (three times)

We see that both (29) and (30) are satisfied ($p = 3$ here).

2. Simple cubic Cu_3Au; T point at

$\vec{k} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\ b)$, $0 < b < \frac{1}{2}$. This is an exterior point (see Fig. 3). The character table for T is identical to that for Δ . For T as chosen here, the 8 operations are identical to those for Δ at

$(2\pi/a)(00b)$, $0<b<\frac{1}{2}$. T as chosen has equivalent points ($\vec{k}' = \vec{k}+\vec{K}$) at $(2\pi/a)(\frac{1}{2}\,\bar{\frac{1}{2}}\,b)$, $(2\pi/a)(\bar{\frac{1}{2}}\,\frac{1}{2}\,b)$, and $(2\pi/a)(\bar{\frac{1}{2}}\,\bar{\frac{1}{2}}\,b)$.

(a) Central atom: Since the same character table (B-III) and the same ℓ character table (C-I) will be used here as in example 1 above (the same operations will be selected out of table C-I as for Δ), we obtain the same pattern of contained a.l.f.'s as for the Δ point central atom, above.

(b) Non-central atoms: Eq. (25) must be used here with $\chi_{nc}^{\ell,\vec{k}}(R)$ determined by using eq. (26). The resultant ℓ character table is given in Appendix C. Table C-III gives $\chi_{nc}^{\ell,\vec{k}}(R)$ constructed as per eq. (26); the $\exp\left[i\vec{k}\cdot(\bar{R}\vec{s}_\nu - \vec{s}_\nu)\right]$ factors are given in Table C-IV. One finds that:

T_1 contains $\ell = 1$

$\ell = 2$ ($\Gamma_{25'}$) (twice)

T_2 contains $\ell = 1$

$\ell = 2$ ($\Gamma_{25'}$)

T_1' contains $\ell = 1$

$\ell = 2$ (Γ_{12})

$\ell = 2$ ($\Gamma_{25'}$)

T_2' contains $\ell = 0$

$\ell = 1$ (twice)

$\ell = 2$ (Γ_{12})

$\ell = 2$ ($\Gamma_{25'}$)

T_5 contains $\ell = 0$

$\ell = 1$ (twice)

$\ell = 2$ (Γ_{12}) (twice)

$\ell = 2$ ($\Gamma_{25'}$) (twice)

We see that eqs. (29) and (30) are satisfied here ($p = 3$).

3. Simple cubic CsCl; T point at $\vec{k} = (2\pi/a)(\frac{1}{2}\,\frac{1}{2}\,b)$, $0 < b < \frac{1}{2}$. This is an exterior point (see Fig. 3).

(a) Central atom: The comments in example 2.(a) above, apply.

(b) Non-central atom: Since there is only one non-central atom in CsCl as opposed to three for Cu_3Au, we need a new ℓ character table. This is given in Appendix C as Table C-VI. (The phase factors used in the construction of this table are given in Table C-VII.) Using eq. (25), Table B-III, and Table C-VI, we find:

T_1 contains $\ell = 2$ ($\Gamma_{25'}$)

T_2 contains no a.l.f.'s

T_1' contains $\ell = 2$ (Γ_{12})

T_2' contains $\ell = 0$

$\ell = 1$

$\ell = 2$ (Γ_{12})

T_5 contains $\ell = 1$

$\ell = 2$ ($\Gamma_{25'}$)

We see that eqs. (29) and (30) are satisfied here ($p = 1$).

D. Working out the actual unsymmetrized and symmetrized a.l.f.'s.

Once the $\mathcal{L}$ character tables have been used as in the preceding section to determine what $\mathcal{L}$-types are contained in the various representations, it is still necessary to determine which <u>particular</u> function is involved and to symmetrize this function. For simple cubic, eg., this means that once we know $\mathcal{L} = 1$ is contained in Δ_1 for instance, do we use x or y or z as the unsymmetrized function. This is determined by trial and error; in many cases the proper choice will be readily apparent. The basic symmetrization recipe, eq. (9) is used.

Before proceeding with specific examples we need to review the general symmetrization of an a.l.f. Using eqn (15) of ref. 3, a symmetrized a.l.f. may be written as

$$\Phi_j^{\lambda}(\vec{r}) = (h/g)\sum_{\mu}\sum_{R}' D_{11}^{\lambda}(R)\, e^{i\vec{k}\cdot R^{-1}\vec{s}_{\mu}}\, \zeta_{q_j}\left[R^{-1}(\vec{r}-\vec{s}_{\mu})\right] \qquad (31)$$

where the prime on the R sum indicates that, for each $\vec{s}_{\mu}$, only those R which satisfy $R^{-1}\vec{s}_{\mu} = \vec{s}_{\nu} + \vec{\tau}$ are allowed if we started with the unsymmetrized function on the $\vec{s}_{\nu}$ atomic site. (The $*$ on $D_{11}(R)$ has been dropped as these elements are all real for Cu_3Au.) We rewrite the exponential factor as

$$e^{i\vec{k}\cdot\vec{s}_{\mu}}\, e^{i\vec{K}(R)\cdot\vec{s}_{\mu}}$$

with $R\vec{k} = \vec{k} + \vec{K}(R)$. Thus (31) becomes

$$\Phi_j^{\lambda}(\vec{r}) = (h/g)\sum_{\mu} e^{i\vec{k}\cdot\vec{s}_{\mu}} \sum_{R}' D_{11}^{\lambda}(R)\, e^{i\vec{K}(R)\cdot\vec{s}_{\mu}}\, \zeta_{q_j}\left[R^{-1}(\vec{r}-\vec{s}_{\mu})\right] \qquad (32)$$

We note that the $\exp(i\vec{k}\cdot\vec{s}_\mu)$ factor in eq. (32) does not depend on R; thus, in finding the explicit a.l.f.'s we may treat this factor as a constant for each site (for a given $\vec{k}$). In the MPW method the symmetrized a.l.f.'s will ultimately be used to form matrix elements such as $\int(\text{a.l.f.})_i^* (\text{a.l.f.})_j d\tau$, $\int(\text{a.l.f.})_i^* H(\text{plane-wave})_j d\tau$, etc. For non-overlapping a.l.f.'s, the function $\delta_{qj}[R^{-1}(\vec{r} - \vec{s}_\mu)]$ is non-zero only for $\vec{r}$ vectors in the $\vec{s}_\mu$ "sphere". For the a.l.f. - a.l.f. matrix elements, then, only the "s_μ part" of $(\text{a.l.f.})_i^*$ will combine with the "s_μ part" of $(\text{a.l.f.})_j$ and the $\exp(i\vec{k}\cdot\vec{s}_\mu)$ of Q_j in eq. (32) will be canceled by the $\exp(-i\vec{k}\cdot\vec{s}_\mu)$ of Q_i^*. For the a.l.f. - plane-wave cases, the $\exp(i\vec{k}\cdot\vec{s}_\mu)$ term may be kept simply as a constant factor. We will, therefore, ignore this factor of eq. (32) in working out the explicit symmetrized a.l.f.'s.

The $\exp\left[i\vec{K}(R)\cdot\vec{s}_\mu\right]$ factors of eq. (32) can not, in general, be factored out of the sum on R for each μ. (For the Cu_3Au and CsCl structures $\vec{K}(R)\cdot\vec{s}_\mu$ will always be $n\pi$, where n is an integer; thus, for these structures, $\exp\left[i\vec{K}(R)\cdot\vec{s}_\mu\right]$ will always be real and equal to ± 1. For more complicated crystal structures this factor can be complex.)

For symmetry points on the zone boundary these factors must be included in the symmetrization; for interior-$\vec{k}$ points $\vec{K}(R)$ is zero so this factor is always +1 for such points. From the discussion associated with eq. (18) we see that the expression $\zeta_{qj}[R^{-1}(\vec{r}-\vec{s}_\mu)]$ in eq. (32) may be considered as a rotation about an axis through the point defined by $\vec{s}_\mu$. If the original ζ_{qj} is centered on $\vec{s}_\nu$ and has an angular part ρ_x/ρ_ν say, then for the R associated with the triad (yxz), the angular part of $\zeta_{qj}[R^{-1}(\vec{r}-\vec{s}_\mu)]$ is just $\rho_{\mu y}/\rho_\mu$ with $\vec{\rho}_\nu = \vec{r}-\vec{s}_\nu$ and $\vec{\rho}_\mu = \vec{r}-\vec{s}_\mu$. Changing language slightly, one says that x on site ν has become y on site μ or x_ν "goes to" y_μ. We now provide a few specific examples.

1. Simple cubic, Cu_3Au structure; $\Delta(z)$ point. $\vec{k} = (2\pi/a)(00b)$, $0 < b < \frac{1}{2}$. Character Table B-III is used. The predicted <u>types</u> of functions are given in sections C.1.(a) and C.1.(b), above. The actual functions (angular parts) are to be chosen from the cubic harmonics given in Table B-II.

(a) Central atom:

Δ_2: From section C.1.(a) we see that only $\ell = 2$ (of the Γ_{12} type) is allowed. This means we must try both $2z^2-x^2-y^2$ and x^2-y^2. Using eq. (9) and the $D_{11}(R)$ for Δ_2 from Table B-III we find that $2z^2-x^2-y^2$ symmetrizes to zero whereas x^2-y^2 symmetrizes to itself. Proceeding similarly with the other Δ representations we find:

Δ_1 $\ell = 0$ $1 \rightarrow 1$

(the arrow means "symmetrizes to")

$\ell = 1$ $z \rightarrow z$

$\ell = 2$ (Γ_{12}) $2z^2-x^2-y^2 \rightarrow 2z^2-x^2-y^2$

Δ_2 $\ell = 2$ (Γ_{12}) $x^2-y^2 \rightarrow x^2-y^2$

Δ_1' no a.l.f.'s

Δ_2' $\ell = 2$ ($\Gamma_{25'}$) $xy \rightarrow xy$

Δ_5 (D_{11}) $\ell = 1$ $x \rightarrow x$

$\ell = 2$ ($\Gamma_{25'}$) $xz \rightarrow xz$

(b) Non-central atoms: (We work out Δ_2' only.) From section C.1.(b), above, we know that $\ell = 2$ ($\Gamma_{25'}$) is contained twice (more precisely; there will be two linearly independent Δ_2' functions of the $\Gamma_{25'}$ type). Let us try all three $\Gamma_{25'}$ functions from Table B-II. We first try these three functions on site 2 (see Fig. 1). Site 2 goes into itself under all eight operations of the $\Delta(z)$ group. We have

	E	$C_4^2(z)$	C_4	C_4	$JC_4^2(x)$	$JC_4^2(y)$	JC_2	JC_2	
	xyz	$\bar{x}\bar{y}z$	$\bar{y}xz$	$y\bar{x}z$	$\bar{x}yz$	$x\bar{y}z$	$\bar{y}\bar{x}z$	yxz	
yz →	yz	-yz	(-xz)	xz	-yz	yz	-xz	xz	= 0
xz →	xz	-xz	yz	-yz	xz	-xz	-yz	yz	= 0
xy →	xy	xy	xy	xy	xy	xy	xy	xy	= 8xy

The entries under the individual operations represent individual $D_{11}(R)P_R f(\vec{r})$ terms in the summation of eq. (9). To obtain the circled entry, eq., one starts with the function yz, replaces this by xz as dictated by the triad $(\bar{y}xz)$, then multiplies by $D_{11}(C_4)$ in the

Δ_2' representation (-1). The expression at the far right is the summation of eq. (9) before multiplying by h/g. (As discussed above, we concern ourselves here with the angular part of $f(\vec{r})$ only.) Since $h = 1$ and $g = 8$ for Δ_2', we obtain xy on site 2 as both unsymmetrized and symmetrized function. For site 3, operations E, $C_4^2(z)$ and the two JC_4^2 take site 3 to site 3; under the two C_4 and the two JC_2 operations site 3 goes to site 4. From the patterns above for site 2, one readily sees that yz and xz on site 3 symmetrize to zero whereas xy on site 3 symmetrizes to $(1/2)\left[(xy)_3 + (xy)_4\right]$. For site 4 we will simply reproduce this last function; thus we see that there are two independent Δ_2' functions as predicted.

2. Simple cubic, Cu_3Au; T point at $\vec{k} = (2\pi/a)(\frac{1}{2}\ \frac{1}{2}\ b)$, $0 < b < \frac{1}{2}$.

(a) Central atom: This will go exactly like a Δ point on the z axis, given above in section D.1.(a).

(b) Non-central atoms: (We consider only T_2' here.) Because of the phase factors discussed above (see eq. (32)), the non-central-atom contained a.l.f.'s for T_2' will <u>not</u> be identical to those for Δ_2'. The predicted <u>types</u> of functions are given in section C.2.(b) above. Site rotations will go as in the Δ example above since the same eight operations are involved. Character Table B-III is used. The $\exp\left[i\vec{K}(R)\cdot\vec{s}_3\right]$ factors of eqn. (32) are given in Table C-V. For the unsymmetrized functions on site 3 we must use the $\exp\left[i\vec{K}(R)\cdot\vec{s}_3\right]$ factors for the four operations which take site 3 into itself (E, $C_4^2(z)$, $2JC_4^2$) and use the $\exp\left[i\vec{K}(R)\cdot\vec{s}_4\right]$ factors for the four operations which take site 3 to site 4 ($2C_4$, $2JC_2$).

