The electron-ion interactions in 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, by making use of simple coordinate axes transformations and lattice symmetry in the case of f.c.c. and b.c.c. structures. It is shown that there are several alternative ways of expressing the interference factor, $S(q)$ and the different expressions given by Sharan and others and Bross and Bohn are just two of these equivalent expressions. By comparing these expressions in the symmetry directions with those obtained under spherical approximation their apparent differences are discussed.

1. Introduction

The electron-ion interactions which play a significant role in the transport properties as well as the lattice dynamical study of metals have been dealt with (a) by self consistent methods (Bardeen 1937, Toya 1958) (b) by phenomenological methods (Sharma and Joshi 1963; Krebs 1965) and (c) by pseudopotential methods (Animalu and Heine 1965, Woo *et al* 1975). In all these methods the effect of the thermal motion of the ion which perturbs the energies of conduction electrons should be evaluated by averaging over the atomic polyhedron. Following the assumptions of Wigner and Seitz (1933), the polyhedron is approximated by a sphere of equivalent volume, with a radius r_s. The integration over this sphere gives the form factors in pseudopotential calculations and the interference factor $G(qr_s)$ in other calculations. However this approximation makes the energy a function of atomic volume only but not of the type of the crystal structure (Wilson 1954). Besides the calculations based on $G(qr_s)$ overestimate the strength of the electron-ion interaction and are not consistent with the symmetry requirements of the lattice. To overcome these difficulties, matrix elements have been expressed as the difference between their values at any wave vector q and at the corresponding reciprocal lattice vector g (Toya, 1965, Fielek 1975) and this is equivalent to assuming arbitrarily the values of $G(gr_s)$ to be zero. In spite of this, additional arbitrary parameters had to be introduced into the argument of G factor to obtain agreement with the experimental results in the case of alkali metals (Dayal and Srivastava, 1963; Srivastava and Prasad 1970).

It is therefore obvious that the evaluation of the sum over the actual shape of the polyhedron is essential to express the matrix elements in a realistic form which conforms with the lattice symmetry. Bross and Bohn (1967) have given a set of expressions for such a sum in the case of f.c.c. and b.c.c. lattices without specifying

the method of evaluation. On the other hand, Ashok Kumar (1973) and Sharan *et al* (1973) have given another set of expressions which they obtained by a laborious vector integration method. A new electron gas model (Ramamurthy and Neelakandan 1978) based on the deformation potential approximation which incorporated the latter expressions has given results which are in complete agreement with the experimental results in the case of alkali metals (Ramamurthy and Singh 1978). However, the two sets of expressions appear to be quite different from each other and are scarcely made use of by others. It is the purpose of the present paper to show that this sum can be evaluated, with ease, by exploiting lattice symmetry and that there are several alternative ways of expressing it. In addition, the expressions obtained for this sum by Sharan *et al* (1973) Ashok Kumar (1973) and Bross and Bohn (1967) are compared with the present ones to establish the relations between them.

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, but treating the electrons as free (the exchange and correlation effects being taken into account through an appropriate screening function (Ramamurthy and Singh 1978), the interference factor, $S(\mathbf{q})$ is given by

$$S(\mathbf{q}) = \frac{\int_\Omega \exp(i\,\mathbf{q}\cdot\mathbf{r})\,d\Omega}{\Omega} \tag{1}$$

where Ω 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,

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

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

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

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

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

Here σ_x, σ_y and σ_z are the Cartesian components of σ defined by

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

where the integration is over the surface of the atomic polyhedron and hence has to be evaluated separately for each crystal structure. This evaluation which turns out to be extremely simple when the lattice symmetry is made use of, is illustrated in § 3 by taking the example of cubic crystals. However this procedure could be extended to other crystal structures as well.

