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# The electron-ion interactions in tetragonal metals

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**Abstract.** The electron-ion interactions are evaluated exactly over the actual shape of the atomic polyhedron, instead of approximating it by a sphere or an ellipsoid, by making use of simple co-ordinate axes transformations and lattice symmetry in the case of fct and bct structures. It is shown that there are several alternative ways of expressing the interference factor, $S(\mathbf{q})$, one of which was obtained by Sharan and others in the case of indium. By comparing these expressions with the latter, with those of corresponding cubic structures as well as with those obtained under spherical approximation respectively, the crystallographic equivalence and stability of tetragonal structures as well as the validity of Wigner-Seitz approximation are discussed.

**Keywords.** Electron-ion interaction; interference factor; coordinate axes transformation; crystallographic equivalence; fct lattice; bct lattice.

## 1. Introduction

The simple evaluation of the electron-ion interactions, by averaging the thermal motion of the ion over the Wigner-Seitz sphere of radius $r_s$, makes the energy of the conduction electrons a function of the atomic volume only and not of the type of the crystal structure (Wilson 1954). Consequently the form factors and the interference factor, $G(qr_s)$ so obtained are insensitive to the symmetry of the lattice. It is therefore essential to evaluate this effect over the actual shape of the atomic polyhedron in order to overcome these deficiencies. The present author has shown in an earlier paper (Ramamurthy 1978, hereinafter referred to as I) that the sum over the actual shape of the polyhedron can be evaluated with ease, in the case of cubic structures by exploiting their lattice symmetry and the apparently different expressions obtained by Bross and Bohn (1967), Ashokkumar (1973) and Sharan *et al* (1973) are just two of the several alternative (but equivalent) ways of expressing the interference factor, $S(\mathbf{q})$.

In the case of tetragonal structures, even the evaluation of this sum over an ellipsoid (instead of a sphere) of equivalent volume (Sharan and Bajpai 1970, Verma and Upadhyaya 1971) suffers from the serious deficiencies mentioned earlier. On the other hand there are no reports of the exact evaluation in literature except the one by Sharan *et al* (1972) who treated the indium structure as bct on the plea that it is crystallographically equivalent to fct. Nevertheless the shape of its atomic polyhedron resembled that of fcc structure. It is therefore the purpose of the present paper to evaluate exactly the interference factor of fct and bct structures by exploiting their lattice symmetry and to show that they can be expressed in several alternative ways.

Further, these expressions are compared with that of Sharan *et al* (1972) as well as with those corresponding to cubic structures in I to gather some information regarding the equivalence and stability of tetragonal structures.

## 2. Theory

When the effect of the thermal motion of the ion is averaged over the conduction electrons present in the atomic polyhedron without approximating it by a sphere or an ellipsoid of equivalent volume, but treating the electrons as free (the band structure effects and the exchange as well as correlation effects being taken into account through appropriate effective mass and screening function (Ramamurthy and Singh 1978), respectively) the interference factor, $S(\mathbf{q})$ is given by

$$S(\mathbf{q}) = \left[ \int_{\Omega} \exp(i\mathbf{q}\cdot\mathbf{r})\, d\Omega \right] / \Omega, \tag{1}$$

where $\Omega$ is the volume of the polyhedron and $\mathbf{q}$ is the wave vector representing the motion of the ion. Making use of the following vector identities,

$$\nabla \exp(i\mathbf{q}\cdot\mathbf{r}) \equiv i(q_x\mathbf{i} + q_y\mathbf{j} + q_z\mathbf{k}) \exp(i\mathbf{q}\cdot\mathbf{r}), \tag{2a}$$

$$\nabla\cdot(\mathbf{i}+\mathbf{j}+\mathbf{k}) \exp(i\mathbf{q}\cdot\mathbf{r}) \equiv i(q_x+q_y+q_z) \exp(i\mathbf{q}\cdot\mathbf{r}), \tag{2b}$$

$$\nabla\cdot\nabla \exp(i\mathbf{q}\cdot\mathbf{r}) \equiv -(q_x^2+q_y^2+q_z^2) \exp(i\mathbf{q}\cdot\mathbf{r}), \tag{2c}$$

and Gauss' divergence theorem, equation (1) could be reduced respectively to the following forms:

$$S_1(\mathbf{q}) = S_2(\mathbf{q}) = \frac{(\sigma_x+\sigma_y+\sigma_z)}{\Omega(q_x+q_y+q_z)}, \tag{3b}$$

$$S_3(\mathbf{q}) = \frac{(q_x\sigma_x+q_y\sigma_y+q_z\sigma_z)}{\Omega(q_x^2+q_y^2+q_z^2)}. \tag{3c}$$

Here $\sigma_x$, $\sigma_y$ and $\sigma_z$ are the Cartesian components of $\boldsymbol{\sigma}$ defined by

$$\boldsymbol{\sigma} = \frac{1}{i} \int_{\mathbf{s}} \exp(i\mathbf{q}\cdot\mathbf{r})\, d\mathbf{s}, \tag{4}$$

where the integration is over the surface of the atomic polyhedron and hence has to be evaluated separately for each crystal structure. In § 3 this integral is evaluated in the case of tetragonal structures by following the procedure adopted in I. Similar evaluation in the case of hexagonal structures is reported elsewhere (Ramamurthy 1979).