We find:

$\ell = 0 \quad (1)_2 \rightarrow (1)_2$

$\ell = 1 \quad (z)_2 \rightarrow (z)_2$

$\quad\quad (y)_3 \rightarrow (1/2)\left[(y)_3 + (x)_4\right]$

$\ell = 2 \ (\Gamma_{12}) \quad (2z^2-x^2-y^2)_2 \rightarrow (2z^2-x^2-y^2)_2$

$\quad\quad (\Gamma_{25'}) \quad (yz)_3 \rightarrow (1/2)\left[(yz)_3 + (xz)_4\right]$

3. Simple cubic, CsCl; T point at $\vec{k} = (2\pi/a)(\frac{1}{2}\frac{1}{2}b)$, $0 < b < \frac{1}{a}$. (See Fig. 3.)

(a) Central atom: This will go exactly like a Δ point on the z axis, given in example 1.(a), above.

(b) Non-central atom: For the CsCl structure (Fig. 2) there is only one non-central site so that eq. (32) becomes

$$Q_j^{\lambda}(\vec{F}) = (h/g)\Sigma_R D_{11}^{\lambda}(R)\, e^{i\vec{K}(R)\cdot\vec{s}}\, S_{qj}\left[R^{-1}(\vec{F}-\vec{s})\right] \qquad (33)$$

and all R take this site into itself or equivalent. (We again ignore the $\exp\left[i\vec{K}\cdot\vec{s}\right]$ factor as discussed in connection with eq. (32).) Thus, the $\exp\left[i\vec{K}(R)\cdot\vec{s}\right]$ factor is identical with the phase factor for R used in forming $\chi^{\ell}_{nc}(R)$ and may be taken directly from Table C-VII. We work out T_2' only here.

From section C.3.(b), above, we expect an $\ell = 0$ function, an $\ell = 1$ function, and an $\ell = 2$ function of type Γ_{12}. Using the $D_{11}(R)$ from Table B-III and the phase factors from Table C-VII with eq. (33) we obtain:

$\ell = 0 \quad 1 \rightarrow 1$

$\ell = 1 \quad z \rightarrow z$

$\ell = 2 \quad 2z^2-x^2-y^2 \rightarrow 2z^2-x^2-y^2$

We note that the product of the T_2, D_{11} elements and the phase factors give "effective" D_{11} elements identical to T_1; it is thus no coincidence that the functions obtained above are identical to those for Δ_1 for the central atom of Cu_3Au (example 1.(a), above)

DETERMINATION OF THE CONTAINED PLANE WAVES

The plane wave expansion functions are considerably simpler than the a.l.f.'s since the plane waves are easily expressed in terms of one origin in contrast to the a.l.f.'s which are centered on different sites. Each plane wave extends throughout the entire crystal.

A. Formation and ordering: simple cubic, fcc, and bcc.

A plane wave is written

$$f_K(\vec{r}) = \exp\left[i(\vec{k}+\vec{K})\cdot\vec{r}\right]. \tag{34}$$

Putting this into the symmetrization recipe, eq. (9), gives

$$Q_K^{\lambda}(\vec{r}) = (h/g)\Sigma_R D_{11}^{\lambda}(R)\, e^{iR(\vec{k}+\vec{K})\cdot\vec{r}} \tag{35}$$

In general,

$$\vec{K} = 2\pi(c_1\vec{b}_1 + c_2\vec{b}_2 + c_3\vec{b}_3) \tag{36}$$

where the $\vec{b}_i$ are primitive translation vectors in the reciprocal space lattice and the c_i are integers. Although we will confine ourselves here to the cubic system, the procedure can readily be generalized to other crystal systems.

For the simple cubic lattice,

$$\vec{K} = (2\pi/a)(bcd)$$

where b,c,d are any integer; positive, negative, or zero. Using Δ_2' as an example, we illustrate how one symmetrizes the plane waves and determines the allowed types. For $\vec{k}$ labeled by $\Delta(z)$, i.e., $\vec{k} = (2\pi/a)(00t)$, $0 < t < \frac{1}{2}$, we have

$$(\vec{k}+\vec{K}) = (2\pi/a)(bcf) \tag{37}$$

where $f = t+d$ so that f is <u>not</u> an integer.

In symmetrizing the plane waves there can easily be confusion between R and R^{-1}. In eqs. (14) to (16) we defined our triads so that if P_R is associated with the triad $(\bar{y}xz)$, then R is given by eq. (16) and

$$R^{-1}\vec{r} = \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \bar{y} \\ x \\ z \end{pmatrix}$$

For the same triad,

$$R(\vec{k}+\vec{K}) = \begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} b \\ c \\ f \end{pmatrix} = \begin{pmatrix} c \\ \bar{b} \\ f \end{pmatrix}$$

In symmetrizing any function of a dot product,

$$A \equiv \sum_R D^*_{\mu\nu}(R)\, f(\vec{s}\cdot R^{-1}\vec{r})$$

$$A = \sum_R D^*_{\mu\nu}(R)\, f(R\vec{s}\cdot\vec{r}) \qquad (38)$$
$$= \sum_{T^{-1}} D^*_{\mu\nu}(T^{-1})\, f(T^{-1}\vec{s}\cdot\vec{r})$$

with $T^{-1} = R$. Since the sum is over an entire group,

$$A = \sum_T D^*_{\mu\nu}(T^{-1})\, f(T^{-1}\vec{s}\cdot\vec{r}).$$

We may write

$$D^*_{\mu\nu}(T^{-1}) = D^{-1\,*}_{\mu\nu}(T)$$
$$= D_{\nu\mu}(T)$$

Since the D's are unitary. Then, replacing T by R,

$$A = \sum_R D_{\nu\mu}(R)\, f(R^{-1}\vec{s}\cdot\vec{r}) \qquad (39)$$

Comparing eqs (38) and (39), we see that, for <u>real</u> D's, and when symmetrization is with a <u>diagonal</u> element of D, we may use either $R^{-1}\vec{s}$ or $R\vec{s}$. In the following we will use $R^{-1}(\vec{k}+\vec{K})$.

For P_R associated with the triad $(\bar{y}xz)$, the corresponding term in the sum on R of eq. (35) becomes (using $R^{-1}(\vec{k}+\vec{K})$ as above)

$$D_{11}(R)\exp\left[i(2\pi/a)(\bar{c}bf)\cdot\vec{r}\right]$$

for $(\vec{k}+\vec{K})$ given by eq. (37). To shorten the notation we write the square bracket above as $(\bar{c}bf)$. Under the $\Delta(z)$ operations we have:

	E	$C_4^2(z)$	C_4	C_4	$JC_4^2(x)$	$JC_4^2(y)$	JC_2	JC_2
triad	xyz	$\bar{x}\bar{y}z$	$\bar{y}xz$	$y\bar{x}z$	$\bar{x}yz$	$x\bar{y}z$	$\bar{y}\bar{x}z$	yxz
(bcf)	bcf	$\bar{b}\bar{c}f$	$\bar{c}bf$	$c\bar{b}f$	$\bar{b}cf$	$b\bar{c}f$	$\bar{c}\bar{b}f$	cbf

Using Table B-III for the D's, the complete symmetrization (except for the h/g factor) of (bcf) under Δ_2' becomes

$$e^{(bcf)} + e^{(\bar{b}\bar{c}f)} - e^{(\bar{c}bf)} - e^{(c\bar{b}f)} - e^{(\bar{b}cf)} - e^{(b\bar{c}f)} + e^{(\bar{c}\bar{b}f)} + e^{(cbf)}.$$

Since this does not add to zero, the $(\vec{k}+\vec{K})$ represented by (bcf) is allowed under Δ_2' (with neither b or c equal to zero). From the above, one readily sees that (b0f) and (0cf) would each symmetrize to zero and are thus not allowed under Δ_2'. In a similar manner, one determines that $\vec{K}$ types (bbd) and (bcd) are allowed under Δ_2' and that $\vec{K}$ type (000) is not allowed. (Since we are dealing here with $\Delta(z)$, there is no need to try both (000) and (00d) for $\vec{K}$, for example, as there will always be some non-zero value in the z "slot" due to $\vec{k}$.) One also soon sees that (bbd) "covers" (in the sense that no new independent functions are created) $(b\bar{b}d)$, $(\bar{b}bd)$, and $(\bar{b}\bar{b}d)$, and that bcd covers $(b\bar{c}d)$, $(\bar{b}cd)$, (cbd), etc. For any combination, however, $\bar{d}$ as well as d is needed in the z slot.

To now form a "list" of $\vec{K}$'s, one finds the square magnitude of the various $(\vec{k}+\vec{K})$ vectors and cuts the list off at some magnitude. A simple bookkeeping method is illustrated below. We take $\vec{k} = (2\pi/a)(00\frac{1}{4})$. Ignoring the $(2\pi/a)$ factor and multiplying by 4 in order to work with integers we have:

$\vec{K}$	$4\vec{K}$	$4(\vec{k}+\vec{K})$	$16(\vec{k}+\vec{K})^2$
(110)	(440)	(441)	33
$(11\bar{1})$	$(44\bar{4})$	$(44\bar{3})$	41
(111)	(444)	(445)	57
$(11\bar{2})$	$(44\bar{8})$	$(44\bar{7})$	81
(112)	(448)	(449)	113
(120)	(480)	(481)	81
$(12\bar{1})$	$(48\bar{4})$	$(48\bar{3})$	89
(121)	(484)	(485)	105
$(12\bar{2})$	$(48\bar{8})$	$(48\bar{7})$	129
(220)	(880)	(881)	129
$(22\bar{1})$	$(88\bar{4})$	$(88\bar{3})$	137
etc.			

These would order as: (110)

$(11\bar{1})$

(111)

$(11\bar{2})$

(120)

$(12\bar{1})$

(121)

(112)

etc.

For fcc and bcc lattices, $\vec{K}$ may also be written as $\vec{K} = (2\pi/a)(bcd)$ but now there are restrictions on the values of b,

c, and d. For fcc the integers b,c,d must either be all odd or all even; for bcc the sum b+c+d must be even. These restrictions[10] come from the fact that $\vec{k}$ must be an integer sum of the three primitive reciprocal space translation vectors as expressed by eq. (36).

B. Examples of allowed types of $\vec{K}$'s. For all lists given here b,c, and d are positive only.

1. Simple cubic, fcc, and bcc. Γ point, $\vec{k} = (000)$.

Γ_1 (000)

(00b) (As x,y, and z are equivalent, this "covers" (b00) and (0b0).)

(0bb) (Covers (b0b) and (bb0).)

(0bc) (Covers (0cb), (b0c), etc.)

(bbb)

(bcc) (Covers (cbc), etc; (cbb) must also be used.)

(bcd) (Covers (cbd), (dcb), etc.)

Γ_2 (0bc)

(bcd)

2. Simple cubic, fcc, and bcc. Δ point. $\vec{k} = (2\pi/a)(00t)$: for simple cubic $0<t<\frac{1}{2}$; for fcc and bcc $0<t<1$. Because z never mixes with x or y we will simply write n in the z slot; for (0bn), e.g., n can be $0,b,\bar{b},c,\bar{c}$.

10. C. Kittel, "Introduction to Solid State Physics" (John Wiley and Sons, 2nd ed., 1956). See Chapter 12.

Δ_1 (00n)

(0bn)

(bbn)

(bcn)

Δ_2 (0bn)

(bcn)

$\Delta_{2'}$ (bbn)

(bcn)

Δ_5 (using D_{11} of Table B-IV)

(b0n)

(bbn)

(bcn) } linearly independent

(cbn) }

For $t \approx 1/4$, the simple cubic (sc), fcc, and bcc lists for $\Delta_2(z)$ would order as follows:

sc	fcc	bcc
010	020	$01\bar{1}$
$01\bar{1}$	$02\bar{2}$	011
011	022	020
020	$13\bar{1}$	$12\bar{1}$
$01\bar{2}$	131	121
$02\bar{1}$	040	$02\bar{2}$
120	$13\bar{3}$	$01\bar{3}$
021	$02\bar{4}$	022
$12\bar{1}$	$04\bar{2}$	$03\bar{1}$
etc.	etc.	etc.

The differences between the lists are due to the restrictions in the fcc and bcc cases discussed in Section A.

Note added in proof: Eq. (12) may also be used to predict allowed plane wave types (pwt) by replacing $\chi^{\ell}(R)$ with $\chi^{pwt}(R)$. As an example, the type (b00) contains six vectors (b00, $\bar{b}$00, 0b0, etc.) and may be considered as a 6x6 array. Under the identity operation all six vectors go into themselves and the trace is 6; under $C_4^2(z)$ only the vectors 00b, 00$\bar{b}$ go into themselves and the trace is 2; traces for C_4, C_2, C_3, J, JC_4^2, JC_4, JC_2, and JC_3 will be 2, 0, 0, 0, 4, 0, 2, and 0 respectively. For Γ_1, eq.(12) thus gives

$n = (1/48)(6+3x2+6x2+0+0+0+3x4+0+6x2+0) = 1$;

and for Γ_2,

$n = (1/48)(6+3x2-6x2+0+0+0+3x4+0-6x2+0) = 0$.

Thus, the type (b00) is allowed once for Γ_1 and not at all for Γ_2 as per B.1.

PART II: REDUCED LATTICE SCHEME FOR PERTURBATION PROBLEMS

INTRODUCTION TO PART II

As a specific example consider a bcc lattice with one atom per primitive cell. Suppose we now apply a phonon perturbation in which half the atoms (corner atoms) move along the z axis with one phase, and the other half (body-center atoms) also move along the z axis but with a different phase (see Fig. 5), the perturbed lattice will be simple cubic with two atoms per primitive cell. One may find it convenient to use a "reduced" group so that the full Hamiltonian, including the perturbation term, is invariant under this "reduced" or "new full group". Thus, in a perturbation such as the bcc to simple cubic case above, one might wish to use the cubic Δ group (8 members) as the reduced group instead of using the full cubic (48 member) group. This was the approach used by Bloom in his Ph.D. Thesis[11].

