# ON THE FORMULATION AND THE CALCULATION OF THE ANHARMONIC CONTRIBUTIONS TO THE DEBYE-WALLER FACTOR IN METALS (Sodium) 

## by

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Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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## April 1979

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## ABSTRACT

The algebraic expressions for the anharmonic contributions to the Debye-Waller factor up to $O\left(\lambda^{2}\right)$ and $O\left(q_{0}^{4}\right)$ [ where $q_{0}$ is the scattering wave-vector] have been derived in a form suitable for cubic metals with small ion cores where the interatomic potential extends to many neighbours. This has been achieved in terms of various wave-vector dependent tensors, following the work of Shukla and Taylor (1974) on the cubic anharmonic Helmholtz free energy. The contribution to the various wave-vector dependent tensors from the coulomb and the electron-ion terms in the interatomic metallic potential has been obtained by the Ewald procedure. All the restricted multiple whole Brillouin zone (B.Z.) sums are reduced to single whole B.Z. sums by using the plane wave representation of the delta function. These single whole B.Z. sums are further reduced to the $\frac{1}{48}$ th portion of the B.Z. following Shukla and Wilk (1974) and Shukla and Taylor (1974).

Numerical calculations have been performed for sodium where the Born-Mayer term in the interatomic potential has been neglected because it is small [ Vosko (1964)]. In order to compare our calculated results with the experimental results of Dawton (1937), we have also calculated the ratio of the intensities at different temperatures for the lowest five reflections (110), (200), (220), (310) and (400) . Our calculated quasi-harmonic results agree reasonably well with the experimental results at temperatures ( $T$ ) of the order of the Debye temperature $\left(\theta_{D}\right)$. For $T \gg \theta_{D}$, our calculated anharmonic results are found to be in good agreement with the experimental results.

The anomalous terms in the Debye-Waller factor are found not to be negligible for certain reflections even for $T \approx \Theta_{D}$. At temperature $T \gg \theta_{D}$, where the temperature is of the order of the melting temperature ( $T_{m}$ ), the anomalous terms are found to be important almost for all the five reflections.

I would like to express my heartfelt gratitude to Dr. Ramesh Chandra Shukla who suggested and supervised all the analytical and numerical works presented in this thesis.

I wish to thank Mr. Martin VanderSchans for offering me various helps regarding computer programming in the initial stage of this work.

I am grateful to Miss Nasim Banu for hel ping me in various ways.

I am grateful to the Department of Physics, Brock University, for offering me financial support, and to the University of Chittagong, Bangladesh, for granting me study leave.

I would like to thank my wife, Jyotsna for typing the first copy of this manuscript, Mrs. J. Cowan for typing the final copy of this manuscript and the Brock University Computing Centre for their excellent services throughout the course of this thesis.

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## I. INTRODUCTION

The intensity of scattered x-rays from a crystal system decreases with increasing temperature which can be formally expressed as (Debye (1914), Waller (1923))

$$
\begin{equation*}
I_{T}=I_{0} e^{-2 M\left(\underline{\varepsilon}_{0}\right)} \tag{1.1}
\end{equation*}
$$

where $I_{\boldsymbol{T}}$ and $I_{0}$ are the intensities of the scattered $x$-rays at the temperatures $T^{0} K$ and $0^{0} K$ respectively, and the factor $e^{-2 M\left(\underline{\varepsilon}_{0}\right)}$ accounts for the decrease of the intensity due to thermal vibration of the atoms. The exponent $2 M\left(\underline{q}_{0}\right)$ is known as the Debye-Waller factor and is a function of the scattering wave-vector $q_{0}$ and also of temperature T.

For a monatomic Bravais lattice, $I_{T}$ is proportional to the sum

$$
\begin{equation*}
\sum_{l} \sum_{l^{\prime}}\left\langle\exp \left[i q_{0} \cdot\left(r_{l}-r_{l^{\prime}}\right)+i^{\prime} q_{0} \cdot\left(\underline{u}^{2}-\underline{u}^{l^{\prime}}\right)\right]\right\rangle \tag{1.2}
\end{equation*}
$$

where ${\underset{\sim}{r}}_{\ell}$ and $\boldsymbol{r}_{\ell}$, are the equilibrium positions of the atoms in the $\underset{\sim}{\ell} \tilde{h}$ and ${\underset{\sim}{\ell}}^{\prime} \bar{\pi}$ unit cells respectively, ${\underset{\sim}{u}}^{\ell}$ and $\underline{u}^{\ell^{\prime}}$ are their corresponding displacements, and $<>$ indicates the thermal average. In the thermal average in Eq. (1.2), neglecting all terms except those which are independent of $\underset{\sim}{l}$ and $\underbrace{\prime}$, and then comparing Eqs. (1.1) and (1.2), we get


At high temperatures, ie., at temperatures greater than the Debye temperature $\theta_{\mathcal{D}}$, calculated values of $2 M\left(\mathcal{Q}_{0}\right)$ for various materials obtained by employing the harmonic approximation of the solid have been found to be quite inadequate to account for the experimental results. The expression for $2 M\left(\varepsilon_{0}\right)$ obtained by performing the harmonic thermal average on the right hand side of Eq. (1.3), is linear in temperature $T$ in the high temperature limit. Formally, it can be written as

$$
\begin{equation*}
2 M\left(q_{0}\right)=V_{H} q_{0}^{2} T \tag{1.4}
\end{equation*}
$$

where, $V_{H}$ is a volume dependent constant. The experimental values of $2 M\left(\underline{q}_{0}\right)$ at high temperatures deviate from the predicted linear temperature dependence as given by Eq. (1.4).

For example, James (1925) has found that for rock-salt (Jael) the experimental value of $2 M\left(\tilde{q}_{0}\right)$ is proportional to $T^{2}$ and not to T at $T \gg \theta_{D}$. Similar results are found by other workers, like James and Brindley (1928) for sylvine (KC1), Boscovites et al (1958) for silver, Dawton (1937) for sodium, and Chipman (1960) for aluminum, lead and beta-brass.

In order to find a proper explanation for the observed temperature dependence of $2 \boldsymbol{M}\left(\underline{\varepsilon}_{0}\right)$, the effect of thermal expansion
has been investigated where $V_{H}$, in Eq. (1.4), is treated not simply as a constant but as a volume dependent quantity. Such calculations where $2 M\left(\tilde{q}_{0}\right)$ is considered to have a linear explicit temperature dependence while $V_{H}$ is allowed to vary with volume, is known as the quasi-harmonic theory, and have been carried out by several workers, e.g. Nicklow and Young (1966), Shukla and Dey (unpublished).

In their work, Nicklow and Young performed their calculation first for a particular volume and then used the volume coefficient of expansion and the Gruneisen constant to account for the volume change in $V_{H}$. On the other hand, Shukla and Dey have used the force constants for various volumes to account for the volume change in $V_{H}$ exactly.

The values of $2 M\left(q_{0}\right)$, obtained by the quasi-harmonic calculations, are certainly in better agreement with the experimental results compared to that of the purely harmonic calculations done at a fixed volume, but still the discrepancies remain at temperatures much greater than $\Theta_{D}$.

Thus, in order to look for some other contributions to $2 M\left(q_{0}\right)$, one is tempted to examine the thermal average in Eq. (1.3). The thermal averaging in Eq. (1.3) can be performed without making the harmonic approximation. This introduces the terms in the hamiltonian which are neglected in making the harmonic approximation. The collection of all these neglected terms in the hamiltonian are known as the anharmonic terms.

Maradudin and Flinn (1963) have derived the expressions for the
harmonic and anharmonic contributions to $2 M\left(q_{0}\right)$ in the classical high temperature limit. Their derivation retained only the lowest order cubic and quartic terms in the anharmonic part of the hamiltonian. They found two types of anharmonic contributions to 2 M ( $\underline{q}_{0}$ ) proportional to $q_{0}^{2}$ and $q_{0}^{4}$ respectively. The latter contribution was dubbed by them as the anomalous part of $2 M\left(\varepsilon_{0}\right)$.

Maradudin and Flinn have also computed the value of the DebyeWaller factor (harmonic and anharmonic) for a central force nearest neighbour fcc cyrstal ( Pb ). Because of the extreme complexity of the anharmonic expressions of $2 M\left(q_{0}\right)$, they used the leading term approximation where one keeps only the highest order radial derivative of the interatomic potential to represent the different cartesian components of the tensor force constants. For calculating the so-called anomalous terms in $2 M\left(\boldsymbol{q}_{0}\right)$, they used one more approximation. This is known as the Ludwig's approximation which is equivalent to the Einstein's approximation. In their calculation, the potential derivatives were obtained from the Morse potential function as well as from other experimental sources.

However, it should be noted that the Morse potential is a poor representation of metallic interatomic potential where, particularly, small ion cores are involved. The leading term approximation also is not very reliable. The error introduced in making this approximation is of the order of $30-47 \%$ (Shukla and Wilk (1974)). Moreover, the Ludwig's approximation, combined with the leading term approximation, gives an error of the order of $100 \%$ (Shukla (unpublished)).

One conclusion of Maradudin and Flinn, based on the above two approximations, is that the anomalous terms in $2 M\left(\mathcal{Q}_{0}\right)$ can be neglected.

Another work in this direction is reported by Wolfe and Goodman (1969). They did their anharmonic calculations for a nearest neighbour model of copper. For the harmonic part of the calculation, which provides the eigenvalues and eigenvectors, they used two sets of force constants. One is the third neighbour model of Lehman et al (1962), and the other is the sixth neighbour model of Sinha (1966). For the anharmonic part, the nearest neighbour potential derivatives were obtained from a Born-Mayer potential function by using four sets of parameters obtained from the works of Mann and Seeger (1967) and Jaswal and Girifalco (1967). Wolfe and Goodman concluded that the anomalous terms in $2 M\left(q_{0}\right)$ are not negligible.