### 3.1. *fct structure with* $t > 1$

The atomic polyhedron of a fct lattice is a dodecahedron consisting of four pairs of

regular ((101)) rhombic faces each of side, $(a^2+2c^2)^{1/2}/4t$ and two pairs of irregular ((110)) hexagonal faces, where $t$ is the ratio of two lattice constants, $(c/a)$. Each pair contributes to two components of $\sigma$. Nevertheless the symmetry of the polyhedron reduces the evaluation of the integral (4) to that of contributions from a pair of rhombic and hexagonal faces, respectively to $\sigma_z$ and $\sigma_x$. Since the co-ordinate axes transformation

$$\mathbf{Z} = \sin\theta(t\mathbf{z}+\mathbf{x}),\ \mathbf{X} = \cos\theta(\mathbf{x}-\mathbf{z}/t) \text{ and } \mathbf{y} = \mathbf{y}, \tag{5}$$

rotates $z$ and $x$ axes through an angle $\theta=\tan^{-1}(a/c)$ about $y$ axis and thus transforms the (101) rhombic faces into square faces perpendicular to $Z$ axis, the contribution from these faces to $\sigma_z$ could be written as

$$\sigma_z(101) = \left[\frac{\exp\{i(tq_z+q_x)Z\}}{i}\right]_{-a/4}^{a/4} \int_{-a/4}^{a/4}\int_{-a/4}^{a/4} \exp\{i(q_x-q_z/t)\chi\}\exp(iq_y y)ds_Z. \tag{6}$$

Making use of the co-ordinate axes transformation

$$\mathbf{Z} = \mathbf{Z},\ \mathbf{X} = \tfrac{1}{2}(\mathbf{X}+\mathbf{y}) \text{ and } \mathbf{Y} = \tfrac{1}{2}(\mathbf{y}-\mathbf{X}), \tag{7}$$

which rotates $X$ and $y$ axes through 45° about $Z$ axis the integral is evaluated to give

$$\sigma_z(101) = \frac{16\sin[(tq_z+q_x)(a/4)]\sin[(q_z/t-q_x+q_y)(a/8)]\sin[(q_z/t-q_x-q_y)(a/8)]}{[(q_z/t-q_x)^2-q_y^2]} \tag{8}$$

The corresponding contributions from (011), $(0\bar{1}1)$ and $(\bar{1}01)$ faces could easily be written as follows by interchanging $q_x$ and $q_y$, $q_x$ and $-q_y$ and replacing $q_x$ by $-q_x$ respectively, in (8):

$$\sigma_z(011) = \frac{16\sin[(tq_z+q_y)(a/4)]\sin[(q_z/t-q_y+q_x)(a/8)]\sin[(q_z/t-q_y-q_x)(a/8)]}{[(q_z/t-q_y)^2-q_x^2]}, \tag{9}$$

$$\sigma_z(0\bar{1}1) = \frac{16\sin[(tq_z-q_y)(a/4)]\sin[(q_z/t+q_y+q_x)(a/8)]\sin[(q_z/t+q_y-q_x)(a/8)]}{[(q_z/t+q_y)^2-q_x^2]}, \tag{10}$$

and

$$\sigma_z(\bar{1}01) = \frac{16\sin[(tq_z-q_x)(a/4)]\sin[(q_z/t+q_x+q_y)(a/8)]\sin[(q_z/t+q_x-q_y)(a/8)]}{[(q_z/t+q_x)^2-q_y^2]}. \tag{11}$$

Further, the co-ordinate axes transformation

$$\mathbf{X} = \frac{1}{\sqrt{2}}(\mathbf{x}+\mathbf{y}),\ \mathbf{Y} = \frac{1}{\sqrt{2}}(\mathbf{y}-\mathbf{x}) \text{ and } \mathbf{Z} = \mathbf{z}, \tag{12}$$

rotates $x$ and $y$ axes through 45° about $Z$ axis and orients the (110) hexagonal faces perpendicular to $X$ axis and hence their contribution to $\sigma_x$ could be written as

$$\sigma_x(110) = \left[\frac{\exp\{i(q_x+q_y)X\}}{i}\right]_{-a/4}^{a/4} \int_{-a/4}^{a/4}\int_{-c/4}^{c/4} \exp\{i(q_y-q_x)\,Y\} \exp(iq_zZ)\, ds_X. \tag{13}$$

The evaluation of this integral yields

$$\sigma_x(110) = \frac{8\sin[(q_x+q_y)(a/4)]}{[(q_x-q_y)^2-(q_z/t)^2]}\left\{\left(\frac{q_x-q_y}{q_z}\right)\sin[(q_x-q_y)(a/4)]\times\right.$$

$$\sin\left[q_z\left(\frac{c^2-a^2}{4c}\right)\right] - \frac{a}{c}\left(\cos[(q_x-q_y)(a/4)]\cos\left[q_z\left(\frac{c^2-a^2}{4c}\right)\right]\right.$$

$$\left.\left. - \cos[q_z\, c/4]\right)\right\}. \tag{14}$$

The corresponding contribution from $(1\bar{1}0)$ faces could be written as follows by interchanging $q_y$ and $-q_y$:

$$\sigma_x(1\bar{1}0) = \frac{8\sin[(q_x-q_y)(a/4)]}{[(q_x+q_y)^2-(q_z/t)^2]}\left\{\left(\frac{q_x+q_y}{q_z}\right)\times\right.$$

$$\sin[(q_x+q_y)(a/4)]\sin\left[q_z\left(\frac{c^2-a^2}{4c}\right)\right]$$

$$\left.-\frac{a}{c}\left(\cos[(q_x+q_y)(a/4)]\cos\left[q_z\left(\frac{c^2-a^2}{4c}\right)\right]-\cos[q_zc/4]\right)\right\}. \tag{15}$$