For an fcc crystal one would go from fcc to simple tetragonal for a phonon perturbation with half the atoms moving with one phase and half with another but both motions being along the z axis. (See Fig. 6). The reduced group for this case would be the simple tetragonal Λ group (8 members). (The full tetragonal group has 16 members.) All eight members of the simple tetragonal Λ group preserve +z. For the remainder of Part II we shall consider only the fcc to simple

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11. F.K. Bloom, Ph.D. Thesis, RPI, 1966 (unpublished).

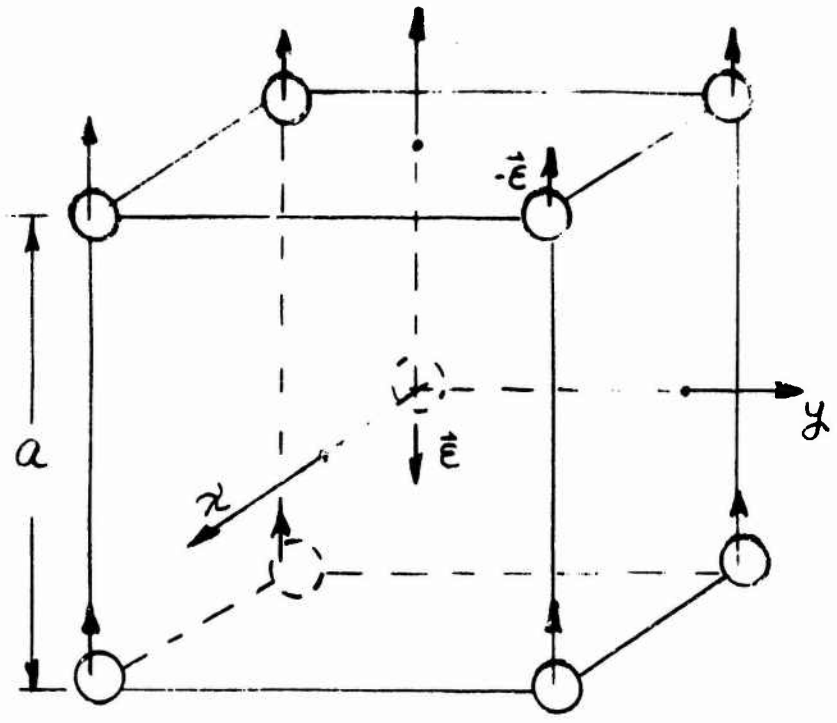
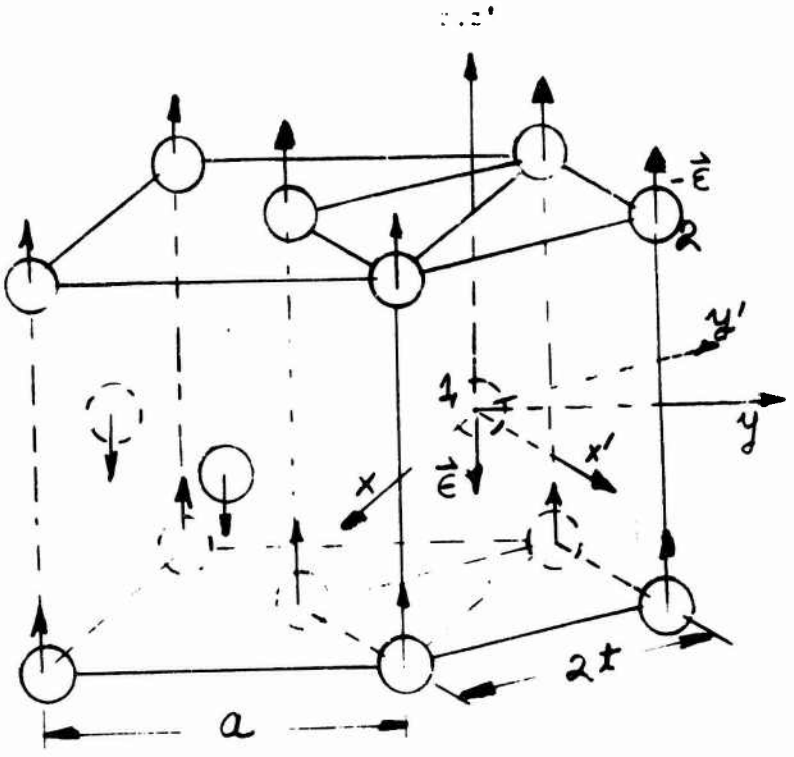


Figure 5. Change in primitive cell from bcc to simple cubic due to a phonon perturbation. For the unperturbed case the bcc primitive cell with one atom is valid. When the perturbation is applied the lattice becomes simple cubic with two atoms per primitive cell; one at (000), the other at (a/2) (111).



$c = a/a$ $\quad 2t = a/\sqrt{2}$

Figure 6. Change in primitive cell from fcc to simple tetragonal due to a phonon perturbation. (Some of the face-centered atoms have been omitted for clarity.) For the unperturbed case the fcc primitive cell with one atom is valid. When the perturbation is applied the lattice becomes simple tetragonal with two atoms per primitive cell; one at (000), the other at (ttc) in the tetragonal (x' y' z') axes. The numbering of the atomic sites is consistent with eqs. (40a) and (40b) of the text.

tetragonal case and shall take the tetragonal Λ group as the reduced or "new full group" for the crystal.

THE "REDUCED GROUP" CHARACTER TABLES: FCC TO SIMPLE TETRAGONAL CASE

For the "Γ" point group for the simple tetragonal lattice (with the added restriction that +z be preserved) one may use the tetragonal Λ point group character table, Table E-I of Appendix E. One must keep in mind that the x' and y' axes of Tables E-I through E-V refer to the simple tetragonal x' and y' axes (perpendicular to the tetragonal faces); when the simple tetragonal is used in conjunction with a "parent" fcc lattice, the x',y' axes of the tetragonal system are rotated 45° from the x, y axes of the fcc system.

To make energy band calculations in the "new" or "perturbed" lattice one needs to determine the contained a.l.f.'s for the various irreducible representations of the symmetry points of this new lattice; in determining these contained a.l.f.'s there are two distinct procedures that may be followed:

1. Determine the contained functions directly as in Part I.
2. Utilize the fcc functions from the "parent" lattice (assuming these have been previously obtained).

We discuss both procedures below.

DETERMINATION OF ATOMIC-LIKE FUNCTIONS: DIRECT PROCEDURE OF PART I

The procedure is exactly as given in Part I; we work out a few examples for comparison with the indirect procedure.

A. $\mathfrak{L}$ Character Tables.

1. Central atom: We take the "body-center" atom at site 1 of Fig. 6 to be the central atom.

$$\vec{s}_1 = (000) \tag{40a}$$

For the central atom one $\mathfrak{L}$ character table suffices for <u>all</u> symmetry points; this is given in Appendix F as Table F-I.

2. Non-central atom: We take the "corner" atom at site 2 of Fig. 6 as the non-central atom in the two-atom basis.

$$\vec{s}_2 = (ttc) \tag{40b}$$

in the $x'y'z'$ axes (tetragonal axes). Since $\vec{s}_1 = 0$ we will simply write $\vec{s}$ for $\vec{s}_2$.

As explained in Part I, the central-atom $\mathfrak{L}$ character table will suffice for the non-central atom for all <u>interior-$\vec{k}$</u> symmetry points; different $\mathfrak{L}$ character tables will be needed, in general, for each of the $\vec{k}$ points on the Brillouin zone boundary. In Appendix F we give the R point $\mathfrak{L}$ character table as an example (Table F-II); the phase factors used in constructing this table are given in Table F-III.

B. Prediction of Contained Functions Using the $\mathfrak{L}$ Characters.

We give three examples for the AB type simple tetragonal lattice using the tetragonal Λ group as the "reduced" or "new full group".

1. Γ point (center of the Brillouin zone). $\vec{k} = (\pi/2)(0/t, 0/t, 0/c)$. See Fig. 7. Since we are using the reduced symmetry the tetragonal Λ group applies. Table E-I of Appendix E may be used as the character table.

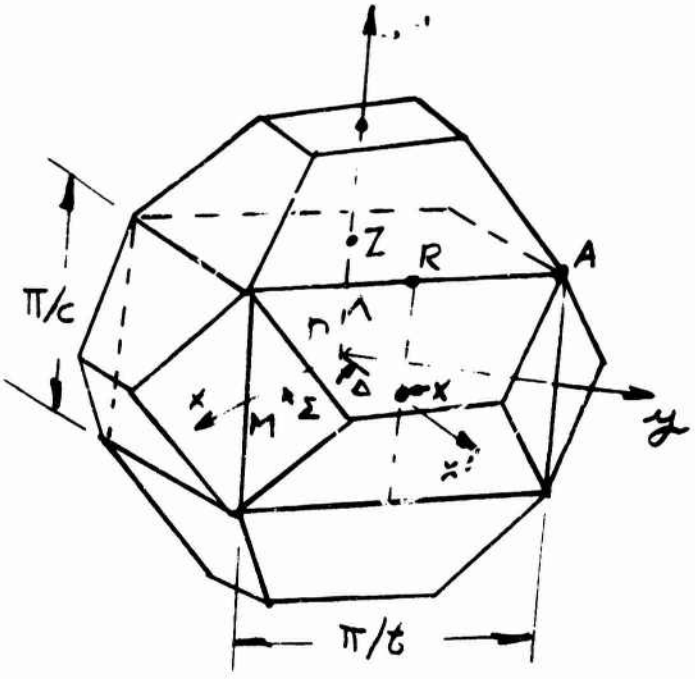


Figure 7. The first Brillouin zone for the simple tetragonal lattice. The first zone of the simple tetragonal resulting from a phonon peturbation of an fcc lattice is shown imbedded in the first Brillouin zone (the truncated octahedron) of the parent fcc lattice. The symmetry labels refer to the simple tetragonal Brillouin zone. The notation is that of Koster (ref. 6).

(a) Central atom: Using Table F-I (App. F), the tetragonal Λ character table (Table E-I), and eq. (12) one finds that:

Λ_1 contains $\ell = 0$

$\ell = 1$ (Λ_1)

$\ell = 2$ (Λ_1)

Λ_2 contains no a.l.f.'s

Λ_3 contains $\ell = 2$ (Λ_3)

Λ_4 contains $\ell = 2$ (Λ_4)

Λ_5 contains $\ell = 1$ (Λ_5)

$\ell = 2$ (Λ_5)

The label in parentheses refers to the "Λ breakdown" of Table F-I. The arrangement above satisfies eqs. (29) and (30). (Λ_5 is 2-dimensional; the other Λ representations are 1-dimensional.) Since we have defined our a.l.f.'s in terms of Λ labels (see Table E-III) the arrangement above was to be expected.

(b) Non-central atom: Since we are dealing with an interior-$\vec{k}$ point and since there is only one non-central atom, the same ℓ character table suffices for both central and non-central atoms (see Part I). The arrangement of contained a.l.f.'s for the non-central atom must, therefore, be identical to that above.

2. $\Delta(x)$ point (interior point). $\vec{k} = (\pi/2)(b/t, 0/t, 0/c)$, $0 < b < 1$. See Fig. 7. For the reduced symmetry scheme the group of

$\vec{k}$ for $\Delta(x')$ consists of that subgroup of the tetragonal Λ group for which the operators preserve $+x'$; this is the two-member group E $(x'y'z')$ and $JC_4^2(y')$ $(\bar{x}y'\bar{z}')$. The character table is given in Appendix E as Table E- IV.

(a) Central atom: Using the character table E- IV and the appropriate parts of the ℓ character table F-I, with eq. (12) one finds:

$\Delta(x')_1$ contains $\ell = 0$ (Λ_1)
$\ell = 1$ (Λ_1)
$\ell = 1$ (Λ_5)
$\ell = 2$ (Λ_1)
$\ell = 2$ (Λ_3)
$\ell = 2$ (Λ_5)

$\Delta(x')_2$ contains $\ell = 1$ (Λ_5)
$\ell = 2$ (Λ_4)
$\ell = 2$ (Λ_5)

It is readily seen that this satisfies eqs. (29) and (30).

(b) Non-central atom: As $\Delta(x')$ is an interior point the non-central atom will have the identical pattern of contained a.l.f.'s as the central atom.

3. R point (exterior point). $\vec{k} = (\pi/2)(1/t, 0/t, 1/c)$. See Fig. 7.

(a) Central atom: Using the R character table (Table E-V) and the appropriate parts of the ℓ character table (Table F-I) with eq. (12), we obtain:

R_1 contains $\ell = 0 \quad (\Lambda_1)$

$\ell = 1 \quad (\Lambda_1)$

$\ell = 2 \quad (\Lambda_1)$

$\ell = 2 \quad (\Lambda_3)$

R_2 contains $\ell = 2 \quad (\Lambda_4)$

R_3 contains $\ell = 1 \quad (\Lambda_5)$

$\ell = 2 \quad (\Lambda_5)$

R_4 contains $\ell = 1 \quad (\Lambda_5)$

$\ell = 2 \quad (\Lambda_5)$

This arrangement satisfies eqs. (29) and (30).