Obviously, the anharmonic calculations of $2 M\left(\varepsilon_{0}\right)$ performed by Maradudin and Flinn, and Wolfe and Goodman are geared to a nearest neighbour model of a crystal. For a metallic crystal with small ion cores where the range of the interatomic potential extends to many neighbours, one has to develop some suitable method for performing the real lattice summations arising in the calculation of the anharmonic contributions to $2 M\left(\mathbb{q}_{0}\right)$. Moreover, to make the calculations consistent, all the harmonic and anharmonic force constants should be derived from the same potential function representing the metal.

The standard method of obtaining such a potential function is to use an effective two-body interatomic potential. This potential in metals consists of three parts (Toya (1958), Cochran (1963)):
(a) direct coulomb interaction of the ion cores, (b) the electron-ion interaction screened by other electrons (electron gas), (c) the Pauli exchange repulsive interaction due to the overlap of closed electron shells of the ion cores, i.e., the Born-Mayer term.

For small ion core metals like sodium, the Born-Mayer contribution is found to be negligible (Vosko (1964)).

Using the force constants derived from the radial derivatives of such a first principle potential function, Shukla and Taylor (1974) have calculated the cubic and quartic anharmonic contributions to the Helmholtz free energy and the specific heat at constant volume of sodium and potassium. This is probably the first work on the calculation of the anharmonic contributions to the Helmholtz free energy where a method is presented to carry out the anharmonic summations out to any neighbour.

Such anharmonic calculations, whether of the Helmholtz free energy or of the Debye-Waller factor, are very difficult to perform because they involve the restricted multiple Brillouin zone sums ( $q$-sums and the delta function $\Delta(\underline{q})$ ), and the direct lattice sums (2-sums) in the calculation of the Fourier transform of the anharmonic force constants.

Here in this thesis, we present a method of performing such difficult calculations of $2 M\left({\underset{\sim}{0}}^{q_{0}}\right)$ in metals with small ion cores.

The main purpose of this thesis is then to derive expressions for the anharmonic contributions to the Debye-Waller factor for cubic metals in such a way that
(1) a calculation becomes possible for metals where the interatomic potential extends to many neighbours, by the introduction of the wave-vector dependent tensors, and
(2) the restricted multiple Brillouin zone sums can be reduced, even in this case, to single Brillouin zone sums thereby making the exact calculation possible.

Other objectives of this thesis are to calculate the harmonic and anharmonic contributions to $2 M\left(\underline{q}_{0}\right)$ for sodium and
(3) see whether or not the anomalous terms in the anharmonic contributions to $2 M\left(\varepsilon_{0}\right)\left[0 f O\left(\varepsilon_{0}^{4}\right)\right]$ are negligible compared to the rest of it $\left[0 f O\left(\tilde{q}_{0}^{2}\right)\right]$ and
(4) compare our calculated results (harmonic and anharmonic) with those obtained experimentally [Dawton (1937)].

The outline of this thesis is as follows. In section 2 , we have presented a summary of the contributions to the Debye-Waller factor in the high temperature limit. In section 3 , the expressions for the anharmonic contributions to the Debye-Waller factor are expressed in terms of different wave-vector dependent tensors. The expressions obtained in section 3 are simplified for cubic metals in section 4. In section 5, the restricted Brillouin zone sums are expressed in terms of single Brillouin zone sums with the help of the plane wave representation of the delta function. Section 6 contains a description of the derivation of the expressions of the various wave-vector dependent tensors using Ewald's method of summation. Our numerical calculations are described and the results are presented in section 7. The discussion and conclusions are presented in sections 8 and 9, respectively.
2. EXPRESSIONS FOR THE ANHARMONIC DEBYE-WALLER FACTOR IN THE HIGH TEMPERATURE LIMIT TO $0\left(\lambda^{2}\right)$ AND $0\left(q_{0}{ }^{4}\right)$

From Equation (I.3), in order to obtain an expression for the exponent $2 \mathrm{M}\left(\underline{q}_{0}\right)$ of Debye-Waller factor, the usual method is to express $\underline{u}^{\ell}$ and $\underline{u}^{\ell^{\prime}}$ in terms of normal coordinates, and then perform the thermal averaging.

For an atom in the $\underline{l}^{\text {th }}$ unit cell, the $\alpha$ component of the displacement, as given by Born and Huang (1954) is

$$
\begin{equation*}
u_{\alpha}^{l}=\frac{1}{\sqrt{N M}} \sum_{\underline{q}_{j}} e_{\alpha}(\underline{q}) Q(\underline{q} j) \exp \left(i q \cdot r_{l}\right) \tag{2.1}
\end{equation*}
$$

where the subscript $\alpha$ denotes a cartesian component, $N$ is the total number of atoms in the crystal, $M$ is the mass of each atom, $q$ is the phonon wave-vector, $j$ the branch index, $e_{\alpha}(\underline{j})$ is the $\alpha$ component of the eigenvector for the phonon mode $(\underline{q} j)$, and $Q(\underline{q})$ is the normal coordinate for the same mode.

In the harmonic approximation, quantum mechanical thermal averaging can be performed by following the procedures outlined in Messiah (1958). In the high temperature limit, the contribution to $2 M\left(\underline{q}_{0}\right)$, as given by the harmonic averaging, is

$$
2 M_{0}\left(q_{0}\right)=q_{0}^{2} \frac{K_{B} T}{3 N M} \sum_{\underline{q} j} \frac{1}{\omega^{2}\left(\underline{q}_{j}\right)}
$$

where $K_{B}$ is the Boltzmann constant, $T$ is the absolute temperature, and $\omega(\underline{q})$ is the angular frequency of the phonon mode $(\underline{q} j)$.

In order to perform the thermal averaging for a weak anharmonic crystal, the usual procedure is to consider the inharmonic part of the Hamiltonian of the crystal as a perturbation. In order to perform such a thermal averaging of a physical quantity, using the perturbation method, certain ordering scheme is needed due to the presence of a double series expansion - one due to the perturbation series expansion of the potential, and the other due to the series expansion of the physical quantity in terms of the perturbing potential.

Following the ordering scheme of Van Hove (1961), we can denote the ordering parameter by $\lambda$ where $\lambda$ is equal in magnitude to the ratio of a typical atomic displacement and the nearest neighbour distance. It has been shown by Maradudin and Fin (1963) that the lowest order anharmonic contributions to the Debye-Waller factor are of $O\left(\lambda^{2}\right)$, and there are four such terms - two of them are of $O\left(\underline{q}_{0}^{2}\right)$ $\left(2 M_{1}\left(\underline{q}_{0}\right)\right.$ and $\left.2 M_{2}\left(\underline{q}_{0}\right)\right)$ and the other two $\left(2 M_{3}\left(\underline{q}_{0}\right)\right.$ and $\left.2 M_{4}\left(q_{0}\right)\right)$ are of $O\left(\underline{q}_{0}^{4}\right)$, where $\underline{q}_{0}$ is the scattering wave-vector. The expressions for these four terms are

$$
\begin{align*}
& 2 M_{1}\left(q_{0}\right)=\frac{-\left(k_{B} T\right)^{2}}{2 N^{2} M} \sum_{q_{1} q_{2}} \sum_{j_{1} j_{2} j_{3}} \frac{\phi\left(q_{1} j_{1},-q_{1} j_{1}, q_{2} j_{2}-q_{2} j_{2}\right)\left[\underline{q}_{0} \cdot \underline{e}\left(q_{2} j_{2}\right)\right]\left[\underline{q}_{0} \cdot e\left(q_{2} j_{3}\right)\right]}{\omega^{2}\left(q_{1} j_{1}\right) \omega^{2}\left(q_{2} j_{2}\right) \omega^{2}\left(q_{2} j_{3}\right)}  \tag{2.3}\\
& \begin{aligned}
2 M_{2}\left(q_{0}\right)=\frac{\left(k_{B} T\right)^{2}}{2 N^{2} M} \sum_{q_{1} q_{2} q_{3}} \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \phi\left(q_{1} j_{1}, \underline{q}_{2} j_{2}, \underline{q}_{3} j_{3}\right) \\
j_{1} j_{2} j_{3} j_{4}
\end{aligned} \quad \times \phi\left(-\underline{q}_{1} j_{1},-\underline{q}_{2} j_{2}^{\prime},-q_{3} j_{4}\right) \\
& \times \frac{\left[q_{0} \cdot e\left(\underline{q}_{3} j_{3}\right)\right]\left[q_{0} \cdot e\left(\underline{q}_{3} j_{4}\right)\right]}{\omega^{2}\left(\underline{q}_{1} j_{1}\right) \omega^{2}\left(\underline{q}_{2} j_{2}^{\prime}\right) \omega^{2}\left(\underline{q}_{3} j_{3}^{\prime}\right) \omega^{2}\left(\underline{q}_{3} j_{4}^{\prime}\right)} \\
& \begin{array}{r}
2 M_{2}\left(q_{0}\right)=\frac{\left(K_{B} T\right)^{2}}{2 N^{2} M} \sum_{j_{1} \underline{q}_{2} q_{3}} \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \phi\left(\underline{q}_{1} j_{1}, \underline{q}_{2} j_{2}, q_{3} j_{3}^{\prime}\right) \\
\times \phi\left(-\underline{q}_{1} j_{1},-\underline{q}_{2} j_{2}^{\prime},\right.
\end{array} \tag{2.4}
\end{align*}
$$