Similar expressions for the contributions to $\sigma_y$ from the hexagonal faces are obtained by interchanging $q_x$ and $q_y$ in (14) and (15). On the contrary, $x$ or $y$ component of the area of rhombic faces is $t^{-1}$ times the corresponding $z$ component and hence their contributions to $\sigma_x$ and $\sigma_y$ are given by

$$\sigma_x(101) + \sigma_x(\bar{1}01) = t^{-1}[\sigma_z(101) - \sigma_z(\bar{1}01)], \tag{16}$$

and
$$\sigma_y(011) + \sigma_y(0\bar{1}1) = t^{-1}[\sigma_z(011) - \sigma_z(0\bar{1}1)]. \tag{17}$$

Since the atomic polyhedron of fct lattice goes over to that of fcc in the limit of $t\to 1$, these expressions for the components of $\boldsymbol{\sigma}$ become equal to one another and reduce to the form obtained in § 3.1 of I.

3.2. *bct structure with $t < 1$*

The atomic polyhedron of a bct lattice is a tetra-kaidecahedron consisting of a pair of (002) square faces and two pairs of ((200)) rhombic faces of sides $(a/4)\,(2-t^2)\,\sqrt{2}$

and $(c/4)\,(1+t^2)^{1/2}$ respectively, as well as four pairs of irregular ((111)) hexagonal faces, where $t$ is the ratio of two lattice constants $(c/a)$. Each pair of the former contributes to one component of $\sigma$ whereas that of the latter contributes to all components. Nevertheless the symmetry of the polyhedron reduces the evaluation of $\sigma$ to that of contributions from a pair of hexagonal faces and rhombic faces to $\sigma_x$ and that from the square faces to $\sigma_z$. Since the latter are perpendicular to $z$ axis, their contribution to $\sigma_z$ could be written as

$$\sigma_z\,(002) = \left[\frac{\exp\,(iq_z\,z)}{i}\right]_{-c/2}^{c/2} \int_{-d}^{d}\int_{-d}^{d} \exp\,(iq_x\,x)\,\exp\,(iq_y\,y)\,ds_z, \tag{18}$$

where $d=(a/4)\,(2-t^2)$. Making use of the co-ordinate axes transformation

$$\mathbf{Z}=\mathbf{z},\ \mathbf{X}=\tfrac{1}{2}\,(\mathbf{x}+\mathbf{y}) \text{ and } \mathbf{Y}=\tfrac{1}{2}\,(\mathbf{y}-\mathbf{x}), \tag{19}$$

which rotates $x$ and $y$ axes through 45° about $Z$ axis the integral is evaluated to obtain

$$\sigma_z\,(002) = \frac{16\,\sin\,[q_z\,c/2]\,\sin\,[(q_x+q_y)\,(d/2)]\,\sin\,[(q_x-q_y)\,(d/2)]}{(q_x^2-q_y^2)}. \tag{20}$$

Similarly the contribution from (200) rhombic faces to $\sigma_x$ could be written as

$$\sigma_x\,(200) = \left[\frac{\exp\,(iq_x\,x)}{i}\right]_{-a/2}^{a/2} \int_{-tc/4}^{tc/4}\int_{-c/4}^{c/4} \exp\,(iq_y\,y)\,\exp\,(iq_z\,z)\,ds_x. \tag{21}$$

Making use of the co-ordinate axes transformation

$$\mathbf{X}=\mathbf{x},\ \mathbf{Y}=\tfrac{1}{2}\,(\mathbf{y}/t+\mathbf{z}) \text{ and } \mathbf{Z}=\tfrac{1}{2}\,(\mathbf{z}-\mathbf{y}/t), \tag{22}$$

which transforms the rhombic faces into square faces and rotates $y$ and $z$ axes through 45° about $X$ axis, the integral is evaluated to obtain

$$\sigma_x(200) = \frac{16t\,\sin\,[q_x\,a/2]\,\sin\,[(tq_y+q_z)\,(c/8)]\,\sin\,[(tq_y-q_z)\,(c/8)]}{[(tq_y)^2-q_z^2]}. \tag{23}$$

Further, the co-ordinate axes transformation

$$\mathbf{X}=\frac{(\mathbf{x}+\mathbf{y}+t\mathbf{z})}{(2+t^2)^{1/2}},\ \mathbf{Y}=\frac{(y-\mathbf{x})}{\sqrt{2}} \text{ and } \mathbf{Z}=\frac{[t(2\mathbf{z}/t-\mathbf{x}-\mathbf{y})]}{\sqrt{2}(2+t^2)^{1/2}} \tag{24}$$

orients the (111) hexagonal faces perpendicular to $X$ axis and hence their contribution to $\sigma_x$ could be written as

$$\sigma_x(111) = \left[\frac{\exp\,\{i(q_x+q_y+tq_z)X\}}{i}\right]_{a/4}^{a/4} \int_{-a/4}^{a/4}\int_{-c/8}^{c/8} \exp\,\{i(q_y-q_x)\,Y\}$$

$$\exp\,\{i\,(2q_z/t-q_x-q_y)\,Z\}\,ds_X. \tag{25}$$

The evaluation of this integral yields

$$\sigma_x(111) = 4\sin[(q_x+q_y+tq_z)(a/4)] \times$$
$$(\{\cos([(q_x-q_y)-t(tq_x-q_z)][a/4]) - \cos[(q_x-q_y)(a/4)]\} /$$
$$[(q_x-q_y)(tq_x-q_z)] - \{\cos([(q_x-q_y)+t(tq_y-q_z)][a/4])$$
$$-\cos[(q_x-q_y)(a/4)]\}/[(q_x-q_y)(tq_y-q_z)]). \quad (26)$$