(b) Non-central atom: Since R is on the zone boundary, phase factors must be considered. The ℓ character table for R for the non-central atom is given in Table F-II. (The phase factors used in constructing this table are given in Table F-III.) Using the R character table (Table E-V) and Table F-II with eq. (25) we obtain:

R_1 contains $\ell = 1 \quad (\Lambda_5)$

$\ell = 2 \quad (\Lambda_5)$

R_2 contains $\ell = 1$ (Λ_5)

$\ell = 2$ (Λ_5)

R_3 contains $\ell = 0$ (Λ_1)

$\ell = 1$ (Λ_1)

$\ell = 2$ (Λ_1)

$\ell = 2$ (Λ_3)

R_4 contains $\ell = 2$ (Λ_4)

This arrangement satisfies eqs. (29) and (30). From the phase factors given in Table F-III one sees that in symmetrizing the a.l.f.'s (see eq. (33) and accompanying discussion) the product of the reduced symmetry R point character table (Table E-V) and the phase factors gives an "effective" R character table for the non-central atom in which R_1 is now like the original R_3, R_2 like R_4, R_3 like R_1, and R_4 like R_2 so that one would expect to get the arrangement above.

C. Working Out the Actual Unsymmetrized and Symmetrized A.L.F.'s.

In this section we list the explicit a.l.f.'s for the three reduced-symmetry, simple tetragonal examples of the previous section.

1. Γ point. $\vec{k} = (\pi/2)(0/t, 0/t, 0/c)$. The central atom and the non-central atom have the identical pattern of contained a.l.f.'s.

Λ_1 $\ell = 0$ $\quad 1 \rightarrow 1$

(the arrow means "symmetrizes to")

$\ell = 1$ $\quad z' \rightarrow z'$

$\ell = 2$ $\quad 2(z')^2 - (x')^2 - (y')^2 \rightarrow 2(z')^2 - (x')^2 - (y')^2$

Λ_2 no a.l.f.'s

Λ_3 $\ell = 2$ $(x')^2-(y')^2 \rightarrow (x')^2-(y')^2$

Λ_4 $\ell = 2$ $x'y' \rightarrow x'y'$

Λ_5 $\ell = 1$ (D_{11}) $x' \rightarrow x'$

$\ell = 2$ (D_{11}) $x'z' \rightarrow x'z'$

2. $\Delta(x')$ point. $\vec{k} = (\pi/2)(b/t,0/t,0/c)$, $0<b<1$. Central and non-central atoms will have identical lists.

$\Delta(x')_1$ $\ell = 0$ (Λ_1) $1 \rightarrow 1$

$\ell = 1$ (Λ_1) $z' \rightarrow z'$

$\ell = 1$ (Λ_5) $x' \rightarrow x'$

$\ell = 2$ (Λ_1) $2(z')^2-(x')^2-(y')^2 \rightarrow 2(z')^2-(x')^2-(y')^2$

$\ell = 2$ (Λ_3) $(x')^2-(y')^2 \rightarrow (x')^2-(y')^2$

$\ell = 2$ (Λ_5) $x'z' \rightarrow x'z'$

$\Delta(x')_2$ $\ell = 1$ (Λ_5) $y' \rightarrow y'$

$\ell = 2$ (Λ_4) $x'y' \rightarrow x'y'$

$\ell = 2$ (Λ_5) $y'z' \rightarrow y'z'$

3. R point. $\vec{k} = (\pi/2)(1/t,0/t,1/c)$.

(a) Central atom:

R_1 $\ell = 0$ (Λ_1) $1 \rightarrow 1$

$\ell = 1$ (Λ_1) $z' \rightarrow z'$

$\ell = 2$ (Λ_1) $2(z')^2-(x')^2-(y')^2 \rightarrow 2(z')^2-(x')^2-(y')^2$

$\ell = 2$ (Λ_3) $(x')^2-(y')^2 \rightarrow (x')^2-(y')^2$

R_2 $\ell = 2$ (Λ_4) $x'y' \rightarrow x'y'$

R_3 $\ell = 1$ (Λ_5) $x' \rightarrow x'$

$\ell = 2$ (Λ_5) $x'z' \rightarrow x'z'$

R_4 $\ell = 1$ (Λ_5) $y' \rightarrow y'$

$\ell = 2$ (Λ_5) $y'z' \rightarrow y'z'$

(b) Non-central atom: As noted in B.3.(b) above, R_1 for the non-central atom will be like R_3 of the central atom, R_2 like R_4, R_3 like R_1, and R_4 like R_2.

DETERMINATION OF ATOMIC-LIKE FUNCTIONS: INDIRECT PROCEDURE

Assuming the contained a.l.f.'s for the various representations in the unperturbed-lattice system to have been previously obtained, one can utilize compatibility relations to obtain the a.l.f.'s for the perturbed-lattice system; in some cases this may be easier than obtaining the perturbed-lattice a.l.f.'s directly. We will first develop the underlying mathematics and then apply the procedure to the three fcc to simple tetragonal examples of the previous section.

A. Mathematics.

Consider a set of functions $f_\mu^{(j)}(\vec{r})$ which transform by ("belong to") the $\mu^{\underline{th}}$ row of the $j^{\underline{th}}$ irreducible representation of a group as per eq. (2). Suppose we now form new functions $F_\mu(\vec{r})$ as linear combinations of the original $f_\mu^{(j)}(\vec{r})$:

$$F_\mu(\vec{r}) = \sum_{\nu=1}^{h_j} f_\nu^{(j)}(\vec{r})\, \alpha_{\nu\mu} \tag{41}$$

where h_j is the dimensionality of the $j^{\underline{th}}$ representation.

The coefficients $\alpha_{\nu\mu}$ form a matrix which we take to be unitary; thus

$$f_\nu^{(j)}(\vec{r}) = \sum_{\kappa=1}^{h_j} \alpha_{\nu\kappa}^{*}\, F_\kappa(\vec{r}). \tag{42}$$

Applying P_R to $F_\mu(\vec{r})$:

$$\begin{aligned} P_R F_\mu(\vec{r}) &= \sum_\nu^{h_j} \alpha_{\nu\mu}\, P_R\, f_\nu^{(j)}(\vec{r}) \\ &= \sum_{\nu,\rho}^{h_j} \alpha_{\nu\mu}\, f_\rho^{(j)}(\vec{r})\, D_{\rho\nu}^{(j)}(R) \quad \text{, using (2);} \\ &= \sum_{\nu,\rho,\kappa}^{h_j} \alpha_{\nu\mu}\alpha_{\rho\kappa}^{*}\, F_\kappa(\vec{r})\, D_{\rho\nu}^{(j)}(R) \quad \text{, using (42);} \\ &= \sum_\kappa^{h_j} F_\kappa(\vec{r}) \sum_{\nu,\rho}^{h_j} (\alpha^{-1})_{\kappa\rho}\, D_{\rho\nu}^{(j)}(R)\, \alpha_{\nu\mu} \\ P_R F_\mu(\vec{r}) &= \sum_\kappa^{h_j} F_\kappa(\vec{r}) \left(\alpha^{-1} D^{(j)}(R) \alpha\right)_{\kappa\mu} \end{aligned} \tag{43}$$

Comparing eqs. (2) and (43) we see that the $F_\mu(\vec{r})$ belong to the $\mu^{\underline{th}}$ row of the representation given by the matrices $\left(\alpha^{-1} D^{(j)}(R) \alpha\right)$.

If the $D^{(j)}(R)$ form an irreducible representation for $\mathcal{G}_{\vec{k}}$, the point group for a given $\vec{k}$ of the unperturbed lattice, then they also form a representation (possibly reducible) for that same $\vec{k}$ point in the perturbed lattice for those cases in which $G_{\vec{k}}$, the point group of $\vec{k}$ in the perturbed-lattice system, is a subgroup of $\mathcal{G}_{\vec{k}}$. Eqs. (41) and (43) then imply that if α brings $\alpha^{-1} D^{(j)}(R) \alpha$ to the

appropriate block form for all R in $G_{\vec{k}}$, and if the $f_{\nu}^{(j)}(\vec{r})$ are the symmetrized a.l.f.'s for $D^{(j)}$, then the $F_{\mu}(\vec{r})$ given by (41) will be the symmetrized a.l.f.'s for the various irreducible representations of $G_{\vec{k}}$ contained in $D^{(j)}$.

For 1-dimensional $D^{(j)}$ eq. (41) tells us that each symmetrized a.l.f. of $D^{(j)}$ will be a symmetrized a.l.f. of $D^{(a)}$ if $D^{(a)}$ is the perturbed-lattice representation compatible with $D^{(j)}(R)$. For multi-dimensional $D^{(j)}$ which are <u>already diagonal</u> for those R of $\mathcal{H}_{\vec{k}}$ which are members of $G_{\vec{k}}$, the α matrix will be $\overline{\overline{1}}$ and the a.l.f.'s for $D^{(a)}$ in G_k will be just those a.l.f.'s belonging to the row of $D^{(j)}$ compatible with $D^{(a)}$. If a multi-dimensional $D^{(j)}$ does not satisfy this diagonal condition it is necessary to determine the $\alpha_{\nu\mu}$ to use with eq. (41); in such cases it may be easier to determine the contained a.l.f.'s for $D^{(a)}$ directly.

In applying the indirect procedure to the fcc to simple tetragonal case one first notes from Figs. 6 and 7 that a choice between two coordinate systems must be made; one may wish to write all operators and functions in terms of the tetragonal $x'y'z'$ axes or to do the entire problem in terms of the original fcc xyz axes. We illustrate both methods using the three examples previously worked out via the direct procedure. In section B, below, we work in the tetragonal axes; in section C we work in the fcc axes.

B. Working in the Tetragonal Axes (x',y', z') - Correspondence Between fcc and Simple Tetragonal.

We first note that our point group for the "Γ" point of the perturbed lattice (labeled Λ in the "reduced" symmetry) is essentially the $\Delta(z)$ group of fcc; thus, we should be able to obtain the contained a.l.f.'s for the various Λ representations from the a.l.f.'s for the various $\Delta(z)$ fcc representations (for $\Delta(z)$, an fcc crystal with one atom per primitive cell will have the same contained a.l.f.'s as the central atom of simple cubic Cu_3Au so we may utilize the $\Delta(z)$ example of D.1.(a) of Part I.). Because the tetragonal x', y' axes are rotated 45° from the x,y axes of fcc (see Figs. 6 and 7) we must be particularly careful with the JC_4^2 and JC_2 operations; taking the $+x'$ axis of the tetragonal system as lying between the +x and +y fcc axes as per Fig. 6 we have the correspondence given in Table I. The correspondence between functions in the two systems is

Table I

Operator Correspondence, fcc - "Reduced" Simple Tetragonal

fcc	$JC_4^2(x)$	$JC_4^2(y)$	$JC_2(\bar{y}\bar{x}z)$	$JC_2(yxz)$
tetrag.	$JC_2(y'x'z')$	$JC_2(\bar{y}'\bar{x}'z')$	$JC_4^2(x')$	$JC_4^2(y')$

given in Table II.

Table II

Function Correspondence, fcc Axes - Tetragonal Axes

fcc	tetragonal
1	1
x	$(1/\sqrt{2})(x'-y')$
y	$(1/\sqrt{2})(x'+y')$
z	z'
$2z^2-x^2-y^2$	$2(z')^2-(x')^2-(y')^2$
x^2-y^2	$-2x'y'$
yz	$(1/\sqrt{2})z'(x'+y')$
xz	$(1/\sqrt{2})z'(x'-y')$
xy	$(1/2)[(x')^2-(y')^2]$

2. Γ point. $\vec{k} = (\pi/2)(0/t,0/t,0/c)$.

(a) Using Tables I and II, above: The fcc $\Delta(z)$ character table is given by Table B-III; the simple tetragonal Λ character table by Table E-I. Using Table I the compatibility relations are given by Table III. To find the list of contained symmetrized a.l.f.'s for Λ_3,

Table III

Compatibility, fcc $\Delta(z)$ - Simple Tetragonal Λ

(Using the operator correspondence of Table I)

fcc	Δ_1	Δ_2	$\Delta_{1'}$	$\Delta_{2'}$	Δ_5
tetrag.	Λ_1	Λ_4	Λ_2	Λ_3	Λ_5

eg., we note from D.1.(a) of Part I that the $\Delta_{2'}$ a.l.f. for fcc (or central-atom, simple cubic) is xy; from Table II this will be $(x')^2-(y')^2$ in the tetragonal axes system. (We ignore the multiplying factor.) Proceeding similarly we may rapidly write down the Λ_1, Λ_2, and Λ_4 a.l.f.'s. Λ_5 is 2-dimensional and is slightly more involved; comparing Tables B-IV and E-II and keeping the correspondence of Table I in mind, we see that the Δ_5 D's are not identical to those of Λ_5 for all R. The α matrix to transform the Δ_5 D's into the Λ_5 D's via $\alpha^{-1}D\alpha$ is

$$\overline{\overline{\alpha}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & \bar{1} \\ 1 & 1 \end{pmatrix}. \qquad (44)$$

From D.1.(a) of Part I, the D_{11} a.l.f.'s of Δ_5 are x and xz. (The D_{22} a.l.f.'s are y and yz.) Substituting into eq. (41) gives

$$\frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y = \frac{x+y}{\sqrt{2}}$$

for one of the D_{11} Λ_5 a.l.f.'s and $(1/\sqrt{2})z(x+y)$ for the other. Putting these into the $x'y'z'$ system via Table II gives x' and $z'x'$ respectively. (The D_{22} Λ_5 a.l.f.'s will be y' and $z'y'$.) Thus we obtain the same contained a.l.f. pattern as via the direct procedure (Section C.1., above).