3.1. *fcc structure*

The atomic polyhedron of a fcc lattice is a dodecahedron consisting of six pairs of ((110)) rhombic faces, each of side $(a/\sqrt{3})/2$ where $2a$ is the lattice constant. Each pair contributes to two components of σ. However the symmetry associated with the polyhedron reduces the evaluation of the integral (4) to that of one of these contributions to one component, say σ_x. Since the coordinate axes transformation

$$\mathbf{X} = \frac{1}{\sqrt{2}}\,(\mathbf{x}+\mathbf{y}),\ \ \eta = \frac{1}{\sqrt{2}}\,(\mathbf{y}-\mathbf{x})\ \text{and}\ \mathbf{z}=\mathbf{z}, \tag{5}$$

rotates x and y axes through 45° about z axis and thus transforms the (110) rhombic faces into square faces perpendicular to X axis, the contribution from these faces to σ_x could be written as

$$\sigma_x\,(110) = \left\{\frac{\exp\,[i\,(q_x+q_y)X]}{i}\right\} \int\limits_{-a/2}^{a/2} \int\limits_{-a/2}^{a/2} \exp\,[-i\,(q_x-q_y)\eta] \times$$

$$\exp\,(i\,q_z\,z)\,ds_X. \tag{6}$$

Making use of the coordinate axes transformation

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

which rotates η and z axes through 45° about X axis the integral is evaluated to give

$$\sigma_x\,(110) = \frac{16\sin(q_x+q_y)(a/2)\sin(q_x-q_y+q_z)(a/4)\sin(q_x-q_y-q_z)(a/4)}{[(q_x-q_y)^2-q_z^2]}. \tag{8}$$

The corresponding contributions from (101), (10$\bar{1}$) and (1$\bar{1}$0) faces could easily be written as follows by interchanging q_y and q_z, q_y and $-q_z$ and replacing q_y by $-q_y$ respectively, in (8):

$$\sigma_x\,(101) = \frac{16\sin(q_x+q_z)(a/2)\sin(q_x+q_y-q_z)(a/4)\sin(q_x-q_y-q_z)(a/4)}{[(q_x-q_z)^2-q_y^2]}, \tag{9}$$

$$\sigma_x\,(10\bar{1}) = \frac{-16\sin(q_x-q_z)(a/2)\sin(q_x+q_y+q_z)(a/4)\sin(q_x-q_y+q_z)(a/4)}{[(q_x+q_z)^2-q_y^2]},$$

$$\tag{10}$$

and

$$\sigma_x\,(1\bar{1}0) = \frac{16\sin(q_x-q_y)(a/2)\sin(q_x+q_y+q_z)(a/4)\sin(q_x+q_y-q_z)(a/4)}{[(q_x+q_y)^2-q_z^2]}\;.\quad(11)$$

Similar expressions for σ_y and σ_z are obtained by cyclic permutation of the expressions for σ_x.

3.2. *bcc structure*

The atomic polyhedron of a bcc lattice is a tetrakaidecahedron consisting of four pairs of ((111)) hexagonal faces and three pairs of ((200)) square faces, each of side $a/\sqrt{2}$ where $2a$ is the lattice constant. One pair of square faces and all pairs of hexagonal faces contribute to each component of σ. However the symmetry associated with the polyhedron reduces the evaluation of σ to that of contributions from the square faces and one pair of hexagonal faces to one component, say σ_x. Since only the (200) square faces are perpendicular to x axis, their contribution to σ_x could be written as

$$\sigma_x\,(200) = \left[\frac{\exp\,(i\,q_x\,x)}{i}\right]_{-a}^{a}\int_{-a/2}^{a/2}\int_{-a/2}^{a/2}\exp\,(i\,q_y\,y)\,\exp\,(i\,q_z\,z)\,ds_x.\quad(12)$$

Making use of the co-ordinate axes transformation

$$X=x,\; Y=\tfrac{1}{2}\,(y+z)\;\text{and}\;Z=\tfrac{1}{2}\,(z-y)\quad(13)$$

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

$$\sigma_x\,(200) = \frac{16\sin\,(q_x a)\sin\,(q_y+q_z)(a/4)\sin\,(q_y-q_z)(a/4)}{(q_y^2-q_z^2)}\;.\quad(14)$$