The corresponding contributions from $(11\bar{1})$, $(1\bar{1}1)$ and $(\bar{1}11)$ faces could easily be written as follows, replacing $q_z$ by $-q_z$, $q_y$ by $-q_y$ and $q_x$ by $-q_x$, respectively in (26):

$$\sigma_x(11\bar{1}) = 4\sin[(q_x+q_y-tq_z)(a/4)] \times$$
$$(\{\cos([(q_x-q_y)-t(tq_x+q_z)][a/4]) - \cos[(q_x-q_y)(a/4)]\} /$$
$$[(q_x-q_y)(tq_x+q_z)] - \{\cos([(q_x-q_y)+t(tq_y+q_z)][a/4])$$
$$-\cos[(q_x-q_y)(a/4)]\} / [(q_x-q_y)(tq_y+q_z)]), \quad (27)$$

$$\sigma_x(1\bar{1}1) = 4\sin[(q_x - q_y + tq_z)(a/4) \times$$
$$(\{\cos([(q_x+q_y)-t(tq_x-q_z)][a/4]) - \cos[(q_x+q_y)(a/4)]\}/[(q_x+q_y)(tq_x-q_z)]$$
$$+ \{\cos([(q_x+q_y)-t(tq_y+q_z)][a/4]) - \cos[(q_x+q_y)(a/4)]\}/[(q_x+q_y)(tq_y+q_z)]), \quad (28)$$

and $\sigma_x(\bar{1}11) = 4\sin[(q_y+tq_z-q_x)(a/4)]$

$$\times(\{\cos([(q_x+q_y)-t(tq_x+q_z)][a/4]) - \cos[(q_x+q_y)(a/4)]\}/[(q_x+q_y)(tq_x+q_z)]$$
$$+\{\cos([(q_x+q_y)-t(tq_y-q_z)][a/4]) - \cos[(q_x+q_y)(a/4)]\}/[(q_x+q_y)(tq_y-q_z)]. \quad (29)$$

Similar expressions for the contributions to $\sigma_y$ are obtained by merely interchanging $q_x$ and $q_y$ in (23) and (26–29). On the contrary, $z$ component of the area of hexagonal faces is $t$ times the corresponding $x$ component and hence their contributions to $\sigma_z$ are given by

$$\sigma_z(111)+\sigma_z(11\bar{1})+\sigma_z(1\bar{1}1)+\sigma_z(\bar{1}11)$$
$$= t[\sigma_x(111)-\sigma_x(11\bar{1})+\sigma_x(1\bar{1}1)-\sigma_x(\bar{1}11)]. \quad (30)$$

Since the atomic polyhedron of bct lattice goes over to that of bcc in the limit of $t\to 1$, these expressions for the components of $\sigma$ become equal to one another and reduce to the form obtained in § 3.2 of I.

### 3.3. *Expressions for* $S(\mathbf{q})$

It is obvious that the interference factor for any crystal structure could be expressed in two different forms by substituting the expressions for $\sigma_x$, $\sigma_y$ and $\sigma_z$ in (3b) and (3c). Since the expressions so obtained for $S_2(\mathbf{q})$ and $S_3(\mathbf{q})$ consist of scalar sums, they could be reduced to convenient forms. In the case of fct structure for instance, the expression for $S_2(\mathbf{q})$ is reduced to (A-1) when the terms with common denominator are collected together whereas that for $S_3(\mathbf{q})$ is reduced to (A-2) when the products of trigonometric functions are transformed into their sums. Similarly the expression for $S_2(\mathbf{q})$ in the case of bct structure goes over to (A-3) when the sums of trigonometric functions are transformed into their products while the reverse transformation reduces that for $S_3(\mathbf{q})$ to (A-4). Thus these expressions which are collected together in appendix A are just two of the several alternative (but equivalent) ways of expressing the interference factor. Further all these expressions reduce to the corresponding expressions of the cubic structures (viz. (A-1) to (A-4) in I) when $t$ tends to unity. Nevertheless, none of these expressions is of the form obtained by Sharan *et al* (1972)*, mainly because the latter cannot be reduced to any of the expressions of fcc or bcc structure in the limit of $t$ tending to unity. On the contrary, expression (A-1) could be written in the latter form by making use of the co-ordinate axes transformation (19) which transforms fct to bct structure with a value of $t > \sqrt{2}$.