(b) An easier method for this example: From Tables B-III, IV and E-I, II we see that $\Delta(z)$ of fcc has the same relationship to the fcc xyz axes as Λ of simple tetragonal has to the $x'y'z'$ axes; thus Λ_1 "corresponds" to Δ_1, Λ_2 to $\Delta_{1'}$, Λ_3 to Δ_2, Λ_4 to $\Delta_{2'}$, and Λ_5 to Δ_5 (with D_{11} of Λ_5 corresponding exactly to D_{11} of Δ_5).

Then, since the Δ_2 a.l.f. eg., is x^2-y^2 (see Section D.1.(a) of Part I), the a.l.f. for Λ_3 will be $(x')^2-(y')^2$. Again, this will be seen to agree with section C.1. of the direct procedure. This method avoids finding an α matrix for Λ_5 and does not require the function transformation of Table II.

2. $\Delta(x')$ point. $\vec{k} = (\pi/2)(b/t,0/t,0/c)$ ($x'y'z'$ axes) $0<b<1$. This is a Σ point of fcc (see Fig. 7). Using Table I, above, the E and $JC_4^2(y')$ operators of $\Delta(x')$ for the reduced simple tetragonal correspond respectively to E and $JC_2(yxz)$ of fcc. Using this operator correspondence and the appropriate character tables (Tables B-V and E-IV) we obtain the compatibility given in Table IV. We may obtain the list of contained symmetrized atomic-like functions for $\Delta(x')_1$,

Table IV

Compatibility, fcc Σ - Reduced Simple Tetragonal $\Delta(x')$

(Using the operator correspondence of Table I)

fcc	Σ_1	Σ_2	Σ_3	Σ_4
tetrag.	$\Delta(x')_1$	$\Delta(x')_2$	$\Delta(x')_1$	$\Delta(x')_2$

eg., from the symmetrized Σ_1 and Σ_3 fcc lists by changing the xyz functions of Σ_1 and Σ_3 to x', y', z' functions as per Table II; this will give the same a.l.f.'s as obtained in section C.2., above, using the direct procedure (the Σ fcc a.l.f.'s are given in Table B-VI of Appendix B.)

3. R point. $\vec{k} = (\pi/2)(1/t,0/t,1/c)$ ($x'y'z'$ axes). This is an L point of fcc (see Fig. 7). Comparision of the R point character

table (Table E-V, App. E) with the fcc L point character table (Table B-IX, App. B) shows that the R point group is not a subgroup of the L point group; thus the $D^{(j)}$ of eq. (43) do not form a representation for the R point. For such cases it is generally easier to obtain the contained a.l.f.'s via the direct procedure; for the example chosen, however, the R point of the reduced simple tetragonal has the same relationship to the tetragonal $x'y'z'$ axes as the Z point of fcc (at $\vec{k} = (2\pi/a)(10b)$ in the xyz axes) has to the xyz axes of fcc. Since the two point groups are identical (compare Tables B-VII and E-V) we may take the central-atom R_1 a.l.f.'s from the Z_1 fcc a.l.f.'s of Table B-VIII, R_2 from Z_2, R_3 from Z_3, and R_4 from Z_4. This agrees with the a.l.f. pattern obtained in section C.3.(a), above, using the direct procedure. Once the central-atom R-point a.l.f.'s have been obtained, the non-central a.l.f.'s may be obtained from them just as in the direct procedure (assuming that the phase factors of Table F-III are known).

C. Working in the Original fcc xyz Axes.

If one has already set up the E^0 calculation in terms of the fcc axes, it is probably most suitable to define the simple tetragonal in terms of the fcc axes. In the perturbation one is, after all, interested mainly in how the various fcc levels shift; it is not particularly important how one labels the tetragonal (perturbed-lattice) representations as long as one is consistent. We illustrate this procedure with the same three examples previously used.

1. Γ point: One may simply label the reduced simple tetragonal

Γ-point representations as Δ_1, Δ_2, etc. of fcc. From Section D.1.(a) of Part I the Δ_2' a.l.f., eg., is xy; then xy is to be used with the "Δ_2" representation of the Γ-point with the group operators all defined in terms of the original fcc axes. From the fcc Γ-Δ compatibility table (Table G-I, App. G) one sees that Δ_1 will give the Γ_1, Γ_{12}, and Γ_{15} levels, Δ_2' will give the Γ_2', Γ_{12}', and Γ_{25}' levels, etc. This method requires no α matrices, no transforming of x,y,z functions to x′,y′, z′ functions, and no relabeling of the group operators.

2. $\Delta(x')$: In the $x'y'z'$ system $\vec{k} = (\pi/2)(b/t,0/t,0/c)$, $0<b<1$; in the xyz system $\vec{k} = (2\pi/a)(b/2,b/2,0)$. The $\Delta(x')$ operators of Table E-IV, App. E, will now be labeled E and $JC_2(yxz)$ using the fcc axes. The two representations may conveniently be labeled as $\Sigma_{(+)}$ and $\Sigma_{(-)}$. Comparing Table E-IV with Table B-V, App. B, we see that the $\Sigma_{(+)}$ a.l.f.'s may be taken directly from Σ_1 and Σ_3 of fcc (see Table B-VI) and the $\Sigma_{(-)}$ a.l.f.'s from Σ_2 and Σ_4; no x,y,z to x′,y′,z′ transformation is needed.

3. R point: In the $x'y'z'$ system $\vec{k} = (\pi/2(1/t,0/t,1/c)$; in the xyz system $\vec{k} = (2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. To work in terms of the fcc axes the most straightforward procedure would be to label the four operators of the R point (Table B-V) in terms of the fcc axes (they would then be E, $C_4^2(z)$, $JC_2(\bar{y}\bar{x}z)$, and $JC_2(yxz)$ respectively) and proceed as in Part I. To use the indirect procedure is quite tedious; for this particular case, one could obtain the contained functions from fcc Z as in B,3, and then transform these functions to the fcc axes using Table II. The R_2 central-atom a.l.f., eg., would be x^2-y^2.

DETERMINATION OF PLANE WAVES: DIRECT PROCEDURE

One proceeds exactly as in Part I. For the simple tetragonal lattice the allowed $\vec{K}$'s are given by

$$\vec{K} = \pi(b/t, d/t, f/c) \tag{45}$$

in the tetragonal axes system with b,d,f any integers. At the Γ point, the allowed $\vec{K}$ types for the "reduced" simple tetragonal representations (defined as per Table E-I, II) are given in Table V. (The notation of Part I is used.) For the reduced simple tetragonal

Table V

Allowed K Types, Reduced Simple Tetragonal

(Components given in the tetragonal axes system)

Λ_1	Λ_2	Λ_3	Λ_4	Λ_5 (D_{11})	
00f	bdf	0bf	bbf	b0f	
0bf		bdf	bdf	bbf	
bbf				bdf }	both must be included
bdf				dbf }	

Table V is valid for any $\vec{k}$ value on the Λ axis (see Fig. 7), i.e., $\vec{k} = (\pi/2)(0/t, 0/t, h/c)$, $0 \leq h \leq 1$. Since the z′ "slot" is an invariant for the Λ group the combination bdf, eg., implies that bd0, bd$\bar{b}$, bdb, bd$\bar{d}$, bdd, bd$\bar{f}$, bdf are all allowed. For the 1-dimensional representations the combinations bdf, $\bar{b}$df, dbf, etc. will all symmetrize to $\pm$ the same function so only one of these should be included. In ordering these plane waves it must be remembered that the z′ slot has a different magnitude than x′ or y′. For the reduced-symmetry simple

tetragonal whose "parent" fcc lattice has cube side equal to a,

$$t = a/(2\sqrt{2}), \qquad c = a/2, \tag{46}$$

so that eq. (45) may be written (still in $x'y'z'$ axes)

$$\vec{K} = (2\pi/a)(\sqrt{2}b, \sqrt{2}d, f) \tag{47}$$

As an example, we list the first few $\vec{K}$'s for Λ_3 (in $x'y'z'$ axes; the b,d,f values are given).

010, $01\bar{1}$, 011, $01\bar{2}$, 012, 020, $02\bar{1}$, 021, 120, etc.

DETERMINATION OF PLANE WAVES: INDIRECT PROCEDURE

A. Labeling in Terms of the Tetragonal Axes.

1. Γ point: Since $\Delta(z)$ of fcc has the same relationship to the fcc xyz axes as Λ of the reduced-symmetry simple tetragonal has to the tetragonal $x'y'z'$ axes, we may utilize the correspondence between Δ and Λ given in section B.1.(b), above, for the a.l.f.'s; the Λ_1 plane waves are then obtained from the Δ_1 list, Λ_2 from Δ_1', Λ_3 from Δ_2, etc. Since the fcc $\vec{K}$'s are restricted to all-odd or all-even components, whereas the simple tetragonal $\vec{K}$'s have no such restriction, one must supplement the fcc lists. (If simple cubic $\Delta(z)$ lists are available no such supplementing is necessary.) This procedure must, of course, lead to the same $\vec{K}$'s as given by the direct procedure, above. (Compare the Λ_3 list of the previous section with the simple cubic Δ_2 list given in Part I; except for changes in ordering these are identical.)

2. $\Delta(x')$: Using the operator correspondence of Table I and the associated Σ fcc (or simple cubic) $-\Delta(x')$ compatibility (Table IV) one may generate the $\Delta(x')_1$ plane waves from the Σ_1 and Σ_3 simple

cubic lists and the $\Delta(x')_2$ plane waves from the Σ_2 and Σ_4 lists using the x,y to x′,y′ transformations of Table II. Comparing the expression for allowed simple cubic $\vec{K}$'s (i.e., $(\vec{K} = (2\pi/a)(\ell mn)$ (xyz axes) with ℓ,m,n any integers) with eq. (47) and using Table II we see that

$$b = \frac{\ell + m}{2}, \qquad d = \frac{m - \ell}{2} \tag{48}$$

so that only those simple cubic $\vec{K}$'s with ℓ,m both even or both odd may be used. This is a quite tedious process and it is probably easier to generate the $\Delta(x')$ plane wave lists directly.

3. R point: $\vec{k} = (\pi/2)(1/t, 0/t, 1/c)$ ($x'y'z'$ axes). Since this R point of the simple tetragonal has the same relationship to the tetragonal $x'y'z'$ axes as the simple cubic Z point (at $\vec{k} = (2\pi/a)(\frac{1}{2}0h)$ with h = 1/2) has to the cubic xyz axes, we may take the R_1 plane wave b,d,f values directly from the simple cubic Z_1 list, R_2 from Z_2, R_3 from Z_3, and R_4 from Z_4. The allowed $\vec{K}$ types for R_2, eg., are 0bf, bbf, bdf, dbf with f equal to $0, \bar{b}, b, \bar{d}, d, \bar{f}, f$ (These are the b,d,f of eq. (45) or (47).)

B. Labeling in Terms of the fcc Axes.

The idea here is the same as that expressed in Section C of the indirect a,l,f, procedure, above; namely, we define the tetragonal lattice in terms of the original fcc xyz axes.

1. Γ point: The Δ_1 fcc plane wave list may be used as is for Δ_1, the Δ_2 list for Δ_2, etc. These lists will be valid for any point on the simple tetragonal Λ axis, i.e., for $\vec{k} = (2\pi/a)(00b)$ in the xyz system, $0 \leqslant b \leqslant 1/2$.

2. $\Delta(x')$ point: In the tetragonal axes, $\vec{k} = (\pi/2)\,(b/t, 0/t, 0/t)$, $0 < b < 1$; in the xyz system, $\vec{k} = (2\pi/a)\,(b/2, b/2, 0)$. Working in the fcc axes we may construct the $\Sigma_{(+)}$ plane wave list from the fcc Σ_1 and Σ_3 lists; the $\Sigma_{(-)}$ list from Σ_2 and Σ_4 of fcc.

3. R point: As in determining the contained a.l.f.'s the most straight forward procedure is to write the four R-point operators in terms of the fcc axes and work out the contained plane waves directly.

USE OF COMPATIBILITY TO MATCH UNPERTURBED-LATTICE AND PERTURBED-LATTICE ENERGY LEVELS

In many cases one is interested in comparing the unperturbed energy levels determined by using the reduced symmetry scheme with the corresponding levels of the parent lattice. In almost all cases one is interested in matching the energy shifts to the proper unperturbed level. The key to this matching is compatibility.

A. THE CONCEPT OF FOLDING.

In real space the simple tetragonal primitive cell is twice as large as the parent fcc primitive cell (since the new lattice has <u>two</u> atoms per primitive cell whereas the original fcc lattice has only one atom per primitive cell). This implies that the simple tetragonal reciprocal space Brillouin zone has only <u>one-half</u> the volume of the parent fcc Brillouin zone. Some of the $\vec{k}$ points of the simple tetragonal Brillouin zone will then correspond to <u>more than one</u> $\vec{k}$ point of the original fcc (see Fig. 7). For example, Γ-point levels of simple tetragonal (labeled Λ in the "reduced" scheme) correspond to both Γ and X(z) levels of fcc.

A $\vec{k}$ point on the Λ axis of simple tetragonal at, say, $\vec{k} = (\pi/2)(00\frac{7}{8c})$ corresponds to both $\vec{k} = (2\pi/a)(00\frac{7}{16})$ and $\vec{k} = (2\pi/a)(00\frac{9}{16})$ of fcc; i.e., the Γ to X(z) axis of fcc is "folded" in half.

B. EXAMPLES USING TETRAGONAL LABELING.

1. Γ point. Compatibility is used to determine which Λ representation of the reduced simple tetragonal corresponds to which Γ and which X(z) representations of fcc. Since the Λ group of reduced simple tetragonal is a subgroup of Γ fcc and of X(z) fcc, the procedure is quite straightforward. Using the Λ simple tetragonal to Δ fcc compatibility (Table III) and the fcc Δ-Γ compatibility (Table G-I, App. G) we construct Table VI. (Λ is defined by Table E-I, Γ by Table B-I.)