$$
\begin{align*}
& 2 M_{3}\left(q_{0}\right)=\frac{\left(K_{B} T\right)^{3}}{12 N^{3} M^{2}} \sum_{q_{1} \underline{q}_{2} q_{3} \underline{q}_{4}} \sum_{j, j_{2} j_{3} j_{4}} \Delta\left(q_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right) \\
& \times \phi\left(q_{1} j_{1}, \underline{q}_{2} j_{2}, q_{3} j_{3}, q_{4} j_{4}\right) \\
& \times \frac{\left[\underline{q}_{0} \cdot \underline{e}\left(\underline{q}_{1} j_{i}\right)\right]\left[\underline{q}_{0} \cdot \underline{e}\left(\underline{q}_{2} j_{2}\right)\right]\left[\underline{q}_{0} \cdot e\left(q_{3} j_{3}^{\prime}\right)\right]\left[\underline{q}_{0} \cdot \underline{e}\left(\underline{q}_{4} j_{4}\right)\right]}{\omega^{2}\left(\underline{q} j_{1}\right) \omega^{2}\left(\underline{q}_{2} j_{2}^{\prime}\right) \omega^{2}\left(\underline{q}_{3} j_{3}^{\prime}\right) \omega^{2}\left(\underline{q}_{4} j_{4}^{\prime}\right)} \\
& 2 M_{4}\left(\underline{q}_{0}\right)=\frac{-\left(k_{B T}\right)^{3}}{4 N^{3} M^{2}} \sum_{q_{1} q_{2} q_{3}} \sum_{j_{1} j_{2} j_{3}} \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \Delta\left(-q_{1}+\underline{q}_{5}+q_{6}\right)  \tag{2.5}\\
& x \phi\left(q_{1} j_{1}, q_{2} j_{2}, q_{3} j_{3}^{\prime}\right) \phi\left(-q_{1} j_{1}, q_{5} j_{5}, q_{6} j_{6}\right) \\
& x \frac{\left[q_{0} \cdot e\left(q_{2} j_{2}\right)\right]\left[q_{0} \cdot e\left(q_{3} j_{3}\right)\right]\left[q_{0} \cdot e\left(q_{5} j_{5}\right)\right]\left[q_{0} \cdot e\left(q_{6} \cdot j_{6}\right)\right]}{\omega^{2}\left(q_{1} j_{1}\right) \omega^{2}\left(q_{2} j_{2}\right) \omega^{2}\left(q_{3} j_{3}\right) \omega^{2}\left(q_{5} j_{5}\right) \omega^{2}\left(q_{6} j_{6}^{\prime}\right)} \tag{2.6}
\end{align*}
$$

where, in Eqs. (2.4), (2.5) and (2.6) the delta function $\Delta\left(\underline{q}_{1}+\underline{q}_{2}+\cdots \underline{q}_{n}\right)$, which conserves the sum of the phonon wave vectors, has the following meaning

$$
\begin{align*}
\Delta\left(\underline{q}_{1}+\underline{q}_{2}+\cdots+q_{n}\right) & =1 \quad \text { if }\left(q_{1}+q_{2}+\cdots \underline{q}_{n}\right)=0 \text { or, } \tau \\
& =0 \quad \text { otherwise } \tag{2.7}
\end{align*}
$$

where $\tau$ is a vector of the reciprocal lattice; the function $\phi\left(q_{1} j_{1}, q_{2} j_{2}, \cdots \underline{q}_{n} j_{n}\right) \quad$ which is the Fourier transform of the atomic force constant $\phi_{\alpha_{1} \alpha_{2} \alpha_{3} \ldots \alpha_{n}}(\ell)$, is defined as

$$
\begin{align*}
& \phi\left(\underline{q}_{1} j_{i}^{\prime}, \underline{q}_{2} j_{2}^{\prime}, \ldots \underline{q}_{n} j_{n}\right)=\frac{1}{2 M^{n / 2}} \sum_{\underline{l}}^{1} \sum_{\alpha_{1} \alpha_{2} \cdot \alpha_{n}} \phi_{\alpha_{1} \alpha_{2}} \ldots \alpha_{n}^{(l)} \\
& \times e_{\alpha_{1}}\left(\underline{q}_{1} j_{1}\right) e_{\alpha_{2}}\left(q_{2} j_{2}\right) \cdots e_{\alpha_{n}}\left(q_{n} j_{n}\right) \\
& x\left(1-e^{-i \underline{q}_{1} \cdot \underline{r}_{l}}\right)\left(1-e^{-i \xi_{2} \cdot \xi_{k}}\right) \cdots\left(1-e^{-i \underline{q}_{n} \cdot r_{k}}\right) \tag{2.8}
\end{align*}
$$

The force constant $\phi_{\alpha_{1} \alpha_{2}} \ldots \alpha_{n}(\ell)$ is the $n^{\text {th }}$ tensor derivative of the two-body potential $\phi(\ell)$ with respect to atomic displacements $\underline{u}^{\ell}$ and evaluated at the equilibrium position $\underline{u}^{\ell}=0$. That is,

$$
\begin{equation*}
\phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(l)=\left.\frac{\partial^{n} \phi\left(\left|\underline{\Omega}_{l}+\underline{u}^{l}\right|\right)}{\partial u_{\alpha_{1}}^{l} \partial u_{\alpha_{2}}^{l} \ldots \cdot \partial u_{\alpha_{n}}^{l}}\right|_{\underline{u}^{l}=0} \tag{2.9}
\end{equation*}
$$

Isolating the $\ell$ dependent terms and the corresponding sum over $\ell$ in Eq. (2.8), we can define the following function

$$
\begin{align*}
\Phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}\left(\underline{q}_{1}, q_{2}, \ldots \underline{q}_{n}\right) & =\sum_{\underline{l}}^{\prime} \phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(l)\left(1-e^{-i \underline{q}_{1} \cdot \underline{r}_{l}}\right) \\
& \times\left(1-e^{-i \underline{q}_{2} \cdot \tilde{r}_{l}}\right) \ldots\left(1-e^{-i \underline{q}_{n} \cdot r_{l}}\right) \tag{2.10}
\end{align*}
$$

We can now express Eq. (2.8) in terms of Eq. (2.10) and this expression is

$$
\begin{aligned}
\phi\left(\underline{q}_{1} \dot{j}_{1}, \underline{q}_{2} j_{2}, \cdots \underline{q}_{n} j_{n}\right) & =\frac{1}{2 M^{n / 2}} \sum_{\alpha_{1} \alpha_{2} \cdot \alpha_{n}} \Phi_{\alpha_{1} q_{2} \ldots \alpha_{n}}\left(\underline{q}_{1}, \underline{q}_{2}, \cdots \underline{q}_{n}\right) \\
& \times e_{\alpha_{1}}\left(q_{1} j_{1}\right) e_{\alpha_{2}}\left(\underline{q}_{2} j_{2}\right) \ldots e_{\alpha_{n}}\left(\underline{q}_{n} j_{n}\right)
\end{aligned}
$$

In Eqs. (2.8) to (2.11), each of the subscripts $\alpha_{1}, \alpha_{2}, \ldots, \alpha_{n}$ is assigned the values of cartesian components $x, y, z$ and $\sum_{\underline{\underline{Z}}}^{\prime}$ indicates the summation over real lattice vectors excluding the origin point $l=0$.

We note from Eqs. (2.2), (2.3), (2.4), (2.5) and (2.6) that each of the expressions for $2 M_{0}\left(\underline{q}_{0}\right), 2 M_{1}\left(q_{0}\right)_{\text {and }} 2 M_{2}\left(\underline{q}_{0}\right)$ is proportional to $q_{0}^{2}$ whereas $2 M_{3}\left(q_{0}\right)$ and $2 M_{4}\left(q_{0}\right)$ are
proportional to $q_{0}^{4}$. In other words, although $2 M_{3}\left(q_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ are of $O\left(\lambda^{2}\right)$ as are $2 M_{1}\left(\underline{q}_{0}\right)$ and $2 M_{2}\left(\underline{q}_{0}\right)$, their $q_{0}$-dependence is different. For this reason, $2 M_{3}\left(\underline{q}_{0}\right)$ and
$2 \mathrm{M}_{4}\left(\underline{q}_{0}\right)$ are known as anomalous terms.

## 3. SIMPLIFICATION OF THE ANHARMONIC DEBYE-WALLER FACTOR IN TERMS OF DIFFERENT WAVE-VECTOR DEPENDENT TENSORS

As has already been mentioned in section 1, the main purpose of this thesis is to simplify the expressions for Debye-Waller factor in such a way that its evaluation becomes possible for metallic crystals where the interaction potential extends to many neighbours. The expressions of $2 M_{1}\left(q_{0}\right), 2 M_{2}\left(q_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$, in Eqs. (2.3), (2.4), (2.5) and (2.6) respectively, are in terms of $\phi\left(\underline{q}_{1}, \underline{q}_{2} \dot{j}_{2}, \ldots \underline{q}_{n} j_{n}\right)$, and they are more appropriate, from computational point of view, for a short range potential where the summation over $\underline{\ell}$ in Eq. (2.10) is restricted to a few neighbours only. In metallic crystals with small ion cores, where the inter-atomic potential extends to many neighbours, it is very difficult to achieve a decent converged value of $\Phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}\left(\boldsymbol{q}_{1}, \underline{q}_{2} ; \underline{\underline{q}}_{n}\right)$ in Eq. (2.10) by performing the summation over $\underline{l}$. For such crystals, here we derive an alternative set of expressions for $2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(q_{0}\right)$, $2 M_{3}\left(q_{0}\right)$ and $2 M_{4}\left(\varepsilon_{0}\right)$ in terms of the function $F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q})$ which is defined as

$$
\begin{align*}
F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q}) & =\sum_{\underline{l}}^{\prime} \phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{l}) e^{i \underline{q} \cdot r_{n}} \\
& =C F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q})+i S F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q}) \tag{3.1}
\end{align*}
$$

where,

$$
S F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q})=\sum_{\underline{l}}^{\prime} \phi_{\alpha_{1}} \alpha_{2} \ldots \alpha_{n}(l) \sin \left(\underline{q} \cdot \underline{\Omega}_{l}\right)
$$

and

$$
c F_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(\underline{q})=\sum_{\underline{l}}^{\prime} \phi_{\alpha_{1} \alpha_{2} \ldots \alpha_{n}}(l) \cos \left(\underline{q}, \underline{r}_{l}\right)
$$

For our purposes in this thesis, in the calculation of $2 M_{1}\left(\underline{q}_{0}\right)$, $2 M_{2}\left(\underline{q}_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$, only $S F_{\alpha_{1} \alpha_{2} \alpha_{3}}(\underline{q})$ and $C F_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}(\underline{q}) \quad$ are needed. For the sake of simplicity of notation, we set

$$
\begin{equation*}
S F_{\alpha_{1} \alpha_{2} \alpha_{3}}(\underline{q}) \equiv F_{\alpha \beta \gamma}(\underline{q}) \tag{3.4}
\end{equation*}
$$

and

$$
\begin{equation*}
C F_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}(\underline{q}) \equiv F_{\alpha \beta \gamma \delta}(\underline{q}) \tag{3.5}
\end{equation*}
$$

We note from Eqs. (2.4) and (2.6) that each of $2 M_{2}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(q_{0}\right)$ are proportional to $\left|\phi\left(q_{1}, j_{1}, q_{2} j_{2}, q_{3} j_{3}\right)\right|^{2}$. Thus, simplification of $2 M_{2}\left(q_{0}\right)$ and $2 M_{4}\left(q_{0}\right)$ in terms of $F_{\alpha \beta \gamma}(\underline{q})$ is similar to that of $F_{3}$, the cubic anharmonic free energy, which is also proportional to $\left|\phi\left(\underline{q}_{1} j_{1}, \underline{q}_{2} j_{2}, \underline{q}_{3} \dot{j}_{3}\right)\right|^{2}$. Shukla and Taylor (1974) have developed a procedure for the computation of $F_{3}$, where $F_{3}$ has been expressed in terms of $F_{\beta \gamma}(\underline{q})$, and so we will not repeat that derivation again.