Further, it could be shown that the apparently different expressions for $S_2(\mathbf{q}, t)$ and $S_3(\mathbf{q}, t)$ reduce to the same expressions in the principal symmetry directions of the crystal by making use of L'Hospital's rule to overcome their singularity. These expressions for the interference factor in $[\zeta 00]$, $[\zeta\zeta 0]$ and $[00\zeta]$ directions denoted respectively by (B-1), (B-2) and (B-3) in the case of fct structure and by (B-4), (B-5) and (B-6) in the case of bct structure, where $\zeta$ is the appropriate reduced wave vector, are included in the appendix B. It can be observed that each of these goes over to the corresponding expression of the cubic structure in the limit of $t \to 1$, tends to unity in the limit of $\zeta \to 0$ and becomes zero when $\zeta$ corresponds to a reciprocal lattice vector, $\mathbf{g} \neq 0$. They have been plotted as a function of $\zeta$ in the case of indium (fct with $t = 1{\cdot}08$) and white tin (bct with $t = 0{\cdot}55$) in figures 1a and b respectively along $[\zeta 00]$, $[00\zeta]$ and $[\zeta\zeta 0]$ directions and in figure 1c along a non-symmetry direction $[\zeta\zeta\zeta]$. For comparison, the corresponding values of the interference factor $G(\zeta r_s)$ obtained from the expression (C-1) in the appendix C, have also been plotted alongside.

## 4. Discussion

It is obvious from figures 1a, b and c that the interference factor, $S(\zeta)$ varies considerably with the direction as well as the crystal structure and goes through zero at values of $\zeta$ corresponding to $\mathbf{g} \neq 0$ while $G(\zeta r_s)$ does not. Further comparison of these figures with those in I reveals that the corresponding cubic and tetragonal structures have same values of $G(\zeta r_s)$ but different values of $S(\zeta)$ and the latter depend on the values of $t$. Thus the difference between $S(\zeta)$ and $G(\zeta r_s)$ which is mainly due to the fact that the surface of the ellipsoid of equivalent volume does not match with that of the polyhedron, manifests itself even at small values of $\zeta$ in all directions. This

*There is a numerical error of 256 in their expression for $S(\mathbf{q})$.

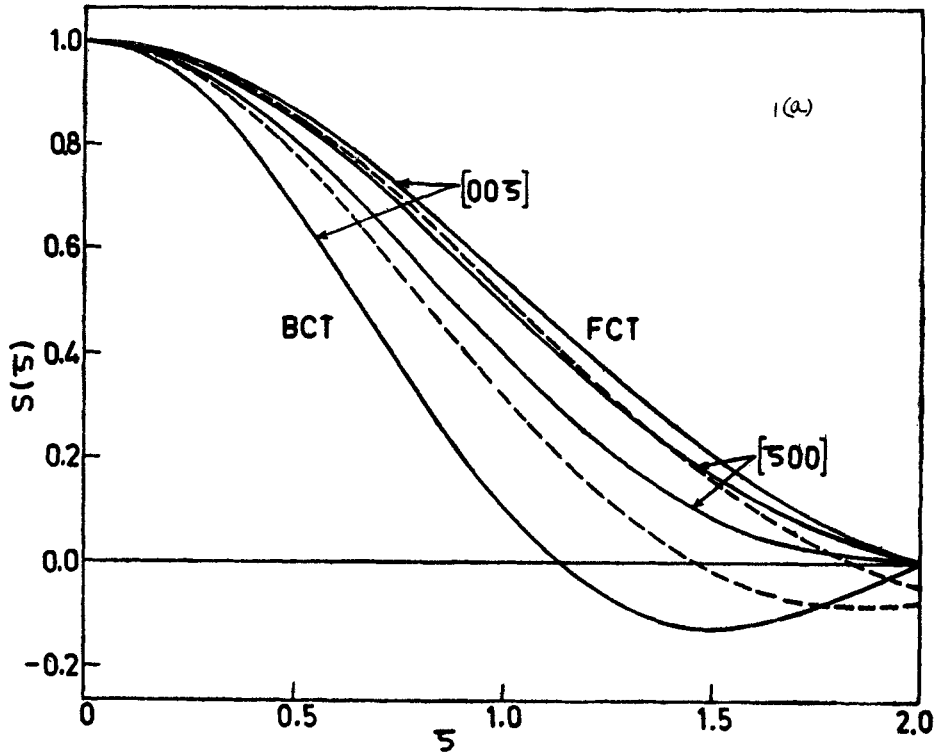


Figure 1(a)