Further, the co-ordinate axes transformation

$$X = \frac{1}{\sqrt{3}}\,(x+y+z),\; Y = \frac{1}{\sqrt{2}}\,(y-x)\;\text{and}\;Z = \frac{1}{\sqrt{6}}\,(2z-x-y)\quad(15)$$

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

$$\sigma_x\,(111) = \left\{\frac{\exp\,[i\,(q_x+q_y+q_z)\,X]}{i}\right\}_{-a/2}^{a/2}\int_{-a/2}^{a/2}\int_{-a/4}^{a/4}\exp\,[i\,(q_y-q_x)Y]\times$$

$$\exp\,[i\,(2q_z-q_x-q_y)\,Z]\,dsx.\quad(16)$$

The evaluation of this integral yields

$$\sigma_x(111) = 4\sin\left[(q_x+q_y+q_z)a/2\right]\left[\frac{\cos(q_y-q_z)(a/2)-\cos(q_x-q_y)(a/2)}{(q_x-q_y)(q_x-q_z)}\right.$$

$$\left.-\frac{\cos(q_x-q_z)(a/2)-\cos(q_x-q_y)(a/2)}{(q_x-q_y)(q_y-q_z)}\right]. \tag{17}$$

The corresponding contributions form $(11\bar{1})$, $(1\bar{1}1)$ 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 (17):

$$\sigma_x(11\bar{1}) = 4\sin\left[(q_x+q_y-q_z)(a/2)\right]\left[\frac{\cos(q_y+q_z)(a/2)-\cos(q_x-q_y)(a/2)}{(q_x-q_y)(q_y+q_z)}\right.$$

$$\left.-\frac{\cos(q_x+q_z)(a/2)-\cos(q_x-q_y)(a/2)}{(q_x-q_y)(q_y+q_z)}\right], \tag{18}$$

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

$$\left.+\frac{\cos(q_x-q_z)(a/2)-\cos(q_x+q_y)(a/2)}{(q_x+q_y)(q_y+q_z)}\right] \tag{19}$$

and

$$\sigma_x(\bar{1}11) = 4\sin\left[(q_y+q_z-q_x)a/2\right]\left[\frac{\cos(q_y-q_z)a/2-\cos(q_x+q_y)a/2}{(q_x+q_y)(q_x+q_z)}\right.$$

$$\left.+\frac{\cos(q_x+q_z)(a/2)-\cos(q_x+q_y)(a/2)}{(q_x+q_y)(q_y-q_z)}\right]. \tag{20}$$

Similar expressions for σ_y and σ_z are obtained by cyclic permutation of the expressions for σ_x.

3.3. *Expressions for S(q)*

It is obvious that the interference factor for any crystal structure could be expressed in two different forms by substituting the expressions for σ_x, σ_y and σ_z in 3(a) and (b). Since the expressions so obtained for $S_2(q)$ and $S_3(q)$ consist of scalar sums, they could be reduced to convenient forms. In the case of fcc structure for instance, the expression for $S_2(q)$ is reduced to the form given by Ashok Kumar (1973) (viz. equation (A-1)) when the terms with common denominator are collected together whereas that for $S_3(q)$ is reduced to the form given by Bross and Bohn (1967) (viz. equation (A-2)) when the products of trigonometric functions are transformed into their sums. Similarly the expression for $S_2(q)$ in the the case of bcc structure goes over to the form given by Sharan *et al* (1973) (viz. equation (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 the form given by Bross and Bohn (1967) (viz. equation (A-4)). Thus it is unequivocally established that the expressions given by Bross and Bohn (1967), Ashok Kumar (1973) and Sharan *et al* (1973) which are reproduced in appendix, are just two of the several alternative (but equivalent) ways of expressing the interference factor.