Now, from Eqs. (2.3) and (2.5) we see that both of $2 M_{1}\left(\underline{q}_{0}\right)$ and $2 M_{3}\left(\underline{q}_{0}\right)$ are proportional to $\phi\left(\underline{q}_{1} j_{1}, \underline{q}_{2} j_{2}, \underline{q}_{3} j_{3}, \underline{q}_{4} \dot{j}_{4}\right)$, and
$2 M_{3}\left(\underline{q}_{0}\right)$ has a delta function $\Delta\left(q_{1}+q_{2}+\underline{q}_{3}+\underline{q}_{4}\right)$ while in $2 M_{1}\left(\underline{q}_{0}\right)$ the delta function is exactly satisfied. Hence, to avoid repetition, we will derive the expression for $2 M_{3}\left(\underline{q}_{0}\right)$ only as this is more complex of the two.

From Eq. (2.5) we see that $2 M_{3}\left(\underline{q}_{0}\right)$ contains the function $\phi\left(q_{1} j_{1}, q_{2} j_{2}, \underline{q}_{3} j_{3}, q_{4} j_{4}\right)$ which depends on the function $\Phi_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}\left(\underline{q}_{1}, \underline{q}_{2}, \underline{q}_{3}, q_{4}\right)$ through Eq. (2.11). The complete expression for $\Phi_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}\left(\underline{q}_{1}, \underline{q}_{2}, \underline{q}_{3}, \underline{q}_{4}\right)$ from Eq. (2.10) is

$$
\begin{gather*}
\Phi_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}\left(\underline{q}_{1}, q_{2}, \underline{q}_{3}, q_{4}\right)=\sum_{l}^{1} \phi_{\alpha_{1} \alpha_{2} \alpha_{3} \alpha_{4}}(l)\left(1-e^{-i \underline{q}_{1} \cdot r_{l}}\right) \\
\times\left(1-e^{-i \underline{q}_{2} \cdot r_{2}}\right)\left(1-e^{-i \underline{q}_{3} \cdot r_{l}}\right)\left(1-e^{-i \underline{q}_{4} \cdot r_{l}}\right) \tag{3.6}
\end{gather*}
$$

Multiplying the last four factors in Eq. (3.6) we get

$$
\begin{aligned}
& {\left[1-e^{-i \underline{q}_{1} \cdot \tilde{r}_{l}}-e^{-i \underline{q}_{2} \cdot r_{l}}-e^{-i \underline{q}_{3} \cdot \underline{r}_{l}}-e^{-i \underline{q}_{4} \cdot r_{l}}+e^{-i\left(\underline{q}_{1}+\underline{q}_{2}\right) \cdot \underline{r}_{l}}\right.} \\
& +e^{-i\left(\underline{q}_{1}+\underline{q}_{3}\right) \cdot r_{l}}+e^{-i\left(\underline{q}_{1}+\underline{q}_{4}\right) \cdot \underline{r}_{1}}+e^{-i\left(\underline{q}_{2}+\underline{q}_{3}\right) \cdot \underline{r}_{l}}+e^{-i\left(\underline{q}_{2}+\underline{q}_{4}\right) \cdot r_{l}} \\
& +e^{-i\left(\underline{q}_{3}+\underline{q}_{4}\right) \cdot r_{l}}-e^{-i\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \cdot r_{l}}-e^{-i\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{4}\right) \cdot r_{l}} \\
& \left.-e^{-i\left(\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right) \cdot r_{l}}-e^{-i\left(\underline{q}_{1}+\underline{q}_{3}+\underline{q}_{4}\right) \cdot r_{l}}+e^{-i\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right) \cdot \underline{r}_{l}}\right]
\end{aligned}
$$

Due to the presence of the delta function $\Delta\left(\underline{q}_{1}+\underline{\underline{q}}_{2}+\underline{q}_{3}+\underline{q}_{4}\right)$ in $2 M_{3}(\underline{q})$, we make the following replacements in expression (3.7):

$$
\begin{aligned}
& \underline{q}_{3}+\underline{q}_{4}=\tau-q_{1}-q_{2} \\
& \underline{q}_{2}+\underline{q}_{4}=\tau-\underline{q}_{1}-\underline{q}_{3} \\
& \underline{q}_{1}+\underline{q}_{4}=\tau-\underline{q}_{2}-\underline{q}_{3} \\
& \underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}=\tau-\underline{q}_{4} \\
& q_{1}+\underline{q}_{2}+q_{4}=\tau-\underline{q}_{3} \\
& q_{2}+\underline{q}_{3}+\underline{q}_{4}=\tau-\underline{q}_{1} \\
& \underline{q}_{1}+\underline{q}_{3}+\underline{q}_{4}=\tau-\underline{q}_{2} \\
& q_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}=I
\end{aligned}
$$

and then, expression (3.7) becomes

$$
\begin{aligned}
& {\left[2-e^{-i \underline{q}_{1} \cdot \pi_{l}}-e^{-i \underline{q}_{2} \cdot \pi_{l}}-e^{-i \underline{q}_{3} \cdot r_{l}}-e^{-i \underline{q}_{4} \cdot r_{l}}\right.} \\
& +e^{-i\left(\underline{q}_{1}+\underline{q}_{2}\right) \cdot \mu_{l}}+e^{-i\left(\underline{q}_{1}+\underline{q}_{3}\right) \cdot \mu_{l}}+e^{+i\left(\underline{q}_{2}+q_{3}\right) \cdot \mu_{l}} \\
& +e^{-i\left(\underline{q}_{2}+\underline{q}_{3}\right) \cdot \underline{\pi}_{l}}+e^{+i\left(q_{1}+\underline{q}_{3}\right) \cdot \underline{\pi}_{2}}+e^{+i^{i}\left(\underline{q}_{1}+\underline{q}_{2}\right) \cdot \pi_{l}} \\
& \left.-e^{+2 \underline{q}_{4} \cdot \underline{r}_{l}}-e^{+i \underline{q}_{3} \cdot r_{l}}-e^{+i \underline{q}_{1} \cdot r_{l}}-e^{+i \underline{\pi}_{2} \cdot \underline{r}_{l}}\right]
\end{aligned}
$$

Substituting Eq. (3.8) for the last four factors into Eq. (3.6) and then employing Eq. (3.5), we can write Eq. (3.6) in the form

$$
\begin{aligned}
\Phi_{\alpha_{1} \alpha_{2} \alpha_{3 \alpha}}\left(q_{1}, q_{2}, q_{3}, q_{4}\right)= & 2\left[F_{\alpha \beta \gamma \delta}(0)-F_{\alpha \beta \gamma \delta}\left(q_{1}\right)-F_{\alpha \beta \gamma \delta}\left(q_{2}\right)\right. \\
& -F_{\alpha \beta \gamma \delta}\left(q_{3}\right)-F_{\alpha \beta \gamma \delta}\left(q_{4}\right)+F_{\alpha \gamma \delta}\left(q_{1}+q_{2}\right) \\
& \left.+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{3}\right)+F_{\alpha \gamma \delta}\left(q_{2}+q_{3}\right)\right]
\end{aligned}
$$

Substituting Eq. (3.9) into Eq. (2.11), we get

$$
\begin{aligned}
\phi\left(q_{1} j_{1}, q_{2} j_{2}, q_{3} j_{3}, q_{4} j_{4}\right)= & \frac{1}{M^{2}} \sum_{\alpha \beta \gamma \delta} e_{\alpha}\left(q_{1} j_{1}\right) e_{\beta}\left(q_{2} j_{2}\right) e_{\gamma}\left(q_{3} j_{3}\right) e_{\delta}\left(q_{4} j_{4}\right) \\
\times & {\left[F_{\alpha \beta \gamma \delta}(0)-F_{\alpha \beta \gamma \delta}\left(q_{1}\right)-F_{\alpha \beta \gamma \delta}\left(q_{2}\right)-F_{\beta \gamma \delta}\left(q_{3}\right)\right.} \\
& -F_{\alpha \beta \gamma \delta}\left(q_{4}\right)+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{3}\right) \\
& \left.+F_{\alpha \beta \gamma \delta}\left(q_{2}+q_{3}\right)\right]
\end{aligned}
$$

In Eqs. (3.9) and (3.10) we have used $F_{\beta \text { 人rб }}(0)$ which is equivalent to $F_{\alpha \beta \gamma \delta}(\underline{q}=0)$.