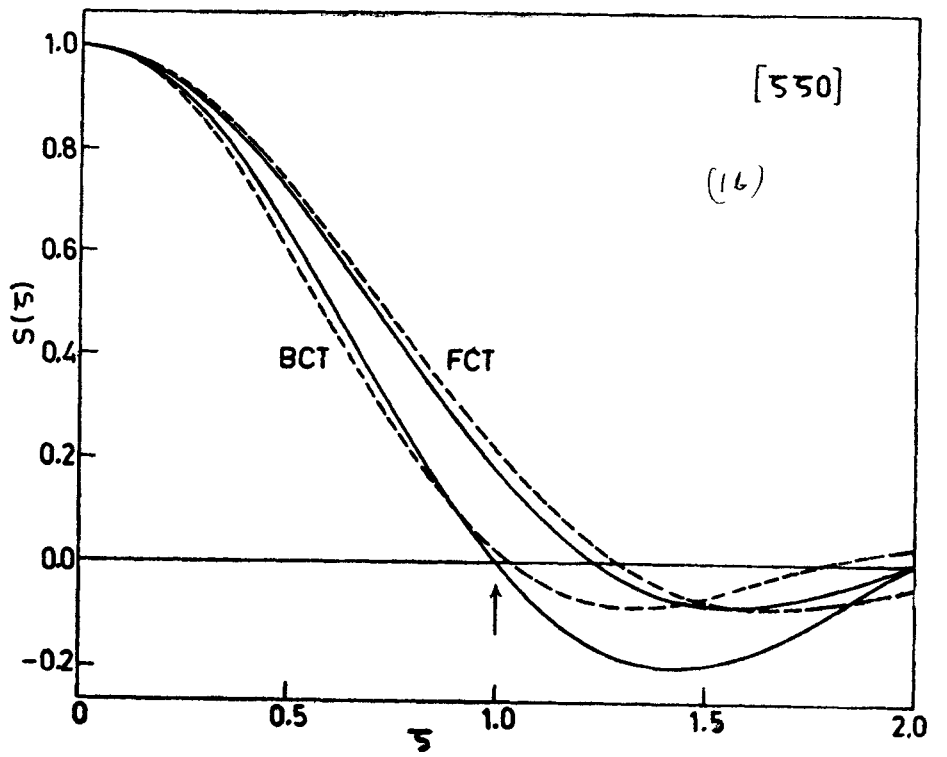


Figure 1(b)

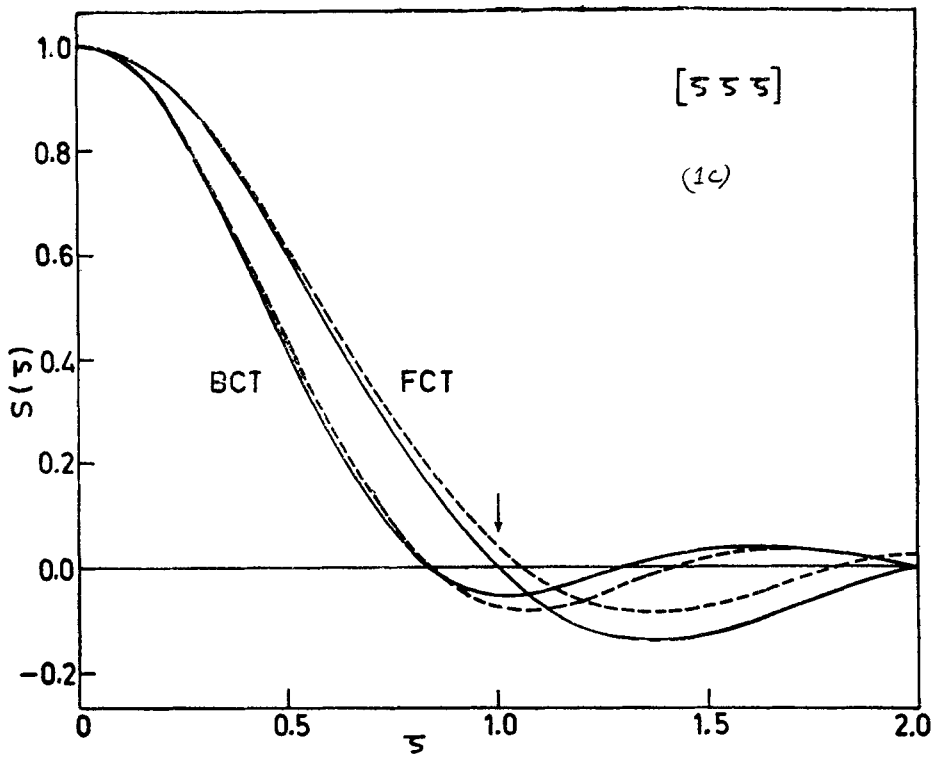


Figure 1(c)

**Figure 1.** $\zeta$-dependence of interference factors in the case of fct indium ($t$=1·08) and bct tin ($t$=0·55) along (a) [$\zeta$00] and [00$\zeta$] directions, (b) [$\zeta\zeta$0] direction and (c) ($\zeta\zeta\zeta$) direction (see appendix B for appropriate expressions): $S(\zeta)$ ———— $G(\zeta r_s)$ — — — — — — — — The arrow in (b) and (c) indicates that $S(\zeta)$ passes through zero whereas $G(\zeta r_s)$ does not, at a reciprocal lattice vector.

difference is positive in those directions where the surface of the ellipsoid lies inside the polyhedron while it is negative in other directions. It is therefore apparent that the Wigner-Seitz approximation leads to an erroneous evaluation of the contributions from normal and umklapp processes to the thermal and electrical properties of tetragonal metals. Since there is no simple and straightforward method of obtaining $S(\zeta)$ from $G(\zeta r_s)$ it is necessary to emphasise that all future calculations should be based on the exact function $S(\zeta)$ as has been done by Sharan and Ashokkumar (1973).

Since the energy difference between different phases is very small compared to the accuracy of calculations, it is extremely difficult to predict the most stable phase for any crystal system. Nevertheless Soma (1976) has shown that fcc indium is unstable against tetragonal distortion mainly because Fuchs (1936) elastic coefficient $A$ is negative. Soma (1977) has also shown that the total energy of indium is minimum at a value of distortion parameter, $\epsilon$ = —0·024 which corresponds to $t$=1·072. Thus the fct structure of indium is obtained by compressing the close packed fcc structure. On the contrary it can be shown that the diamond cubic structure transforms into a bct structure by only changing the value of $t$ and atomic volume continuously. Morita and Soma (1972) have shown that the energy of this structure is minimum at a value of $\epsilon$=0·37 which corresponds to $t$=0·55 in the case of tin. Thus the bct

structure of white tin is obtained by dialating the fcc structure of equivalent volume. According to the present calculations, the interference factor, which represents the strength of electron-ion interactions, of fct structures decreases as $t$ increases whereas that of bct structures increases as $t$ decreases. At the same time the strength of ion-ion interactions of the former decreases whereas that of the latter increases as a consequence of the change in the co-ordination number. Hence the two structures become stable at specific values of $t$.