TABLE VI

Compatibility, fcc Γ - Simple Tetragonal Λ
(Using the operator correspondence of Table I)

fcc levels for	show up on
Γ_1	Λ_1
Γ_{12}	Λ_1, Λ_4
Γ_{15}	Λ_1, Λ_5
$\Gamma_{25'}$	Λ_3, Λ_5

Using Table III with the fcc Δ-X compatibility (Table G-III, App. G) we construct Table VII. (X is defined by Table B-X.)

TABLE VII

Compatibility, fcc X(z) - Simple Tetragonal Λ
(Using the operator correspondence of Table I)

fcc levels for	show up on
X_1	Λ_1
X_2	Λ_4
X_3	Λ_3
$X_{4'}$	Λ_1
X_5	Λ_5
$X_{5'}$	Λ_5

2. Λ point of simple tetragonal at $\hat{k} = (\pi/2)(0/t, 0/t, b/c)$ ($x'y'z'$ axes), $0 < b < 1$. This corresponds to both $\hat{k} = (2\pi/a)(0,0,b/2)$ and $\hat{k} = (2\pi/a)(0,0,1-b/2)$ of fcc (xyz axes). The Δ levels of fcc will show up on the Λ representations as per Table III.

C. EXAMPLES USING THE FCC AXES IN ALL LABELING.

1. Λ axis of simple tetragonal: (See section C.1. of the indirect procedure for determining the a.l.f.'s.) When the reduced simple tetragonal "Γ" group is labeled by the Δ representations of fcc, the fcc Γ-Δ compatibility (Table G-I, App. G) suffices to determine which Δ representations will give which fcc Γ levels; the fcc X-Δ compatibility (Table G-III, App. G) suffices for the fcc X levels. The Δ-Δ correspondence is trivial.

2. $\Delta(x')$ of the reduced simple tetragonal: (See section C.2. of the indirect a.1.f. procedure.) The $\Delta(x')$ point at $\vec{k} = (\pi/2)(b/t,0/t,0/c)$ ($x'y'z'$ axes) is $\vec{k} = (2\pi/a)(b/2,b/2,0)$ in the fcc xyz axes. For $0 < b \leq 1/2$, the $\Delta(x')$ point of reduced simple tetragonal corresponds to fcc Σ and fcc S ($\vec{k} = (2\pi/a)(b/2,b/2,1)$ running from X(z) to U). For $\frac{1}{2} \leq b < 1$, the $\Delta(x')$ point corresponds both to fcc Σ at $(2\pi/a)(b/2,b/2,0)$ and to fcc Σ at $(2\pi/a)(1-b/2,1-b/2,0)$; i.e., the fcc Σ axis from (1/4,1/4,0) to K at (3/4,3/4,0) is "folded" onto the $\Delta(x')$ axis from $1/2 < b < 1$. Compatibility is given in Table VIII.

TABLE VIII
COMPATIBILITY, fcc Σ,S - REDUCED SIMPLE TETRAGONAL $\Delta(x')$
(All labeling in terms of the original fcc axes)

fcc levels for	show up on
Σ_1 , S_1	$\Sigma_{(+)}$
Σ_2, S_2	$\Sigma_{(-)}$
Σ_3, S_3	$\Sigma_{(+)}$
Σ_4, S_4	$\Sigma_{(-)}$

3. R point of simple tetragonal at $\vec{k} = (\pi/2)(1/t,0/t,1/c)$. This is an L point of fcc. Neither group is a subgroup of the other so we proceed somewhat differently from the previous examples. The most straightforward procedure is to utilize the space groups associated with the R point of the reduced simple tetragonal (rst) and with the L point of fcc. One may also use the Γ(fcc)-R(rst) compatibility (Table IX) with the Γ-L compatibility (Table G-IV). The resultant correspondence is given in Table X.

TABLE IX

Compatibility, Γ(fc - R(red. simple tet.)

Γ(fcc)	R(red. simple tet.)
Γ_1	R_1
Γ_2	R_2
Γ_{12}	R_1, R_2
$\Gamma_{15'}$	R_2, R_3, R_4
$\Gamma_{25'}$	R_1, R_3, R_4
$\Gamma_{1'}$	R_2
$\Gamma_{2'}$	R_1
$\Gamma_{12'}$	R_2, R_1
Γ_{15}	R_1, R_3, R_4
Γ_{25}	R_2, R_3, R_4

TABLE X

Compatibility, fcc L - Reduced Simple Tetragonal R

fcc levels for	show up on
L_1	R_1, R_3
L_2	R_2, R_4
$L_{1'}$	R_2, R_4
$L_{2'}$	R_1, R_3
L_3	all R
$L_{3'}$	all R

COMMENTS ON PRESSURE PERTURBATION

There is a fundamental difference in the type of lattice-symmetry change due to a phonon perturbation as discussed in this report and the symmetry change due to a pressure perturbation. In a phonon perturbation the difference in motion of the atoms causes a change in the number of atoms per primitive cell; for many pressure perturbations the new symmetry will still have the same number of atoms per primitive cell as in the parent lattice.

For the phonon perturbation discussed in this report, fcc to tetragonal, we go from fcc with one atom per primitive cell to simple tetragonal with two atoms per primitive cell (See Fig. 6). This causes the Brillouin zone (B.Z.) of the new symmetry to be one-half the volume of the original B.Z. (see Fig. 7) resulting in the "folding" as discussed above. (For the bcc lattice of Fig. 5 one would go from bcc to simple cubic, again introducing folding.)

As an example of a pressure perturbation, consider fcc under a tetragonal strain. The new lattice would be tetragonal as per Fig. 6 but now both "center" atom and "corner" atoms are still identical so that the new lattice would be body-centered tetragonal with one atom per primitive cell. The B. Z. of this bct (before the perturbation is applied) will be identical with the fcc B. Z. Under small strain the perturbed B.Z. will depart only slightly from the original truncated-octahedron B.Z.; there would be no "folding".

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APPENDIX A

"TRIADS" FOR THE CUBIC GROUP OPERATORS

In Table A-I we list the cubic group triads. These triads are consistent with Table II of ref. 4. These triads are also valid for the tetragonal and trigonal systems (for the appropriate operators).

The triad $(\bar{y},x,z)$ associated with R implies that $P_R f(x',y',z') = f(\bar{y}',x',z')$ and that $x=-y'$, $y=x'$, $z=z'$ in $P_R f(x',y',z') = f(x,y,z)$ with $x_i = \Sigma_k R_{ki} x'_k$, i.e., $\vec{r}=R^{-1}\vec{r}'$. See the discussion in the main text associated with eqs. (14) - (16).

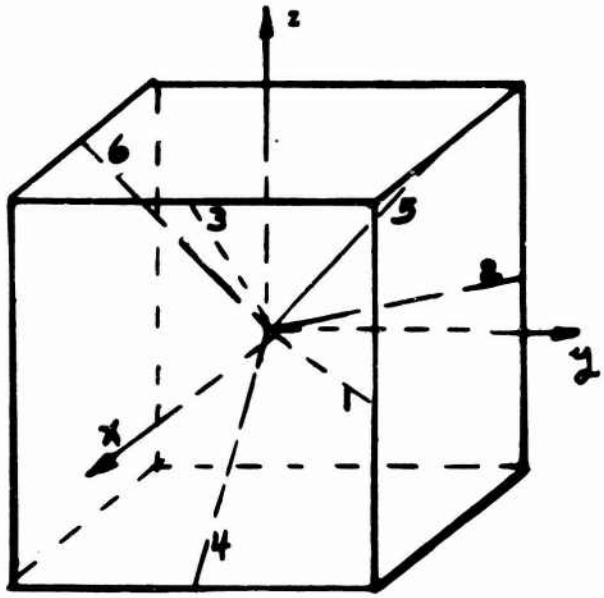
Table A-I

Triads for the Cubic Group Operators

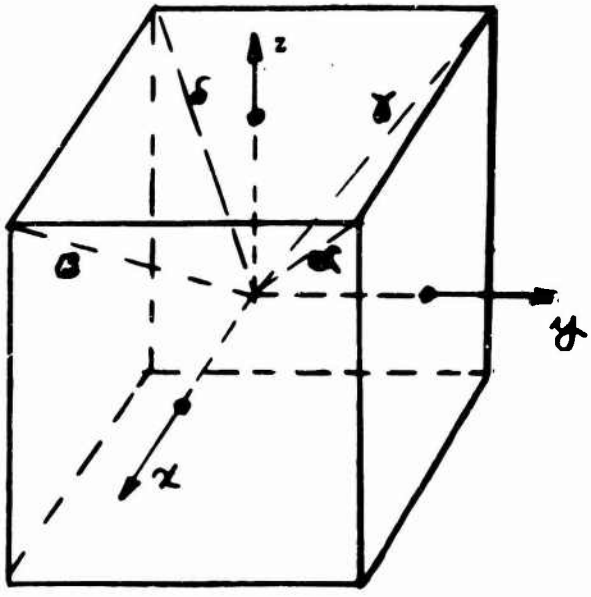
The 24 triads for the proper rotations of the full cubic group are given explicitly. The numbering is such that the number for JR is n+24 where n is the number for R. To obtain the triad for JR simply take the negative of the triad for the corresponding R. Thus the triad for #35 is $(\bar{y},\bar{x},z)$. The C_2 rotation axes are shown in Fig. 8a, those for C_3 in Fig. 8b.

Number	BSW Symbol (ref. 5)	Triad
1	$\bar{E}$	(x,y,z)
2	$C_4^2(z)$	$(\bar{x},\bar{y},z)$
3	$C_4^2(x)$	$(x,\bar{y},\bar{z})$
4	$C_4^2(y)$	$(\bar{x},y,\bar{z})$
5	$C_4(z)$	$(\bar{y},x,z)$
6	$C_4(z)$	$(y,\bar{x},z)$

Number	BSN Symbol (ref. 5)	Triad
7	$C_4(x)$	$(x,\bar{z},y)$
8	$C_4(x)$	$(x,z,\bar{y})$
9	$C_4(y)$	$(z,y,\bar{x})$
10	$C_4(y)$	$(\bar{z},y,x)$
11	$C_2(1)$	$(y,x,\bar{z})$
12	$C_2(3)$	$(z,\bar{y},x)$
13	$C_2(5)$	$(\bar{x},z,y)$
14	$C_2(2)$	$(\bar{y},\bar{x},\bar{z})$
15	$C_2(4)$	$(\bar{z},\bar{y},\bar{x})$
16	$C_2(6)$	$(\bar{x},\bar{z},\bar{y})$
17	$C_3(\alpha)$	(z,x,y)
18	$C_3(\alpha)$	(y,z,x)
19	$C_3(\beta)$	$(z,\bar{x},\bar{y})$
20	$C_3(\beta)$	$(\bar{y},\bar{z},x)$
21	$C_3(\gamma)$	$(\bar{z},\bar{x},y)$
22	$C_3(\gamma)$	$(\bar{y},z,\bar{x})$
23	$C_3(\delta)$	$(\bar{z},x,\bar{y})$
24	$C_3(\delta)$	$(y,\bar{z},\bar{x})$



(a) Rotation axes for the C_2 operators (see Table A-I).



(b) Rotation axes for the C_3 operators (see Table A-I).

Figure 8. Axes for the Cubic Rotations.

APPENDIX B

SELECTED CHARACTER TABLES FOR THE CUBIC SYSTEM

The representation labels and class labels in all Tables in App. B are those of BSW (ref. 5). The number in front of the BSW class symbol gives the number of members in the class.

Table B-I is valid for the Γ point of simple cubic, fcc, and bcc and also for the R point of simple cubic and the H point of bcc.

Table B-I

Character Table, Cubic Γ

Characters for the 24 proper rotations are given explicitly. For the first five representations listed, the characters for the J operators are identical to the corresponding non-J characters; for the last five representations, the characters for the J operators are (-1) times the corresponding non-J characters

	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$
Γ_1	1	1	1	1	1
Γ_2	1	1	-1	-1	1
Γ_{12}	2	2	0	0	-1
$\Gamma_{15'}$	3	-1	1	-1	0
$\Gamma_{25'}$	3	-1	-1	1	0
$\Gamma_{1'}$	1	1	1	1	1
$\Gamma_{2'}$	1	1	-1	-1	1
$\Gamma_{12'}$	2	2	0	0	-1
Γ_{15}	3	-1	1	-1	0
Γ_{25}	3	-1	-1	1	0

Koster's Table XXXI for O_h (ref. 6), Tinkham's Table (pg 70 of ref. 8), and Slater's Table A3-20 (ref. 9), all use the representation labeling of BSW; class and operator notation differ somewhat from that used here (BSW C_4^2 is C_2 in Koster or Tinkham; BSW C_2 is Koster's C_2'). Care must be taken with the primes of Slater's Table A3-20; his unprimed operators are those of the tetrahedral group T_d (E, C_4^2, C_3, JC_4 and JC_2 in BSW notation).