Substituting Eq. (3.10) into Eq. (2.5) we obtain

$$
\begin{aligned}
& 2 M_{3}\left(q_{0}\right)=\frac{\left(k_{B T}\right)^{3}}{12 N^{3} M^{4}} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} q_{2} q_{3} q_{4}} \Delta\left(q_{1}+q_{2}+q_{3}+q_{4}\right) \\
& j_{1}^{\prime} j_{2} j_{3} j_{4} \times e_{\alpha}\left(q_{1} j_{1}\right) e_{\beta}\left(q_{2} j_{2}\right) e_{\gamma}\left(q_{3} j_{3}\right) e_{\delta}\left(q_{4} j_{4}\right) \\
& \times \frac{\left[q_{0} \cdot e\left(q_{1} j_{1}\right)\right]\left[\underline{q}_{0} \cdot e\left(q_{2} j_{2}\right)\right]\left[q_{0} \cdot e\left(q_{3} j_{3}\right)\right]\left[q_{0} \cdot e\left(q_{4} j_{4}\right)\right]}{\omega^{2}\left(q_{1} j_{1}\right)} \omega^{2}\left(\underline{q}_{2} j_{2}^{\prime}\right) \\
& \omega^{2}\left(\underline{q}_{3} j_{3}\right) \omega^{2}\left(q_{4} j_{4}\right) \\
& \times\left[F_{\alpha \beta \gamma \delta}(0)-F_{\alpha \beta \gamma \delta}\left(q_{1}\right)-F_{\alpha \beta \gamma \delta}\left(\underline{q}_{2}\right)-F_{\alpha \beta \gamma \delta}\left(q_{3}\right)-F_{\alpha \beta \gamma}\left(q_{4}\right)\right. \\
&+F_{\left.\alpha \beta \gamma \delta\left(q_{1}+q_{2}\right)+F_{\alpha \gamma \delta}\left(q_{1}+q_{3}\right)+F_{\alpha \beta \gamma \delta}\left(q_{2}+q_{3}\right)\right]}
\end{aligned}
$$

Relabelling the wave-vectors in Eq. (3.11), it is seen that, in the square bracket, the $2 n d, 3 r d, 4$ th and 5 th terms are equivalent, and so are the 6 th, 7 th and 8 th terms.

Taking this into account, and using the following notations

$$
\begin{aligned}
& \underline{q}_{0} \cdot e\left(\underline{q}_{1} j_{1}\right)=\sum_{\lambda} \underline{q}_{\lambda} e_{\lambda}\left(q_{1} j_{1}\right) \\
& \underline{q}_{0} \cdot e\left(\underline{q}_{2} j_{2}\right)=\sum \underline{q}_{\mu} e_{\mu}\left(q_{2} j_{2}\right)
\end{aligned}
$$

$$
\begin{aligned}
& \underline{q}_{0} \cdot \underline{e}\left(q_{3} j_{3}\right)=\sum_{\nu} \underline{q}_{0} e_{\nu}\left(\underline{q}_{3} j_{3}\right) \\
& \underline{q}_{0}, \underline{e}\left(\underline{q}_{4} j_{4}\right)=\sum_{\epsilon} \underline{q}_{\epsilon} e_{\epsilon}\left(\underline{q}_{4} j_{4}\right)
\end{aligned}
$$

Eq. (3.11) can be written as

$$
\begin{equation*}
2 M_{3}\left(q_{0}\right)=\frac{\left(k_{B} T\right)^{3}}{12 N^{3} M^{4}} \sum_{\lambda \mu \nu \epsilon} q_{\lambda} q_{0} q_{\mu} q_{0} N_{\lambda \mu \nu \epsilon}^{c} \tag{3.12}
\end{equation*}
$$

where

$$
\begin{align*}
N_{N \mu \nu \in}^{c}= & \sum_{\alpha \beta \gamma \delta} \sum_{j_{1} q_{1} q_{2} q_{3} q_{4} q_{3} j_{4}} \times\left(\frac{e_{\alpha} e_{1}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\nu}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{0} e_{\epsilon}}{\omega^{2}}\right)_{q_{4} j_{4}} \\
& \times\left[F_{\alpha \beta \gamma \delta}(0)-4 F_{\alpha \beta \gamma}\left(q_{1}\right)+3 F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)\right]
\end{align*}
$$

Similar expressions for $2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ in terms of $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(q)$ are

$$
\begin{equation*}
2 M_{1}\left(q_{0}\right)=\frac{-\left(K_{B} T\right)^{2}}{N^{2} M^{3}} \sum_{\lambda \mu} q_{0} q_{o_{\mu}} N_{\lambda \mu}^{A} \tag{3.14}
\end{equation*}
$$

where,

$$
\begin{aligned}
& \times\left[F_{\alpha \beta \gamma \delta}(0)-F_{\alpha \beta \gamma \delta}\left(q_{1}\right)-F_{\alpha \beta \gamma \delta}\left(q_{2}\right)+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)\right]
\end{aligned}
$$

$$
\begin{equation*}
2 M_{2}\left(q_{0}\right)=\frac{\left(K_{B} T\right)^{2}}{2 N^{2} M^{4}} \sum_{\delta \epsilon} q_{0} q_{0} \in N_{\delta \epsilon}^{B} \tag{3.15}
\end{equation*}
$$

where

$$
\begin{aligned}
& N_{\delta \in}^{B}=\sum_{q_{1} q_{2} q_{3}} \sum_{\alpha \beta \gamma} \Delta\left(q_{1}+q_{2}+q_{3}\right)
\end{aligned}
$$

$$
\begin{align*}
& x\left[F_{\alpha \beta \gamma}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right)\right]\left[F_{\lambda \mu \nu}\left(q_{1}\right)+F_{\mu \mu \nu}\left(q_{2}\right)+F_{\mu \nu \nu}\left(q_{3}\right)\right] \\
& 2 M_{4}\left(q_{0}\right)=\frac{-\left(K_{B} T\right)^{3}}{4 N^{3} M^{5}} \sum_{\epsilon \eta \xi \xi} q_{\theta} q_{0} q_{0} q_{0} N_{\in \eta \xi \xi}^{D} \tag{3.17}
\end{align*}
$$

where

$$
\begin{aligned}
& N_{\in \eta \xi\}}^{D}=\sum_{\substack{q_{1} q_{2} q_{3} \\
j_{1}^{\prime} j_{2}^{\prime} j_{3} j_{5} q_{6} j_{6}}} \sum_{\alpha \beta \gamma} \Delta\left(\underline{q}_{1}+q_{2}+q_{3}\right) \Delta\left(-q_{1}+q_{5}+q_{6}\right) \\
& \times\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\epsilon} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\eta} e_{\gamma}}{w^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{j} e_{\mu}}{\omega^{2}}\right)_{q_{5} j_{5}}\left(\frac{e_{5} e_{\nu}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& x\left[F_{\alpha \beta \gamma}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right)\right] \\
& \times\left[F_{\lambda \mu \nu}\left(q_{5}\right)+F_{\lambda \mu \nu}\left(q_{6}\right)-F_{\lambda \mu \nu}\left(q_{1}\right)\right]
\end{aligned}
$$

The superscripts A, B, C and D over $N$ are used for some identification purposes only and they do not bear any physical significance.
4. THE ANHARMONIC CONTRIBUTION TO THE DEBYE-WALLER FACTOR FOR CUBIC CRYSTALS

Expressions of $2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(\underline{q}_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$, given by equations (3.12) to (3.19) are true for any crystal.

Symbolically, they can be written as

$$
\begin{align*}
& 2 M_{1}\left(\underline{q}_{0}\right)  \tag{4.1}\\
& \left.\begin{array}{c}
\text { or } \\
2 M_{2}\left(\underline{q}_{0}\right)
\end{array}\right\}=\sum_{\alpha \beta} q_{0} q_{0} Z_{\alpha \beta}^{1 \text { or } 2}  \tag{4.2}\\
& \left.\begin{array}{l}
2 M_{3}\left(\underline{q}_{0}\right) \\
\text { or } \\
2 M_{4}\left(\underline{q}_{0}\right)
\end{array}\right\}=\sum_{\alpha \beta \gamma \delta} q_{\alpha} q_{\beta} q_{0} q_{0} q_{0} Z_{\alpha \beta \gamma \delta}^{3 \text { or } 4}
\end{align*}
$$

In general, for any crystal system, the calculation of $2 M_{1}\left(\underline{q}_{0}\right)$ or $2 M_{2}\left(\underline{q}_{0}\right)$ will require the computation of nine components of $Z_{\alpha \beta}^{10 r} 2$, and the calculation of $2 M_{3}\left(q_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ will require the computation of eighty-one components of $Z_{\alpha \beta \gamma \delta,}^{30 \pi} 4$, and this indeed is a prohibitive task. For cubic crystals, the second and fourth rank tensors $Z_{\alpha \beta}^{1 \text { or } 2}$ and $Z_{\alpha \beta \gamma \delta}^{30 \% 4}$ respectively, can be reduced considerably.

For example, we take the expression for $2 M_{1}\left(\underline{q}_{0}\right)$ or $2 M_{2}\left(\underline{q}_{0}\right)$ in Eq. (4.1) which can be written as

$$
\begin{aligned}
& +q_{0} q_{0}\left[z_{x z}^{10 r 2}+z_{z x}^{\text {10r } 2}\right]+q_{0} q_{0}\left[z_{y z}^{\text {or } 2}+z_{z y}^{10 r 2}\right]
\end{aligned}
$$

If $2 M_{1}\left(\underline{q}_{0}\right)$ and $2 M_{2}\left(\underline{q}_{0}\right)$ represent the contributions to $2 M\left(q_{0}\right)$ for a cubic crystal, they will remain invariant under all the forty-eight symmetry operations of a cube applied on the wavevector $\underline{q}_{0} \cdot z_{\alpha \beta}^{10 \pi 2}$ will also remain unchanged since it is independent of $\underline{q}_{0}$.