Although the fct structure is crystallographically equivalent to the bct structure, it is obvious from § 3 that the shape of the atomic polyhedron of the former with $t>1$ resembles that of fcc structure whereas that of the latter with $t<1$ resembles that of bcc structure and they should be treated as such. Even if the former is treated as bct with $t>\sqrt{2}$ (Sharan *et al* 1972) or the latter as fct with $t\sqrt{2}<1$, the shape of the polyhedron does not change and hence the expressions so obtained for $S(\mathbf{q}, t)$ do not reduce to those of the corresponding cubic structures in the appropriate limit for $t$. As long as $t>1$ the perpendicular bisector planes at $\pm c/2$ do not intersect the atomic polyhedron of fct structure, but they do intersect and transform it into that of bct as soon as $t$ becomes $< 1$ and the latter goes over to that of bcc structure when $t\sqrt{2}=1$. It is therefore appropriate to treat the existing crystallographic fct structures with $t<1$ and bct structures with $t>1$ (Wyckoff 1965) as bct structures in the evaluation of the interference factor, but the expressions obtained for $S(\mathbf{q}, t)$ in this range have not been included in the appendix. It may be observed that the other two tetragonal structures are actually distorted forms of fcc structures and they do not transform into bcc structure even at high pressures or low temperatures. Nevertheless it is the shape of the atomic polyhedron which suggests that the white tin structure should be treated as bct by making use its crystallographic equivalence with fct.

## 5. Conclusions

The symmetry of the atomic polyhedron reduces the complexity of the exact evaluation of the electron-ion matrix elements over its actual shape and these expressions are required for the proper evaluation of thermal and electrical properties of tetragonal metals since the Wigner-Seitz approximation is not valid even at small wave vectors. One of the two alternative expressions for $S(\mathbf{q})$ in the case of fct structure can be transformed to the form given by Sharan *et al* (1972) for bct indium. The shape of the atomic polyhedron suggests that fct with $t>1$ and bct with $t<1$ should be treated as such, whereas the other tetragonal structures should be treated as bct. Consequently the white tin structure which is a distorted form of fcc, is treated as bct by making use of its crystallographic equivalence with fct.

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## Appendix A. Expressions for $S(\mathbf{q}, t)$: general direction

*(a) fct structure with $t > 1$*

$$S_2(\mathbf{q}, t) = \left[\frac{8}{t^2(u+v+w)}\right]\left\{\frac{\sin\left(\frac{u+v}{2}\right)\left[\left(\frac{u-v}{w'}\right)\sin\left(\frac{u-v}{2}\right)\sin(\alpha w) - \cos\left(\frac{u-v}{2}\right)\cos(\alpha w) + \cos(tw/2)\right]}{[(u-v)^2 - (w')^2]}\right.$$
$$+\left[\frac{(1+t)\sin\left(\frac{v+tw}{2}\right)\sin\left(\frac{v-w'+u}{4}\right)\sin\left(\frac{v-w'-u}{4}\right)}{[(v-w')^2 - u^2]} + \frac{(1-t)\sin\left(\frac{v-tw}{2}\right)\sin\left(\frac{v+w'+u}{4}\right)\sin\left(\frac{v+w'-u}{4}\right)}{[(v+w')^2 - u^2]}\right.$$
$$\left.\left. + 2 \text{ additional terms with } u \text{ and } v \text{ interchanged}\right]\right\}. \tag{A-1}$$

$$S_3(\mathbf{q}, t) = \left[\frac{-2}{t^2(u^2+v^2+w^2)}\right]\left(\left[(u+v)\left\{\left(\frac{u-v+w'}{2w'}\right)[\sin(u+\alpha w) + \sin(v-\alpha w)] - \sin\left(\frac{u+v+tw}{2}\right)\right.\right.$$
$$\left.\left. - \left(\frac{u-v-w'}{2w'}\right)\left[\sin(u-\alpha w) + \sin(v+\alpha w) - \sin\left(\frac{u+v-tw}{2}\right)\right\}\right] / [(u-v)^2 - (w')^2]\right.$$
$$\left. + \text{an additional term, with } v \text{ and } -v \text{ interchanged}\right] +$$
$$+\left[(v+tw)\left\{\sin\left(\frac{v+\alpha w}{2}\right) + \sin(\beta w) + \sin\left(\frac{u-v-tw}{2}\right) - \sin\left(\frac{u+v+tw}{2}\right)\right\} / [(v-w')^2 - u^2]\right.$$
$$+ (v-tw)\left\{\sin\left(\frac{v-\alpha w}{2}\right) - \sin(\beta w) + \sin\left(\frac{u-v+tw}{2}\right) - \sin\left(\frac{u+v-tw}{2}\right)\right\} / [(v+w')^2 - u^2]$$
$$\left.\left. + 2 \text{ additional terms with } u \text{ and } v \text{ interchanged}\right]\right). \tag{A-2}$$