Table B-II

Basis Functions (Cubic Harmonics) for $\ell = 0,1,2$ for the Cubic System

ℓ	Functions	Transform like
0	1	Γ_1
1	x y z	Γ_{15}
2	$2z^2-x^2-y^2$ x^2-y^2	Γ_{12}
2	yz xz xy	$\Gamma_{25'}$

Table B-III

Character Table, Cubic Δ (and Simple Cubic T)

	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
Δ_1	1	1	1	1	1
Δ_2	1	1	-1	1	-1
Δ_1'	1	1	1	-1	-1
Δ_2'	1	1	-1	-1	1
Δ_5	2	-2	0	0	0

For $\Delta(z)$ the operators are $E, C_4^2(z), 2C_4(z), JC_4^2(x), JC_4^2(y)$, and JC_2 about axes in the xy plane. In the numbering system of Table A-I these are 1,2,5,6,27,28,35, and 38. $\vec{k} = (2\pi/a)(00b)$; for simple cubic, $0 < b < \frac{1}{2}$; for fcc and bcc, $0 < b < 1$. For simple cubic T, $\vec{k} = (2\pi/a) \times (\frac{1}{2}\frac{1}{2}\, b)$, $0 < b < \frac{1}{2}$.

Koster's Table XII for C_{4v} (ref. 6) and Slater's Table A3-21 (ref. 9) use the BSW representation labeling. The class labels C_4^2, JC_4^2, JC_2 of Table B-III are C_2, σ_v, σ_d respectively, in Koster's notation.

TABLE B-IV

D Matrices for Δ_5 (and T_5) of Table B-III

$$E \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_4^2 \begin{bmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{bmatrix} \quad C_4 \begin{bmatrix} 0 & 1 \\ \bar{1} & 0 \end{bmatrix} \quad C_4 \begin{bmatrix} 0 & \bar{1} \\ 1 & 0 \end{bmatrix}$$

1 2 5 6

$$JC_4^2 \begin{bmatrix} \bar{1} & 0 \\ 0 & 1 \end{bmatrix} \quad JC_4^2 \begin{bmatrix} 1 & 0 \\ 0 & \bar{1} \end{bmatrix} \quad JC_2 \begin{bmatrix} 0 & \bar{1} \\ \bar{1} & 0 \end{bmatrix} \quad JC_2 \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

27 28 35 38

By cyclic permutation the Δ_5 D matrices in Slater's Table A3-21 are identical to these. (Slater's Δ point is on the x axis).

Table B-V

Character Table, Cubic Σ

	E	C_2	JC_4^2	JC_2
Σ_1	1	1	1	1
Σ_2	1	1	-1	-1
Σ_3	1	-1	-1	1
Σ_4	1	-1	1	-1

For Σ located as in Fig. 3, the four operators are numbers 1, 11, 26, 38 (see Table A-I). $\hat{k} = (2\pi/a)(bb0)$: For simple cubic and bcc, $0<b<\frac{1}{2}$; for fcc, $0<b<\frac{1}{4}$. The representation labeling is the same as Slater's Table A3-23 (ref. 9) and Koster's Table V for C_{2v} (ref. 6) if we interpret Koster's class labels σ_v, σ_v' as JC_2, JC_4^3 respectively.

Table B-VI

Contained A.L.F.'s for the Irreducible Representations of Cubic Σ for fcc Cu

the arrow means "symmetrizes to".

Σ_1

$1 \rightarrow 1$

$x \rightarrow (1/2)(x+y)$

$2z^2-x^2-y^2 \rightarrow 2z^2-x^2-y^2$

$xy \rightarrow xy$

Σ_2

$yz \rightarrow (1/2)(yz-xz)$

Σ_3

$z \rightarrow z$

$yz \rightarrow (1/2)(yz+xz)$

Σ_4

$y \rightarrow (1/2)(y-x)$

$x^2-y^2 \rightarrow x^2-y^2$

Table B-VII

Character Table, Simple Cubic and fcc Z

	E	C_4^2	JC_4^2	$JC_4^2(\frac{1}{4})$
Z_1	1	1	1	1
Z_2	1	1	-1	-1
Z_3	1	-1	-1	1
Z_4	1	-1	1	-1

For Z located as in Fig. 3, the four operators are numbers 1, 2, 27, 28 (see Table A-I). For simple cubic, $\vec{k} = (2\pi/a)(\frac{1}{2}0b)$, $0<b<\frac{1}{2}$; for fcc, $\vec{k} = (2\pi/a)(10b)$, $0<b<\frac{1}{2}$. The representation labeling is the same as in Slater's Table A3-27 (ref. 9); consistent with his location of Z (see his Fig. A3-2, pg 369), his R_1' is JC_4^2, his R_4' is $JC_4^3(1)$.

Table B-VIII

Contained A.L.F.'s for the Irreducible Representations of Cubic Z for fcc Cu

the arrow means "symmetrizes to".

Z_1 $\quad 1 \longrightarrow 1$

$z \longrightarrow z$

$2z^2-x^2-y^2 \longrightarrow 2z^2-x^2-y^2$

$x^2-y^2 \longrightarrow x^2-y^2$

Z_2 $\quad xy \longrightarrow xy$

Z_3 $\quad x \longrightarrow x$

$xz \longrightarrow xz$

Z_4 $\quad y \longrightarrow y$

$yz \longrightarrow yz$

Table B-IX

Character Table, fcc L

	E	$3C_2$	$2C_3$	J	$3JC_2$	$2JC_3$
L_1	1	1	1	1	1	1
L_2	1	-1	1	1	-1	1
L_3	2	0	-1	2	0	-1
L_1'	1	1	1	-1	-1	-1
L_2'	1	-1	1	-1	1	-1
L_3'	2	0	-1	-2	0	1

L points are located at the centers of the hexagonal faces of the truncated octahedron reciprocal space unit cell for fcc lattices. For L at $\vec{k} = (2\pi/a)(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$, the 12 operators are 1, 14, 15, 16, 17, 18 (non-J) and 25, 38, 39, 40, 41, 42 (J) in the numbering system of Table A-I. Slater's Table A3-26 (ref. 9) has the same representation labeling except that his L_4 is our L_3'. Koster's Table XIX for D_{3d} (ref. 6) has the BSW representation labeling except that Koster's L_1', L_2' are the BSW L_2', L_1' respectively. Koster's class labels C_2', I, σ_v, S_6 are the BSW C_2, J, JC_2, JC_3 respectively.

Table B-X

Character Table, Cubic X

Characters for the eight proper rotations are given explicitly. For the first five representations listed, the characters for the J operators are identical to the corresponding non-J characters; for the last five representations, the characters for the J operators are (-1) times the corresponding non-J characters.

	E	$C_4^2(11)$	$2C_4^2(\bar{1}1)$	$2C_4$	$2C_2$
X_1	1	1	1	1	1
X_2	1	1	1	-1	-1
X_3	1	1	-1	-1	1
X_4	1	1	-1	1	-1
X_5	2	-2	0	0	0
$X_{1'}$	1	1	1	1	1
$X_{2'}$	1	1	1	-1	-1
$X_{3'}$	1	1	-1	-1	1
$X_{4'}$	1	1	-1	1	-1
$X_{5'}$	2	-2	0	0	0

APPENDIX C

SELECTED ℓ CHARACTER TABLES FOR THE CUBIC SYSTEM

For explanation and use of these tables see Part I of the main text. The representation labels and class labels in all tables in App. C are those of BSW (ref. 5). The number in front of the class labels in Tables C-III and C-VI gives the number of members in the class. No such number is given in Tables C-I and C-II as this number will depend on the $\vec{k}$ point being considered. In Tables C-IV, C-V, and C-VII the individual operators are listed.

Table C-I

ℓ Character Table, Cubic System, for Central Atom, All $\vec{k}$ Points

For the central atom, these characters (including the ℓ=2,3 breakdowns) may be used for $\chi^{\ell}(R)$ in eq. (12) of the main text for all $\vec{k}$ points. The appropriate operators for the group of $\vec{k}$ are to be selected.

	E	C_4^2	C_4	C_2	C_3	J	JC_4^2	JC_4	JC_2	JC_3	
ℓ=0	1	1	1	1	1	1	1	1	1	1	(Γ_1)
ℓ=1	3	-1	1	-1	0	-3	1	-1	1	0	(Γ_{15})
ℓ=2	5	1	-1	1	-1	5	1	-1	1	-1	
ℓ=3	7	-1	-1	-1	1	-7	1	1	1	-1	

The ℓ=0 and ℓ=1 representations are irreducible for the cubic Γ point (they are equivalent to Γ_1, and Γ_{15} respectively. The ℓ=2 and ℓ=3 representations are reducible; their breakdown into irreducible representations is given below.

	E	C_4^2	C_4	C_2	C_3	J	JC_4^2	JC_4	JC_2	JC_3	
ℓ=2	2	2	0	0	-1	2	2	0	0	-1	(Γ_{12})
	3	-1	-1	1	0	3	-1	-1	1	0	($\Gamma_{25'}$)

	E	C_4^2	C_4	C_2	C_3	J	JC_4^2	JC_4	JC_2	JC_3	
$\ell=3$	1	1	-1	-1	1	-1	-1	1	1	-1	($\Gamma_{2'}$)
	3	-1	1	-1	0	-3	1	-1	1	0	(Γ_{15})
	3	-1	-1	1	0	-3	1	1	-1	0	(Γ_{25})

Table C-II

ℓ Character Table, Cu_3Au, for the Non-Central Atoms, All Interior $\vec{k}$ Points

By confining oneself to the operators appropriate to the $\vec{k}$ point in question these characters may be used for $\chi^{\ell}_{nc}(R)$ in eq. (25) of the main text for all interior $\vec{k}$ points. (For $\vec{k}$ points on the zone boundary, phase factors are involved.)

	E	C_4^2	C_4	C_2	C_3	J	JC_4^2	JC_4	JC_2	JC_3	
$\ell=0$	3	3	1	1	0	3	3	1	1	0	(Γ_1)
$\ell=1$	9	-3	1	-1	0	-9	3	-1	1	0	(Γ_{15})
$\ell=2$	15	3	-1	1	0	15	3	-1	1	0	

The decomposed $\ell=2$ characters are as follows:

$\ell=2$	6	6	0	0	0	6	6	0	0	0	(Γ_{12})
	9	-3	-1	1	0	9	-3	-1	1	0	($\Gamma_{25'}$)

Note: Table C-II is not just 3x (Table C-I) because not all non-central sites go into themselves (or equivalent sites) under every operation. The operators E, C_4^2, J, and JC_4^2 take all three non-central sites of the Cu_3Au structure into themselves; C_4, C_2, JC_4, and JC_2 each take only one non-central site into itself; C_3 and JC_3 take no non-central site into itself.

Table C-III

ℓ Character Table for the Non-central Atoms, T Point of Cu_3Au.

For the Cu_3Au structure, these characters are to be used for $\chi^{\ell,T}_{nc}(R)$ in eq. (25) of the main text. For T at $\vec{k} = (2\pi/a)(\frac{1}{2}, \frac{1}{2}, b)$, $0 < b < \frac{1}{2}$, in Fig. 3, the eight operators are 1, 2, 5, 6, 27, 28, 35, 38 in the numbering system of Table A-I.

	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$	
$\ell=0$	3	-1	-1	-1	1	(Γ_1)
$\ell=1$	9	1	-1	-1	1	(Γ_{15})
$\ell=2$	6	-2	0	-2	0	(Γ_{12})
	9	1	1	1	1	$(\Gamma_{25'})$

Table C-IV

Phase Factors in the Construction of Table C-III

The factors listed under each operator R for each site s_ν (at left) are $\exp[i\hat{k}\cdot(R\vec{s}_\nu - \vec{s}_\nu)]$ of eq. (26) of the main text for the $\hat{k}$ of Table C-III. Site locations are given in Fig. 1. A zero entry indicates that $R\vec{s}_\nu$ is not an equivalent site to $\vec{s}_\nu$. The bottom row gives the summation involved in eq. (26).

	E	$C_4^2(z)$	C_4	C_4	$JC_4^2(x)$	$JC_4^2(y)$	JC_2	JC_2
	1*	2	5	6	27	28	35	38
s_2	1	1	-1	-1	-1	-1	1	1
s_3	1	-1	0	0	-1	1	0	0
s_4	1	-1	0	0	1	-1	0	0
sum	3	-1	-1	-1	-1	-1	1	1

* Operators are numbered as per Table A-I.

Phase factors for function symmetrization; T point of Table C-III as example: All eight operations of T take site 2 into itself or equivalent (see Fig. 1). Thus, starting with an unsymmetrized function on site 2, eq. (32) of the main text becomes

$$Q_j^\lambda(\vec{r}) = (h/8)\, e^{i\vec{k}\cdot\vec{s}_2} \sum_{all\ R} D_{11}^\lambda(R)\, e^{i\vec{k}(R)\cdot\vec{s}_2} \chi_{q_j}[R^{-1}(\vec{r}-\vec{s}_2)] .$$

The $\exp[i\vec{k}(R)\cdot\vec{s}_2]$ are listed in the first row of Table C-V. Site 3 goes into itself or equivalent under E, $C_4^2(z)$, and the two JC_4^2 but into site 4 under the two C_4 and the two JC_2. For site 3, then, eq.

(32) becomes

$$Q_j^{\lambda}(\vec{r}) = (h/8)\left\{ e^{i\vec{k}\cdot\vec{s}_3} \Sigma' D_{11}^{\lambda}(R) e^{i\vec{K}(R)\cdot\vec{s}_3} \chi_{qj}\left[R^{-1}(\vec{r}-\vec{s}_3)\right] + e^{i\vec{k}\cdot\vec{s}_4} \Sigma'' D_{11}^{\lambda}(R) e^{i\vec{K}(R)\cdot\vec{s}_4} \chi_{qj}\left[R^{-1}(\vec{r}-\vec{s}_4)\right] \right.$$

with the Σ' over the first set of operators and Σ'' over the second set. The $\exp\left[i\vec{K}(R)\cdot\vec{s}_3\right]$ are listed in the first s_3 row of Table C-V; the $\exp\left[i\vec{K}(R)\cdot\vec{s}_4\right]$ are listed in the second s_3 row. The arrangement for site 4 is similar to that for site 3.