The application of one four-fold rotation on the wave-vector $\underline{q}_{0}$ about the $x$-axis changes $q_{o y}$ to $q_{0 z}, q_{0 z}$ to $-q_{o y}$, and changes the Eq. (4.3) into the following

$$
\left.\begin{array}{l}
2 M_{1}\left(q_{0}\right) \\
\quad \text { or } \\
2 M_{2}\left(q_{0}\right)
\end{array}\right\}=q_{0 x}^{2} z_{x x}^{10 \pi 2}+q_{0}^{2} z_{y y}^{10 r 2}+q_{0 y}^{2} z_{z z}^{1002}+q_{0} q_{x}\left[z_{x y}^{10 \pi 2}+z_{y x}^{10 \pi 2}\right]
$$

The application of another four-fold rotation on the wave-vector $q_{0}$ about the $y$-axis changes $q_{o_{Z}}$ to $q_{x}, q_{0}$ to $-q_{0}$, and the Eq. (4.3) into the following


In a similar manner, the application of one four-fold rotation about the $z$-axis changes $q_{o_{x}}$ to $q_{o_{y}}, \varepsilon_{o y}$ to $-\varepsilon_{o_{x}}$, and for Eq. (4.3) we have

Comparing the coefficients of different components of $\underline{q}_{0}$ in Eq. (4.3), (4.4), (4.5) and (4.6) we see that

$$
\begin{align*}
& Z_{x x}^{\operatorname{lor} 2}=Z_{y y}^{10 \pi 2}=Z_{z z}^{\text {ore } 2} \\
& z_{x y}^{10 \pi 2}+z_{y x}^{1 \text { or } 2}=0 \\
& z_{y Z}^{\text {dor } 2}+z_{z Y}^{\text {dor } 2}=0 \\
& z_{x z}^{10 r 2}+z_{z x}^{10 x^{2}}=0 \tag{4.7}
\end{align*}
$$

Employing the relations given by Eq. (4.7), Eq. (4.1) reduces to

$$
\left.\begin{array}{c}
2 M_{1}\left(\underline{q}_{0}\right)  \tag{4.8}\\
\text { or } \\
2 M_{2}\left(\underline{q}_{0}\right)
\end{array}\right\}=\left(q_{0 x}^{2}+q_{0 y}^{2}+q_{0}^{2}\right) z_{x x}^{1 \text { or } 2}
$$

or, in full form, the expressions for $2 M_{1}\left(q_{0}\right)$ and $2 M_{2}\left(q_{0}\right)$ for cubic crystals can be written from Eqs. (3.14) and (3.16) as

$$
\begin{align*}
& 2 M_{1}\left(q_{0}\right)=\frac{-\left(K_{B} T\right)^{2}}{N^{2} M^{3}}\left(q_{0 x}^{2}+q_{0 y}^{2}+q_{0}^{2}\right) N_{0}^{A} \\
& 2 M_{2}\left(q_{0}\right)=\frac{\left(K_{B} T\right)^{2}}{2 N^{2} M^{4}}\left(q_{0 x}^{2}+q_{0 y}^{2}+q_{0}^{2}\right) N_{0}^{B} \tag{4.9}
\end{align*}
$$

where $\quad N_{0}^{A}=N_{x x}^{A}=N_{y y}^{A}=N_{Z Z}^{A}$
or, $\quad N_{0}^{A}=\frac{1}{3}\left[N_{x X}^{A}+N_{y y}^{A}+N_{z Z}^{A}\right]$
and $\quad N_{0}^{B}=N_{x x}^{B}=N_{y y}^{B}=N_{z z}^{B}$
or,

$$
\begin{equation*}
N_{0}^{B}=\frac{1}{3}\left[N_{x x}^{B}+N_{y y}^{B}+N_{z z}^{B}\right] \tag{4.12}
\end{equation*}
$$

Substituting for $N_{X x}^{A}, N_{y y}^{A}$ and $N_{Z Z}^{A}$ from Eq. (3.15) into Eq. (4.11) we obtain

$$
\begin{aligned}
& N_{0}^{A}=\frac{1}{3} \sum_{\underline{q}_{1} \underline{q}_{2}} \sum_{j_{1} j_{2} j_{3}} \sum_{\alpha \beta \gamma \delta}\left(\frac{e_{\alpha} e_{\beta}^{*}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\gamma}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{q}^{*}}{\omega^{2}}\right)_{\underline{q}_{2} j_{3}} \\
& \quad \times\left[e_{x}\left(q_{2} j_{2}\right) e_{x}\left(q_{2} j_{3}\right)+e_{y}\left(q_{2} j_{2}\right) e_{y}\left(q_{2} j_{3}\right)+e_{z}\left(q_{2} j_{2}\right) e_{z}\left(q_{2} j_{3}\right)\right] \\
& \quad \times\left[F_{\alpha \beta \gamma \delta}(0)-F_{\beta \gamma \gamma}\left(q_{1}\right)-\sigma_{\beta \gamma \delta}\left(q_{2}\right)+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)\right]
\end{aligned}
$$

But

$$
\begin{equation*}
\left[e_{x}\left(q_{2} j_{2}\right) e_{x}\left(\underline{q}_{2} j_{3}\right)+e_{y}\left(q_{2} j_{2}\right) e_{y}\left(q_{2} j_{3}\right)+e_{z}\left(q_{2} j_{2}\right) e_{z}\left(q_{2} j_{3}\right)\right]=\delta_{j_{2}} j_{3} \tag{4.14}
\end{equation*}
$$

Performing the summation over $j_{3}$ in Eq. (4.13) with the help of Eq. (4.14), we get

$$
\begin{align*}
N_{0}^{A} & =\frac{1}{3} \sum_{\bar{q}_{1}^{\prime} q_{2}} \sum_{\alpha \beta \gamma \delta}\left(\frac{e_{\alpha} e_{\beta}^{*}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\gamma} e_{\delta}^{*}}{\omega^{4}}\right)_{q_{2} j_{2}} \\
& \times\left[F_{\alpha \beta \gamma \delta}(0)-F_{\alpha \beta \gamma \delta}\left(q_{1}\right)-F_{\alpha \beta \gamma \delta}\left(q_{2}\right)+F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)\right] \tag{4.15}
\end{align*}
$$

Similarly, substituting for $N_{x x}^{B}, N_{y y}^{B}$ and $N_{z z}^{B}$ from Eq. (3.17) into Eq. (4.12), and using Eq. (4.14), we obtain

$$
\begin{aligned}
& N_{0}^{B}=\frac{1}{3} \sum_{\substack{q_{1} q_{2} q_{3} \\
j_{1} j_{2} j_{3}}} \sum_{\substack{\alpha \beta \nu}} \Delta\left(q_{1}+q_{2}+q_{3}\right)\left(\frac{e_{\alpha} e^{*}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{2}}{\omega^{4} \underline{q}_{3} j_{3}}\right. \\
& X\left[F_{\alpha \beta \gamma}\left(\underline{q}_{1}\right)+E_{\beta \gamma \gamma}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right)\right]\left[F_{\lambda \mu \nu}\left(q_{1}\right)+F_{\mu \nu}\left(\underline{q}_{2}\right)+F_{\mu \nu \nu}\left(\underline{q}_{3}\right)\right]
\end{aligned}
$$

Following the same procedure as has been used in the derivation of equation (4.8), and after some lengthy algebra, we find the following relationship among the components of the fourth rank tensor $Z_{\alpha \beta \gamma \delta}^{30 r 4}$ : $z_{x \times x \times x}^{3 \text { on } 4}=z_{y y y y}^{3 \text { or } 4}=Z_{z z z z}^{3 \text { or } 4}$
$\left\{z_{\text {xxyy }}^{3 \text { or } 4}\right\}=\left\{z_{x x z z}^{3 \text { or } 4}\right\}=\left\{z_{y \text { oz }}^{3 \text { or } 4}\right\}$
$\left\{z_{x x \times y}^{3 \text { or } 4}\right\}=\left\{\begin{array}{c}3 \text { or } 4 \\ x \times x z\end{array}\right\}=\left\{z_{y \text { pyx }}^{3 \text { or } 4}\right\}=\left\{z_{y \text { byz }}^{3 \text { or } 4}\right\}$
$=\left\{z_{z z z x}^{3 \operatorname{or} 4}\right\}=\left\{z_{z z z y}^{3 \text { or } 4}\right\}=0$
$\left\{z_{x x y z}^{3 \text { or } 4}\right\}=\left\{z_{y y x z}^{3 \text { or } 4}\right\}=\left\{z_{z z x y}^{3 \text { or } 4}\right\}=0$

In these equations, the curly brackets $\{\quad\}$ indicate the sum of all the tensors obtained by permuting the explicit cartesian components of the tensor under consideration. Explicitly it is given by

$$
\begin{align*}
\left\{z_{x x y y}^{3}\right\}=z_{x x y y}^{3}+z_{y y x x}^{3} & +z_{x y y x}^{3}+z_{y x x y}^{3} \\
& +z_{x y x y}^{3}+z_{y x y x}^{3} \tag{4.18}
\end{align*}
$$

Making use of the relations given by equation (4.17), equation (4.2) takes the following form

$$
\left.\begin{array}{l}
\left.2 M_{3}\left(q_{0}\right)\right\}=\left(q_{0}^{4}+q_{0 y}^{4}+q_{0 z}^{4}\right) z_{x x x x}^{3 \text { or } 4}  \tag{4.19}\\
2 M_{4}\left(\underline{q}_{0}\right)
\end{array}\right\} \begin{aligned}
& +\left(q_{0}^{2} q_{0 y}^{2}+q_{0}^{2} q_{0}^{2}+q_{0 y}^{2} q_{0}^{2}\right)\left\{z_{x x y y}^{3 \text { or }}\right\}
\end{aligned}
$$

Or, with all the factors put in, the complete form of $2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ for cubic crystals can be written as (from Eqs. (3.12) and (3.18))

$$
2 M_{3}\left(q_{0}\right)=\frac{\left(K_{B} T\right)^{3}}{12 N^{3} M^{4}}\left[N_{x \times x x}^{c}\left(q_{0 x}^{4}+q_{0 y}^{4}+q_{0}^{4}\right)\right.
$$

$$
\begin{equation*}
\left.+\left\{N_{x x y y}^{c}\right\}\left(q_{x}^{2} q_{0}^{2}+q_{0}^{2} q_{0}^{2}+q_{0}^{2} q_{0}^{2}\right)\right] \tag{4.20}
\end{equation*}
$$

$$
2 M_{4}\left(q_{0}\right)=\frac{-\left(K_{B} T\right)^{3}}{4 N^{3} M^{5}}\left[N_{x \times x x}^{D}\left(q_{0}^{4}+q_{0}^{4}+q_{0 z}^{4}\right)\right.
$$

$$
\begin{equation*}
\left.+\left\{N_{x x y y}^{D}\right\}\left(q_{x}^{2} q_{0}^{2}+q_{x}^{2} q_{0}^{2}+q_{0}^{2} q_{0}^{2}\right)\right] \tag{4.21}
\end{equation*}
$$