In spite of the significant difference between the expressions for $S_2(\mathbf{q})$ and $S_3(\mathbf{q})$, it could be shown that they reduce to the same expressions in the principal symmetry directions of the crystal. Since the expressions are singular in these directions, they are reduced by making use of L'Hospital's rule. These expressions for the interference factor in [ζ00], [$\zeta\zeta$0] and [$\zeta\zeta\zeta$] directions denoted respectively by (A-5), (A-6) and (A-7) in the case of fcc structure and by (A-8), (A-9) and (A-10) in the case of bcc structure, where ζ is the reduced wave vector, are also included in appendix. It can be observed that each of the above expressions tends to unity in the limit of $\zeta \rightarrow 0$, and becomes zero when ζ corresponds to a reciprocal lattice vector, $\mathbf{g} \neq 0$. These expressions have been plotted as a function of ζ in figures 1a, b and c respectively along [ζ00], [$\zeta\zeta$0] and [$\zeta\zeta\zeta$] directions. For comparison the interference factor $G(\zeta r_s)$ is also plotted alongside.

4. Discussion

It is obvious from figures 1a, b and c that the interference factor varies considerably with the direction as well as the crystal structure. Nevertheless there is hardly any difference between $S(\zeta)$ and $G(\zeta r_s)$ in any of these cases at small values of ζ and hence
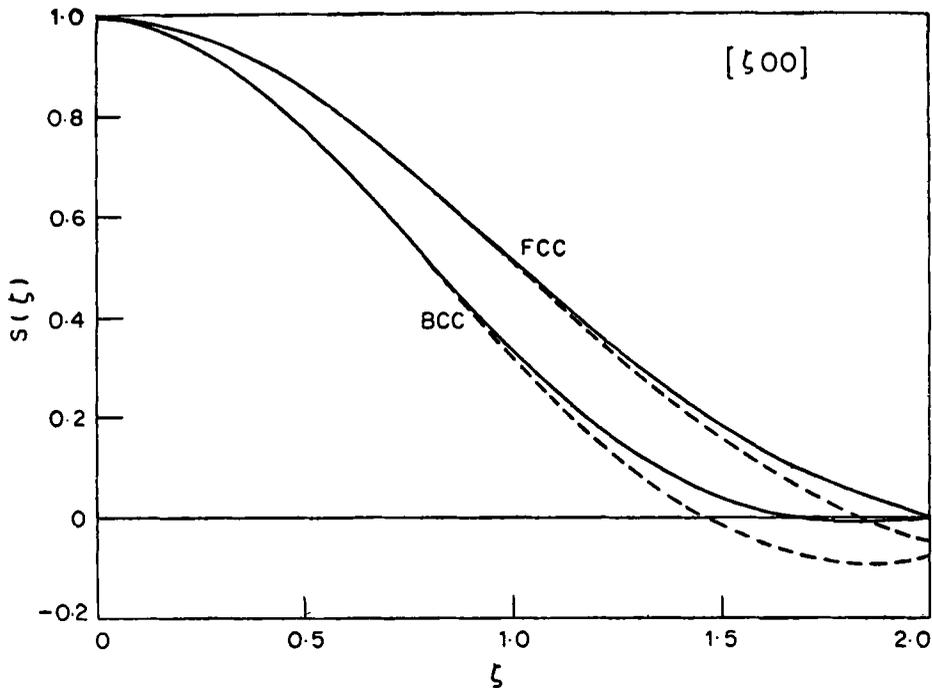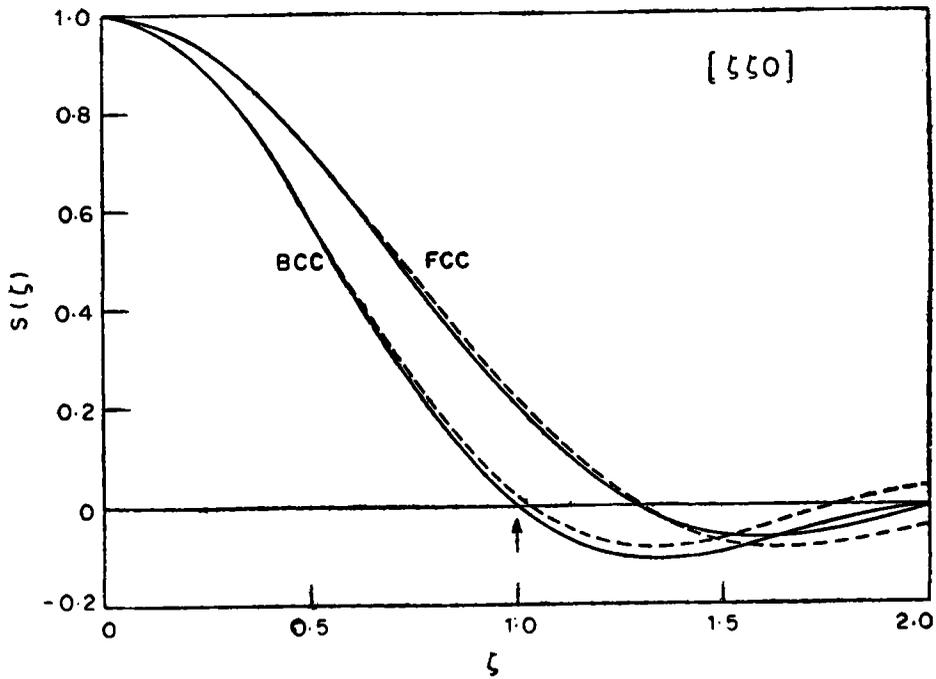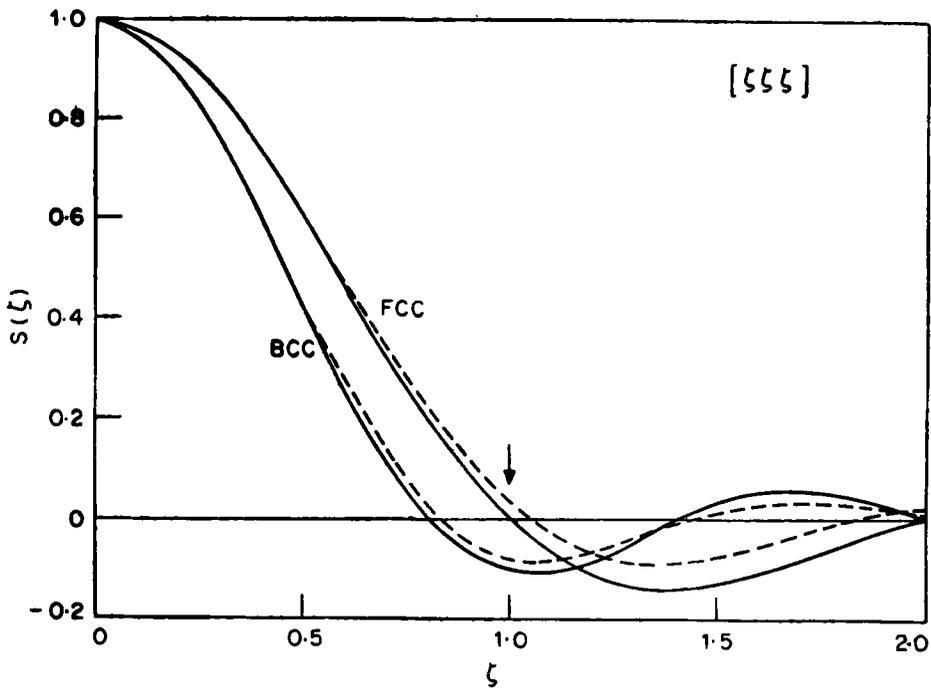