(*b*) *bct structure with* $t<1$

$$S_2(\mathbf{q}, t) = \left[\frac{2}{t^2(u+v+w)}\right]\left\{2\left[\frac{\sin u \sin\left\{\frac{\delta(v+w')}{4}\right\}\sin\left\{\frac{\delta(v-w')}{4}\right\}}{[v^2-(\omega')^2]} + \frac{\sin v \sin\left\{\frac{\delta(u+w')}{4}\right\}\sin\left\{\frac{\delta(u-w')}{4}\right\}}{[u^2-(\omega')^2]}\right.\right.$$

$$\left. + \frac{t \sin(tw) \sin\left\{\frac{\gamma(u+v)}{4}\right\}\sin\left\{\frac{\gamma(u-v)}{4}\right\}}{(u^2-v^2)}\right] - \left((2+t)\left[\frac{\sin\left(\frac{u+v+tw}{2}\right)}{(u-v)(v-w')(w'-u)}\left\{u \sin\left(\frac{2u-\gamma v-tw}{4}\right)\times\right.\right.\right.$$

$$\left.\times \sin\left[\frac{\delta(v-w')}{4}\right] + v \sin\left(\frac{2v-tw-\gamma u}{4}\right)\sin\left[\frac{\delta(w'-u)}{4}\right] + w' \sin\left[\frac{2tw-\delta(u+v)}{4}\right]\sin\left[\frac{\gamma(u-v)}{4}\right]\right\}\Bigg]$$

$$+ t\,[\text{a term with } u \text{ and } -u \text{ interchanged}] + t\,[\text{a term with } v \text{ and } -v \text{ interchanged}]$$

$$\left.\left. + (2-t)\,[\text{a term with } w \text{ and } -w \text{ interchanged}]\right)\right\}. \tag{A-3}$$

$$S_3(\mathbf{q}, t) = \left(\frac{-2}{t^2}\right)\left(\frac{\{w' \sin(tw/2)\,[\cos u + \cos v) + \cos(tw/2)\,[u \sin u + v \sin v]\}}{[(w')^2-u^2]\,[v^2-(w')^2]}\right.$$

$$+ \left[\frac{\{u\,[\sin(\delta u/2)\cos v + \sin(\gamma u/2)\cos(tw)] + v \sin v \cos(\delta u/2) + w' \sin(tw)\cos(\gamma u/2)\}}{[u^2-v^2]\,[(w')^2-u^2]}\right.$$

$$\left.\left. + \text{an additional term with } u \text{ and } v \text{ interchanged}\right]\right). \tag{A-4}$$

where $u = q_x a/2$, $v = q_y a/2$, $w = q_z a/2$ and $w' = w/t$

$\alpha = (t^2-1)/2t$, $\beta = (t^2+1)/2t$ (with $t > 1$), $\gamma = (2-t^2)$ and $\delta = t^2$ (with $t < 1$)

## Appendix B. Expressions for $S(\mathbf{q}, t)$: symmetry directions

(*a*) *fct structure with* $t > 1$

[$\zeta$00] direction

$$S(\zeta, t) = \frac{8 \sin(\pi \zeta/2)}{(t \pi \zeta)^2}\{\alpha t \sin(\pi \zeta/2) + 4 \sin^2(\pi \zeta/4)/(\pi \zeta)\} \tag{B-1}$$

[$\zeta\zeta$0] direction

$$S(\zeta, t) = \frac{\sin(\pi \zeta/2)}{(t^2 \pi \zeta)}\{(2t^2 - 1)\cos(\pi \zeta/2) + 2 \sin(\pi \zeta/2)/(\pi \zeta)\} \tag{B-2}$$

[00$\zeta$] direction

$$S(\zeta, t) = 32 t^4 (\pi \zeta)^{-3} \sin(\pi \zeta/2) \sin^2(\pi \zeta/4 t^2) \tag{B-3}$$

(*b*) *bct structure with* $t < 1$

[$\zeta$00] direction

$$S(\zeta, t) = \frac{\sin(\pi \zeta/2)}{(\pi \zeta/2)}\left[\frac{\sin(\pi \zeta/2)}{(\pi \zeta)} + \frac{4 \sin(\gamma \pi \zeta/4) \sin(\delta \pi \zeta/4)}{(t \pi \zeta)^2} + \frac{\delta \cos(\pi \zeta/2)}{4}\right] \tag{B-4}$$

[$\zeta\zeta$0] direction

$$S(\zeta, t) = \frac{\sin(\pi \zeta)}{(\pi \zeta)}\left[\frac{\gamma \sin(\delta \pi \zeta/2)}{(\delta \pi \zeta)} + \frac{8 \sin^2(\delta \pi \zeta/4)}{(t \pi \zeta)^2}\right] \tag{B-5}$$

(00$\zeta$) direction

$$S(\zeta, t) = \frac{\sin(\pi \zeta/2)}{(\pi \zeta/2)}\left[\frac{\gamma \delta \sin(\pi \zeta/2)}{(\pi \zeta)} + \frac{4\delta^2 \sin^2(\pi \zeta/4)}{(\pi \zeta)^2} + \frac{\gamma^2 \cos(\pi \zeta/2)}{4}\right] \tag{B-6}$$

where the reduced wave vector, $\zeta = qa/2\pi$ in $x$ and $y$ directions
and $= qc/2\pi$ in $z$ direction

## Appendix C. Expression for $G(qr_s)$

$$G(qr_s) = 3\,[\sin(qr_s) - (qr_s)\cos(qr_s)]/(qr_s)^3 \tag{C.1}$$

where $qr_s = (3/4\pi\nu)^{1/3}\,[u^2 + v^2 + (\omega')^2]^{1/2}$

and $\nu$ is the number of lattice points in a unit cell.

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