The expressions for $N_{X x X X}^{C}$ and $N_{X x Y Y}^{C}$ are obtained by first putting $\quad \lambda=\mu=\nu=\epsilon=X$ and then putting $\lambda=\mu=x$ and $\nu=\epsilon=y$ in Eq. (3.13). These expressions are

$$
\begin{align*}
& N_{x x x x}^{c}=\sum_{\substack{\alpha \gamma \delta \\
q_{1} q_{2} q_{3} q_{4}}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{\underline{q}_{3} j_{3}}\left(\frac{e_{x} e_{z}}{\omega^{2}}\right)_{q_{4} j_{4}} \\
& \bar{j}_{1} \bar{j}_{2} \bar{j}_{3} \bar{j}_{4} \\
& x \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right)\left[E_{\beta \gamma \delta}(0)-4 F_{\alpha \gamma \delta}\left(\underline{q}_{1}\right)+3 F_{\alpha \beta \gamma \delta}\left(\underline{q}_{1}+\underline{q}_{2}\right)\right] \tag{4.22}
\end{align*}
$$

and

$$
\begin{align*}
& N_{x x y y}^{c}=\sum_{\alpha \beta \gamma \delta}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{y} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{y} e_{\delta}}{w^{2}}\right)_{q_{4} j_{4}} \\
& j_{1} \dot{q}_{3} q_{4} j_{3} j_{4} \\
& x \Delta\left(q_{1}+\underline{q}_{2}+q_{3}+q_{4}\right)\left[F_{\alpha \beta \gamma \delta}(0)-4 F_{\alpha \beta \gamma \delta}\left(\underline{q}_{1}\right)+3 F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)\right] \tag{4.23}
\end{align*}
$$

Expressions for other tensors in $\left\{N_{x x y y}^{c}\right\}$ are obtained in a similar manner as in Eq. (4.23).

Similarly, expressions for $N_{x \times x x}^{D}$ and $N_{x \times y y}^{D}$ are obtained by first putting $\epsilon=\eta=\xi=\xi=x$ and then putting $\epsilon=\eta=x$ and $\xi=\xi=\mathrm{y}$ in Eq. (3.19). These expressions are

$$
\begin{aligned}
N_{x \times x x} & =\sum_{\frac{q_{1} q_{2} q_{3}}{} \sum_{q_{5} q_{6}} \sum_{\alpha \beta \gamma}^{j_{1} j_{2} j_{3} j_{5} j_{6}} \Delta\left(q_{1}+q_{2}+q_{3}\right) \Delta\left(-q_{1}+q_{5}+q_{6}\right)} \\
& \times\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{x} e_{\mu}}{\omega^{2}}\right)_{q_{5 j}}\left(\frac{e_{x} e_{\nu}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& x\left[F_{\alpha \beta \gamma}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right)\right]\left[F_{\lambda \mu \nu}\left(q_{5}\right)+F_{\mu \nu}\left(\underline{q}_{6}\right)-F_{\mu \nu \nu}\left(q_{1}\right)\right]
\end{aligned}
$$

and

$$
\begin{aligned}
N_{x x y y}^{D}= & \sum_{\substack{q_{1} q_{2} q_{3}}} \sum_{\dot{q}_{5} q_{6}} \sum_{\alpha \beta \gamma} \Delta\left(q_{1}+q_{2}+q_{3}\right) \Delta\left(-\underline{q}_{1}+\underline{q}_{5}+q_{6}\right) \\
& x\left(\frac{e_{\alpha} e_{j}}{\omega^{2}}\right)_{q_{j} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{y} e_{\mu}}{\omega^{2}}\right)_{q_{5 j}}\left(\frac{e_{y} e_{\nu}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& x\left[F_{\alpha \beta \gamma}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right)\right]\left[F_{\mu \mu \nu}\left(q_{5}\right)+F_{\mu \nu \nu}\left(q_{6}\right)-F_{\mu \nu}\left(q_{1}\right)\right]
\end{aligned}
$$

Expressions for other tensors in $\left\{N_{x x y y}^{D}\right\} \quad$ can be obtained in the same manner as in Eq. (4.25).

## 5. SIMPLIFICATION OF DEBYE-WALLER FACTOR FOR CUBIC CYRSTALS FROM THE NUMERICAL POINT OF VIEW

From Eq. (4.9), (4.10), (4.20) and (4.21) of section 4, we see that the calculations of $2 M_{1}\left(\underline{q}_{0}\right)$ and $2 M_{2}\left(\underline{q}_{0}\right)$ require the knowledge of $N_{0}^{A}$ and $N_{0}^{B}$ respectively, the calculation of $2 M_{3}\left(q_{0}\right)$ requires the knowledge of $N_{x x \times x}^{c}$ and $\left\{N_{x x y y}^{c}\right\}$, and the calculation of $2 \mathrm{M}_{4}\left(\underline{q}_{0}\right)$ requires the knowledge of $N_{\times \times \times \times}^{D}$ and $\left\{N_{x x y y}^{D}\right\}$. The expressions for $N_{0}^{A}, N_{0}^{B}, N_{x x x x}^{C}$, $\left\{N_{x x y y}^{C}\right\}, \quad N_{x X x X}^{D} \quad$ and $\left\{N_{x X y Y}^{D}\right\}$, as presented in Eq. (4.15), (4.16), (4.22), (4.23), (4.24) and (4.25) are not suitable for numerical calculation because of the presence of multiple Brillouin zone sums (ie. $q$ sums) and the delta functions in them. However, we can derive more suitable expressions from the numberical viewpoint where only single Brillouin zone sums are involved and the delta functions are removed.

To factorize these multiple Brillouin zone sums, we will use the following plane-wave representation of the delta function $\Delta\left(\underline{q}_{1}+\underline{q}_{2}+\cdots+\underline{q}_{n}\right)$ :

$$
\begin{equation*}
\Delta\left(q_{1}+\underline{q}_{2}+\cdots+\underline{q}_{n}\right)=\frac{1}{N} \sum_{\underline{\leq}} e^{i\left(\underline{q}_{1}+\underline{q}_{2}+\cdots+\underline{q}_{n}\right) \cdot \underline{q}_{l}} \tag{5.1}
\end{equation*}
$$

Also, as will be seen later, we require the following seven types of Brillouin zone sums, viz.,

$$
\begin{equation*}
H_{\alpha \beta}(\underline{l})=\sum_{q j^{j}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{\underline{j} j} \cos \left(\underline{q} \cdot \underline{r}_{l}\right) \tag{5.2}
\end{equation*}
$$

$$
\begin{align*}
& T_{\alpha \beta}(\underline{l})=\sum_{\underline{q} j^{\prime}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{4}}\right)_{\underline{q} j^{\prime}} \cos \left(\underline{q} \cdot \underline{\pi}_{\rho}\right) \\
& A_{\alpha \beta \gamma \delta}(\underline{l})=\sum_{\underline{q}} F_{\alpha \beta \gamma \delta}(\underline{q}) \cos \left(\underline{q}, \underline{\pi}_{l}\right) \\
& B_{\beta \gamma_{0} \mu \nu}(\underline{l})=\sum_{\frac{q}{\alpha} j_{\lambda}^{\prime}}\left(\frac{e_{\alpha,}^{e}}{\omega^{2}}\right)_{q j} F_{\alpha \beta \gamma}(\underline{q}) F_{\lambda \mu \nu}(\underline{q}) \cos \left(\underline{q}, \underline{r}_{l}\right)  \tag{5.5}\\
& C_{\beta \gamma, \mu \nu}(\underline{l})=\sum_{\alpha_{j} j}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{4}}\right)_{q_{j}} F_{\alpha \gamma \gamma}(\underline{q}) F_{\lambda \mu \nu}(\underline{q}) \cos \left(\underline{q}, \pi_{l}\right)  \tag{5.6}\\
& D_{\lambda \beta \gamma}(\underline{l})=\sum_{\frac{q j}{\alpha}}\left(\frac{e_{\alpha} e_{j}}{\left.\omega^{2}\right)_{q j}} F_{\alpha \beta \gamma}(q) \sin \left(\underline{q}, \underline{r}_{l}\right)\right.  \tag{5.7}\\
& E_{\lambda \beta \gamma}(\underline{l})=\sum_{\frac{q}{\alpha} j^{\prime}}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{4}}\right)_{q_{j},} F_{\alpha \beta \gamma}(\underline{q}) \sin \left(\underline{q}, \underline{\pi}_{l}\right) \tag{5.8}
\end{align*}
$$

$$
G_{\lambda \beta \gamma \delta}(\underline{l})=\sum_{\frac{q}{\alpha}}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{q j} F_{\alpha \beta \gamma \delta}(\underline{q}) \cos \left(\underline{q}, \underline{\varepsilon}_{\ell}\right)
$$

The harmonic contribution to the Debye-Waller factor, defined in Eq. (2.2), can also be expressed in terms of $H_{\alpha \beta}(\underline{l})$.