Table C-V

Phase Factors for Function Symmetrization, T Point of Cu_3Au

For explanation of this table see text above. T is located as per Table C-III.

		E	$C_4^2(z)$	C_4	C_4	$JC_4^2(x)$	$JC_4^2(y)$	JC_2	JC_2
		1*	2	5	6	27	28	35	38
site 2	$\exp\left[i\vec{K}(R)\cdot\vec{s}_2\right]$	1	1	-1	-1	-1	-1	1	1
site 3	$\exp\left[i\vec{K}(R)\cdot\vec{s}_3\right]$	1	-1			-1	1		
	$\exp\left[i\vec{K}(R)\cdot\vec{s}_4\right]$			-1	1			-1	1
site 4	$\exp\left[i\vec{K}(R)\cdot\vec{s}_4\right]$	1	-1			1	-1		
	$\exp\left[i\vec{K}(R)\cdot\vec{s}_3\right]$			1	-1			-1	1

* Operators are numbered as per Table A-I.

Table C-VI

χ^{ℓ} Character Table for the Non-Central Atom, T Point of CsCl

For T at $\vec{k} = (2\pi/a)(\frac{1}{2}\ \frac{1}{2}\ b)$, $0 < b < \frac{1}{2}$ in Fig. 3, the eight operators are 1, 2, 5, 6, 27, 28, 35, and 38 in the numbering system of Table A-I. For the CsCl structure these characters are to be used for $\chi_{nc}^{\ell jT}(R)$ in eq. (25) of the main text.

		E	$C_4^2(z)$	$2C_4$	$2JC_4^2$	$2JC_2$	
$\ell=0$		1	1	-1	-1	1	(Γ_1)
$\ell=1$		3	-1	-1	-1	1	(Γ_{15})
$\ell=2$	{	2	2	0	-2	0	(Γ_{12})
	{	3	-1	1	1	1	($\Gamma_{25'}$)

Table C-VII

Phase Factors in the Construction of Table C-VI

The factors listed under each operator R are $\exp\left[i\vec{k}\cdot(R\vec{s}_2-\vec{s}_2)\right]$ for eq. (26) of the main text for the $\vec{k}$ of Table C-VI. Since there is only one non-central site (see Fig. 2), these factors are also Σ'_ν of eq. (26).

	E	$C_4^2(z)$	C_4	C_4	$JC_4^2(x)$	$JC_4^2(y)$	JC_2	JC_2
	1*	2	5	6	27	28	35	38
factor	1	1	-1	-1	-1	-1	1	1

* Operators are numbered as per Table A-I.

APPENDIX D

ALTERNATIVE DERIVATION OF THE PARALLEL AXIS THEOREM

This is an alternative derivation of the substance of eq. (22) of the main text.

From eqn (17) of the main text, we know that for <u>rotation about $\vec{r} = 0$</u>,

$$P_R f(\vec{r}-\vec{s}) = f(R^{-1}\vec{r}-\vec{s}) \qquad \text{(D-1)}$$

From eqns (14) and (15) of the main text, for <u>rotation about $\vec{r} = \vec{s}$</u>,

$$P_R f(\vec{r}-\vec{s}) = f(R^{-1}(\vec{r}-\vec{s})) \qquad \text{(D-2)}$$

$$= f(R^{-1}\vec{r}-\vec{s}+\vec{t})$$

if

$$\vec{t} = \vec{s} - R^{-1}\vec{s} \ . \qquad \text{(D-3)}$$

For Bloch functions,

$$f(R^{-1}\vec{r}-\vec{s}+\vec{t}) = f(R^{-1}\vec{r}-\vec{s})\exp\left[i\vec{k}\cdot\vec{t}\right]$$

so that

$$f(R^{-1}\vec{r}-\vec{s}) = f(R^{-1}\vec{r}-\vec{s}+\vec{t})\exp\left[-i\vec{k}\cdot(\vec{s}-R^{-1}\vec{s})\right].$$

Then, from (D-1) and (D-2),

$$\underset{(\text{about } \vec{r}=0)}{P_R f(\vec{r}-\vec{s})} = \underset{(\text{about } \vec{r}=\vec{s})}{P_R f(\vec{r}-\vec{s})}\exp\left[-i\vec{k}\cdot(\vec{s}-R^{-1}\vec{s})\right]. \qquad \text{(D-4)}$$

Since $R\vec{k} = \vec{k} + \vec{K}_R$ for any R in the group of $\vec{k}$, we may write

$$-i\vec{k}\cdot(\vec{s}-R^{-1}\vec{s}) = -iR\vec{k}\cdot(R\vec{s}-\vec{s}) = -i\vec{k}\cdot(R\vec{s}-\vec{s})-i\vec{K}_R\cdot(R\vec{s}-\vec{s}).$$

Since $\vec{s}-R^{-1}\vec{s}$ is a $\vec{t}$ vector, $R\vec{s}-\vec{s}$ is also so that $\exp\left[-i\vec{K}_R\cdot(R\vec{s}-\vec{s})\right] = 1$, and

$$\underset{(\text{about } \vec{r}=0)}{P_R f(\vec{r}-\vec{s})} = \underset{(\text{about } \vec{r}=\vec{s})}{P_R f(\vec{r}-\vec{s})}\exp\left[-i\vec{k}\cdot(R\vec{s}-\vec{s})\right] . \qquad \text{(D-5)}$$

This is exactly what is expressed by eq. (22) of the main text.

APPENDIX E

SELECTED CHARACTER TABLES, "REDUCED" SIMPLE TETRAGONAL

"Reduced" simply means we restrict our group operators to those that preserve +z. Thus, the full tetragonal group of 16 members is reduced to an 8-member group. This is equivalent to using the standard Λ subgroup of simple tetragonal as the "reduced" full crystal group. For the Γ point of the reduced simple tetragonal we will label the representations with Λ labels. In this appendix the representation labels follow Koster (ref. 6) as far as possible. The class and operator labels are those of BSW (ref. 5). In Table E-I the numbers in front of the class labels give the number of members in the class. The individual operators are identified by their effect on the $x'y'z'$ triad (tetragonal axes).

Table E-I

Character Table, Γ Point of "Reduced" Simple Tetragonal

	E	$C_4^2(z')$	$2C_4(z')$	$2JC_4^2$	$2JC_2$
	$x'y'z'$	$\bar{x}'\bar{y}'z'$	$\bar{y}'x'z', y'\bar{x}'z'$	$\bar{x}'y'z', x'\bar{y}'z'$	$\bar{y}'\bar{x}'z, y'x'z'$
Λ_1	1	1	1	1	1
Λ_2	1	1	1	-1	-1
Λ_3	1	1	-1	1	-1
Λ_4	1	1	-1	-1	1
Λ_5	2	-2	0	0	0

Table E-II

D Matrices for Λ_5 of "Reduced" Simple Tetragonal

E	$C_4^2(z')$	$C_4(z')$	$C_4(z')$	$JC_4^2(x')$	$JC_4^2(y')$	JC_2	JC_2
$x'y'z'$	$\bar{x}'\bar{y}'z'$	$\bar{y}'x'z'$	$y'\bar{x}'z'$	$\bar{x}'y'z'$	$x'\bar{y}'z'$	$\bar{y}'\bar{x}'z'$	$y'x'z'$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ \bar{1} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ \bar{1} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Table E-III

Basis Functions for $\ell = 0, 1, 2$ for the "Reduced" Simple Tetragonal

ℓ	Functions	Representation
0	1	Λ_1
1	z'	Λ_1
	x' y'	Λ_5
2	$2z'^2-x'^2-y'^2$	Λ_1
	$x'^2-y'^2$	Λ_3
	$x'y'$	Λ_4
	$x'z'$ $y'z'$	Λ_5

Table E-IV

Character Table, "Reduced" Simple Tetragonal, $\Delta(x')$

$\vec{k} = (\pi/2)$ (b/t, 0/t, 0/c)

	E	$JC_4^2(y')$
	$x'y'z'$	$x'\bar{y}'z'$
$\Delta(x')_1$	1	1
$\Delta(x')_2$	1	-1

Table E-V

Character Table, "Reduced" Simple Tetragonal, R

$\vec{k} = (\pi/2)$ (1/t, 0/t, 1/c)

	E	$C_4^2(z')$	$JC_4^2(x')$	$JC_4^2(y')$
	$x'y'z'$	$\bar{x}'\bar{y}'z'$	$\bar{x}'y'z'$	$x'\bar{y}'z'$
R_1	1	1	1	1
R_2	1	1	-1	-1
R_3	1	-1	-1	1
R_4	1	-1	1	-1

APPENDIX F

SELECTED ℓ CHARACTER TABLES, "REDUCED" SIMPLE TETRAGONAL

For explanation and use of these tables see the main text.

Table F-I

ℓ Character Table, "Reduced" Simple Tetragonal, for the Central Atom, All $\hat{k}$ Points

The ℓ=1,2 representations are reducible to the tetragonal representations as indicated.
For the central atom, in the reduced simple tetragonal (AB type), these characters may be used for $\chi^{\ell}(R)$ in eq. (12) of the main text for all $\hat{k}$ points.

	E	$C_4^2(z')$	$2C_4(z')$	$2JC_4^2$	$2JC_2$	
	$x'y'z'$	$\bar{x}'\bar{y}'z'$	$\bar{y}'x'z', y'\bar{x}'z'$	$\bar{x}'y'z', x'\bar{y}'z'$	$\bar{y}'\bar{x}'z', y'x'z'$	
ℓ=0	1	1	1	1	1	Λ_1
ℓ=1	3	-1	1	1	1	
	1	1	1	1	1	Λ_1
	2	-2	0	0	0	Λ_5
ℓ=2	5	1	-1	1	1	
	1	1	1	1	1	Λ_1
	1	1	-1	1	-1	Λ_3
	1	1	-1	-1	1	Λ_4
	2	-2	0	0	0	Λ_5

Non-central atom: By selecting the appropriate operators for the $\vec{k}$ point in question, the characters listed in Table F-I may be used for $\chi^{\ell,\vec{k}}_{nc}(R)$ in eq. (25) of the main text for all <u>interior-$\vec{k}$</u> points. For $\vec{k}$ points on the zone boundary a different ℓ character table must, in general, be used for each $\vec{k}$ point; an example of such a table is given in Table F-II.

Table F-II

ℓ Character Table for the Non-Central Atom, R Point of "Reduced" Simple Tetragonal (AB Type)

$\vec{k} = (\pi/2)\ (1/t,\ 0/t,\ 1/c)$

	E	$C_4^2(z')$	$JC_4^2(x')$	$JC_4^2(y')$	
	$x'y'z'$	$\bar{x}'\bar{y}'z'$	$\bar{x}'y'z'$	$x'\bar{y}'z'$	
$\ell=0$	1	-1	-1	1	Λ_1
$\ell=1$	3	1	-1	1	
	1	-1	-1	1	Λ_1
	2	2	0	0	Λ_5
$\ell=2$	5	-1	-1	1	
	1	-1	-1	1	Λ_1
	1	-1	-1	1	Λ_3

(Table F-II, continued)

1	-1	1	-1	Λ_4
2	2	0	0	Λ_5

Table F-III

Phase Factors in the Construction of Table F-II

The factors listed under each operator R are $\exp[i\vec{k} \cdot (R\vec{s}_2 - \vec{s}_2)]$ for eq. (26) of the main text. For the simple tetragonal of type AB there is only one non-central atom site with $\vec{s}_2$ = (ttc), see Fig. 6. Thus, the factors listed are also Σ_v' of eq. (26).

	E	$C_4^2(z')$	$JC_4^2(x')$	$JC_4^2(y')$
Factor	1	-1	-1	1

APPENDIX G

SELECTED COMPATIBILITY TABLES, CUBIC SYSTEM

The representation labels are those of BSW (Ref. 5) and are consistent with Tables B-I, B-III, B-IX, and B-X of Appendix B.

Table G-I

Γ-Δ Compatibility; Simple Cubic, fcc, and bcc

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'	Γ_1'	Γ_2'	Γ_{12}'	Γ_{15}	Γ_{25}
Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$	Δ_1'	Δ_2'	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_2\Delta_5$

Table G-II

Γ-X Compatibility, Simple Cubic and fcc

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'	Γ_1'	Γ_2'	Γ_{12}'	Γ_{15}	Γ_{25}
X_1	X_2	X_1X_2	X_4X_5	X_3X_5	X_1'	X_2'	$X_1'X_2'$	$X_4'X_5'$	$X_3'X_5'$

Table G-III

Δ-X Compatibility, Simple Cubic and fcc

X_1	X_2	X_3	X_4	X_5	$X_{1'}$	$X_{2'}$	$X_{3'}$	$X_{4'}$	$X_{5'}$
Δ_1	Δ_2	$\Delta_{2'}$	$\Delta_{1'}$	Δ_5	$\Delta_{1'}$	$\Delta_{2'}$	Δ_2	Δ_1	Δ_5

Table G-IV

Γ-L Compatibility, fcc

Γ_1	Γ_2	Γ_{12}	$\Gamma_{15'}$	$\Gamma_{25'}$	$\Gamma_{1'}$	$\Gamma_{2'}$	$\Gamma_{12'}$	Γ_{15}	Γ_{25}
L_1	L_2	L_3	L_2L_3	L_1L_3	$L_{1'}$	$L_{2'}$	$L_{3'}$	$L_{2'}L_{3'}$	$L_{1'}L_{3'}$