Figure 1a

Figure 1b

Figure 1c

Figure 1. ζ Dependence of the interference factors in the case of fcc and bcc structures along (a) $[\zeta 00]$ direction (b) $[\zeta\zeta 0]$ direction and (c) $[\zeta\zeta\zeta]$ direction: $S(\zeta)$ ——— $G(\zeta r_s)$ — — — — — — 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.

the assumptions of Wigner and Seitz (1933) is valid in this region. However, the difference between them manifests itself as ζ approaches the zone boundary value and it could be seen from the figures that $S(\zeta)$ goes through zero at values of ζ corresponding to a non-zero reciprocal lattice vector, g while $G(\zeta r_s)$ does not. This difference is a consequence of the fact that the surface of the sphere of equivalent volume does not match with that of the polyhedron in any direction. For instance, in [ζ00] direction this surface lies inside the polyhedron and hence the values of $S(\zeta)$ are higher than the corresponding values of $G(\zeta r_s)$ whereas in other symmetry directions the former are lower than the latter because the spherical surface lies outside the polyhedron. However, the proximity of these surfaces gives rise to the least difference between the two along [$\zeta\zeta$0] direction in the case of fcc structure and along [$\zeta\zeta\zeta$] direction in the case of bcc structure.

It is apparent from the above discussion that Wigner-Seitz approximation leads to an erroneous evaluation of the contribution of umklapp processes to the thermal and electrical properties of metals. There is no simple and straightforward method of obtaining $S(\zeta)$ from $G(\zeta r_s)$ and the use of additional analytical expressions (Toya 1965) or arbitrary parameters (Dayal and Srivastava, 1963; Srivastava and Prasad 1970) in the latter are nothing but some sort of end corrections. It is therefore necessary to emphasize that in future all calculations should be based on the exact function $S(\zeta)$, instead of $G(\zeta r_s)$, as has been done by Goel *et al* (1974a, b) and Sunil Kumar (1977).

5. Conclusions

The exact evaluation of the electron-ion matrix elements over the actual shape of the atomic polyhedron turns out to be extremely simple when the lattice symmetry is made use of. The apparently different expressions for the interference factor, $S(\mathbf{q})$ given by Bross and Bohn (1967) and Sharan *et al* (1973) happen to be exactly equivalent to one another. Wigner-Seitz approximation is valid for normal processes only but not for umklapp processes. Hence exact expressions are required for the proper evaluation of the thermal and electrical properties of metals and to satisfy the symmetry requirements of the lattice.

Acknowledgements

Appendix

1. *Expressions for $S(\mathbf{q})$: general direction*

(a) *fcc structure*

$$S_2(\mathbf{q}) = \left(\frac{16}{u+v+w}\right)\left[\frac{\sin\left(\frac{u+v}{2}\right)\sin\left(\frac{u-v+w}{4}\right)\sin\left(\frac{u-v-w}{4}\right)}{(u-v)^2-w^2}\right]$$

$$\left. + \text{ 2 additional cyclic permuted terms} \right] \tag{A1}$$

$$S_3(\mathbf{q}) = \left(\frac{-2}{u^2 + v^2 + w^2} \right)$$

$$\times \Biggl\{ \frac{(u+v)\left[\sin u + \sin v - \sin\left(\frac{u+v+w}{2}\right) - \sin\left(\frac{u+v-w}{2}\right) \right]}{(u-v)^2 - w^2}$$

$$+ \frac{(u-v)\left[\sin u - \sin v - \sin\left(\frac{u-v+w}{2}\right) - \sin\left(\frac{u-v-w}{2}\right) \right]}{(u+v)^2 - w^2}$$

$$\left. + \text{ 4 additional cyclic permuted terms} \right\} \tag{A2}$$

(b) bcc structure

$$S_2(\mathbf{q}) = \left(\frac{2}{u+v+w} \right) \Biggl\{ \frac{-3\sin\left(\frac{u+v+w}{2}\right)}{(u-v)(v-w)(w-u)}$$

$$\times \left[u \sin\left(\frac{2u-v-w}{4}\right) \sin\left(\frac{v-w}{4}\right) + \text{ 2 cyclic terms} \right]$$

$$- \left(\frac{\sin\left(\frac{u-v-w}{2}\right)}{(u+v)(v-w)(w+u)} \left[u \sin\left(\frac{2u+v+w}{4}\right) \sin\left(\frac{v-w}{4}\right) \right. \right.$$

$$+ v \sin\left(\frac{2v-w+u}{4}\right) \sin\left(\frac{w+u}{4}\right)$$

$$\left. + w \sin\left(\frac{v-2w-u}{4}\right) \sin\left(\frac{u+v}{4}\right) \right] + \text{ 2 cyclic terms} \Biggr)$$

$$+ \left[\frac{2\sin u \sin\left(\frac{v+w}{4}\right) \sin\left(\frac{v-w}{4}\right)}{v^2 - w^2} + \text{ 2 cyclic terms} \right] \Biggr\} \tag{A3}$$

$$S_3(\mathbf{q}) = \Biggl\{ \frac{-2}{(u^2-v^2)(w^2-u^2)} \left[\cos\left(\frac{u}{2}\right) (u \sin u + v \sin v + w \sin w) \right.$$

$$- u \sin \left(\frac{3u}{2}\right) + u \sin \left(\frac{u}{2}\right) (\cos u + \cos v + \cos w) \Big]$$

$$+ 2 \text{ additional cyclic terms} \Big\}$$ (A4)

where $u = q_x a$, $v = q_y a$ and $w = q_z a$.

2. *Expressions for $S(\mathbf{q})$: symmetry directions*

(a) *fcc structure*

($\zeta 00$) direction

$$S(\zeta) = 32 \, (\pi \zeta)^{-3} \sin \left(\frac{\pi \zeta}{2}\right) \sin^2 \left(\frac{\pi \zeta}{4}\right)$$ (A5)

($\zeta \zeta 0$) direction

$$S(\zeta) = (\pi \zeta)^{-2} \sin \left(\frac{\pi \zeta}{2}\right) \left[(\pi \zeta) \cos \left(\frac{\pi \zeta}{2}\right) + 2 \sin \left(\frac{\pi \zeta}{2}\right)\right]$$ (A6)

($\zeta \zeta \zeta$) direction

$$S(\zeta) = 16 (\pi \zeta)^{-3} \sin (\pi \zeta) \sin^2 \left(\frac{\pi \zeta}{4}\right)$$ (A7)

(b) *bcc structure*

($\zeta 00$) direction

$$S(\zeta) = \frac{\sin (\pi \zeta)}{4 \pi \zeta} + \frac{2 \sin^2 (\pi \zeta/2)}{(\pi \zeta)^2} + \frac{8 \sin (\pi \zeta/2) \sin^2 (\pi \zeta/4)}{(\pi \zeta)^3}$$ (A8)

($\zeta \zeta 0$) direction

$$S(\zeta) = \frac{\sin (\pi \zeta) \sin (\pi \zeta/2)}{(\pi \zeta)^2} + \frac{8 \sin (\pi \zeta) \sin^2 (\pi \zeta/4)}{(\pi \zeta)^3}$$ (A9)

($\zeta \zeta \zeta$) direction

$$S(\zeta) = \frac{3 \sin (3 \pi \zeta/2)}{8 \pi \zeta} + \frac{3 \sin (\pi \zeta) \sin (\pi \zeta/2)}{(2 \pi \zeta)^2} + \frac{\sin^3 (\pi \zeta/2)}{2 (\pi \zeta)^3}$$ (A10)

where $\zeta = (qa/\pi)$ is the reduced wave vector.

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