### 5.1 SIMPLIFICATION OF $2 \mathrm{M}_{0}\left(\mathrm{q}_{0}\right)$

Employing the following relation for the components of the eigenvectors $e(q j)$,

$$
e_{x}^{2}(q j)+e_{y}^{2}(q j)+e_{z}^{2}(q j)=1
$$

Eq. (2.2) can be written as
$2 M_{0}\left(q_{0}\right)=q_{0}^{2} \frac{K_{B} T}{3 N M} \sum_{q_{j}} \frac{\left[e_{x}^{2}\left(q_{j}\right)+e_{y}^{2}\left(q_{j}\right)+e_{z}^{2}\left(q_{j}\right)\right]}{\omega^{2}(\underline{q})}$
which, employing Eq. (5.2) can be expressed in terms of $H_{\alpha \beta}(0)$ as

$$
=q_{0}^{2} \frac{k_{B} T}{3 M}\left[H_{x x}(0)+H_{y y}(0)+H_{z z}(0)\right]
$$

where

$$
\begin{equation*}
H_{\alpha \beta}(0) \equiv H_{\alpha \beta}(\underline{l}=0) . \tag{5.10}
\end{equation*}
$$

Eq. (5.10) can also be written as

$$
\begin{equation*}
2 M_{0}\left(\underline{q}_{0}\right)=q_{0}^{2} \frac{k_{B T}}{M} N_{H} \tag{5.11a}
\end{equation*}
$$

where

$$
N_{H}=\frac{1}{3}\left[H_{x x}(0)+H_{y y}(0)+H_{z z}(0)\right]
$$

5.2 SIMPLIFICATION OF $2 \mathrm{M}_{1}\left(\mathrm{q}_{\mathrm{o}}\right)$

Equation (4.15) can be written as

$$
N_{0}^{A}=N_{0}^{A(1)}+N_{0}^{A(2)}+N_{0}^{A(3)}+N_{0}^{A} \text { (4) }
$$

where

$$
N_{0}^{A(1)}=\frac{1}{3} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} j_{1}}\left(\frac{e_{\alpha} e_{\beta}}{w^{2}}\right)_{q_{1} j_{1}} \sum_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\delta}}{\omega^{4}}\right)_{q_{2 j} j_{2}} F_{\alpha \beta \gamma \delta} \text { (0) }
$$

$$
\begin{equation*}
N_{0}^{A(2)}=\frac{-1}{3} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} j_{1}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{q_{1} j_{1}} F_{\alpha \beta \gamma \varepsilon}\left(\underline{q}_{1}\right) \sum_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\delta}}{\omega^{4}}\right)_{q_{2} j_{2}} \tag{5.13}
\end{equation*}
$$

$$
\begin{align*}
& N_{0}^{A(3)}=\frac{-1}{3} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} j_{1}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{q_{i j} j_{1}} \sum_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\delta}}{\omega^{4}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(q_{2}\right)  \tag{5.14}\\
& N_{0}^{A(4)}=\frac{1}{3} \sum_{\alpha \beta \gamma \delta} \sum_{\substack{q_{1} q_{2} \\
j_{1} j_{2}}}\left(\frac{e_{1} e_{\beta}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\gamma} e_{\delta}}{\left.\omega^{4}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(q_{1}+q_{2}\right)} .\right. \tag{5.15}
\end{align*}
$$

Using Eqs. (5.2) and (5.3), Eq. (5.13) can be written as

$$
N_{0}^{A(1)}=\frac{N^{2}}{3} \sum_{\alpha \beta \gamma \delta} H_{\alpha \beta}(0) T_{\gamma \delta}(0) F_{\alpha \beta \gamma \delta}(0)
$$

where $T_{\alpha \beta}(0) \equiv T_{\alpha \beta}(\underline{l}=0)$.

Although the $\underline{q}_{1}$ and $\underline{q}_{2}$ sums are already factorized in Eqs. (5.14) and (5.15) we can simplify the expressions further in terms of $H_{\alpha \beta}(l), T_{\alpha \beta}(l)$ etc., by introducing the following identity

$$
\begin{aligned}
& \sum_{q_{1} j_{1}}\left(\frac{e_{\alpha} e_{\beta}}{w^{2}}\right)_{q_{1} j_{1}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{1}\right) \\
& \equiv \sum_{q_{1}, \dot{q}_{n}}\left(\frac{e_{\alpha} e_{\beta}}{w^{2}}\right)_{q_{i}, j} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \Delta\left(q_{1}-\underline{q}_{n}\right)
\end{aligned}
$$

or, using Eq. (5.1) we get

$$
\begin{aligned}
& =\frac{1}{N} \sum_{\underline{l}} \sum_{\varepsilon_{1} j_{1}, \underline{q}_{n}}\left(\frac{\varepsilon_{\alpha} e_{\beta}}{\omega^{2}}\right)_{\underline{q}_{1} \dot{j}_{1}} F_{\alpha \beta \gamma}\left(\underline{q}_{n}\right) e^{i\left(\underline{q}_{1}-\underline{q}_{n}\right) \cdot \underline{\varepsilon}_{l}} \\
& =\frac{1}{N} \sum_{\underline{\leq}} \sum_{\varepsilon_{1} j_{1}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{q_{i j}} \cos \left(\underline{q}_{1}, \underline{r}_{l}\right) \sum_{\underline{q}_{n}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \cos \left(\underline{q}_{n} \cdot \underline{r}_{l}\right)
\end{aligned}
$$

which, with the help of Eqs. (5.2) and (5.4), reduces to

$$
\begin{equation*}
=\frac{N^{2}}{N} \sum_{l} H_{\alpha \beta}(\underline{l}) A_{\alpha \beta \gamma \varepsilon}(\underline{l}) \tag{5.18}
\end{equation*}
$$

Using Eq. (5.18) and (5.3), Eq. (5.14) can be written as

$$
\begin{equation*}
N_{0}^{A(2)}=\frac{-N^{2}}{3} \sum_{\underline{I}} \sum_{\alpha \beta \gamma \delta} H_{\alpha \beta}(\underline{l}) A_{\alpha \beta \gamma \delta}(l) T_{\gamma \delta}(0) \tag{5.19}
\end{equation*}
$$

Following exactly similar method as used in the derivation of
Eq. (5.18), we can write

$$
\begin{align*}
& \sum_{q_{2 j_{2}}}\left(\frac{e_{\gamma} e_{\delta}}{\omega^{4}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(q_{2}\right) \\
&=N \sum_{l} T_{\gamma \delta}(\underline{l}) A_{\alpha \beta \gamma \delta}(\underline{l}) \tag{5.20}
\end{align*}
$$

With the help of Eqs. (5.20) and (5.2), Eq. (5.15) can be written as

$$
\begin{equation*}
N_{0}^{A(3)}=\frac{-N^{2}}{3} \sum_{\underline{\varrho}} \sum_{\alpha \beta \gamma \delta} H_{\alpha \beta}(0) A_{\alpha \beta \gamma \delta}(\underline{1}) T_{\gamma \delta}(\underline{l}) \tag{5.21}
\end{equation*}
$$

To factorize the $\underline{q}_{1}$ and $\underline{q}_{2}$ sums in Eq. (5.16) we set $\underline{q}_{1}+\underline{q}_{2}=\underline{q}_{n}$, or equivalently, we introduce a delta function $\Delta\left(\underline{q}_{1}+\underline{q}_{2}-\underline{q}_{n}\right)$. This gives

$$
\begin{array}{r}
N_{0}^{A(4)}=\frac{1}{3} \sum_{\alpha \beta \gamma \delta} \sum_{\frac{q_{1} q_{2}}{j_{1}, j_{2}}} \sum_{q_{n}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{\frac{e_{\gamma}}{q_{\delta}}}{w^{4}}\right)_{q_{2 j_{2}}} F_{\alpha \beta \times \delta}\left(\underline{q}_{n}\right) \\
\times \Delta\left(q_{1}+q_{2}-\underline{q}_{n}\right)
\end{array}
$$

or, using Eq. (5.1) for $\Delta\left(\underline{q}_{1}+\underline{q}_{2}-\underline{q}_{n}\right)$

$$
\begin{aligned}
& \begin{array}{r}
=\frac{1}{3 N} \sum_{\underline{l}} \sum_{\alpha \beta \gamma \delta} \sum_{\substack{q_{1} q_{2}}} \sum_{q_{n}}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2} j_{2}}\right)_{q_{1 j},}\left(\frac{e_{\gamma} e_{\delta}}{w^{4}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \\
x e^{i\left(\underline{q}_{1}+q_{2}-q_{n}\right) \cdot \underline{r}_{l}}
\end{array} \\
& =\frac{1}{3 N} \sum_{\underline{s}} \sum_{\alpha \beta \gamma \delta} \sum_{q_{i j} j}\left(\frac{e_{\alpha} e_{\beta}}{\omega^{2}}\right)_{q_{j} j,} \cos \left(\underline{q}_{1} \cdot \underline{r}_{l}\right) \\
& x \sum_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\delta}}{\left.\omega^{4}\right)_{q_{2} j_{2}}} \cos \left(\underline{q}_{2} \cdot \underline{r}_{l}\right) \sum_{q_{n}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \cos \left(\underline{q}_{n} \cdot \underline{r}_{l}\right)\right.
\end{aligned}
$$

which, using Eqs. (5.2), (5.3) and (5.4), further reduces to $N_{0}^{A(4)}=\frac{N^{2}}{3} \sum_{l} \sum_{\alpha \beta \gamma \delta} H_{\alpha \beta}(\underline{l}) T_{\gamma \delta}(\underline{l}) A_{\alpha \beta \gamma \delta}(1)$

Eq. (5.12) combined with Eqs. (5.17), (5.19), (5.21) and (5.22) gives the most suitable simplified expressions for $N_{0}^{A}$ from a numerical viewpoint.
5.3 SIMPLIFICATION OF $2 \mathrm{M}_{2}\left(\mathrm{q}_{\mathrm{o}}\right)$

Equation (4.16) can be written as

$$
\begin{aligned}
N_{0}^{B}= & \frac{1}{3} \sum_{\substack{q_{1} q_{2} q_{3}}} \sum_{\alpha \beta \gamma}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\nu}}{\omega^{4}}\right)_{q_{3} j_{3}} \Delta\left(q_{1}+q_{2}+q_{3}\right) \\
& \times\left[F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\lambda \mu \nu}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\mu \mu \nu}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\mu \mu \nu}\left(q_{3}\right)\right. \\
& +F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\lambda \mu \nu}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\lambda \mu \nu}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\lambda \mu \nu}\left(q_{3}\right) \\
& \left.+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{1}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{2}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{3}\right)\right]
\end{aligned}
$$

By relabelling the wave-vectors, it can be shown that of all the tensors in the square bracket in Eq. (5.23), the equivalent terms in pairs are: first and fifth, and second and fourth; and the third, sixth, seventh and eights are also equivalent to each other. When these equivalences are taken into account, Eq. (5.23) reduces to

$$
\begin{align*}
N_{0}^{B}= & \frac{1}{3} \sum_{q_{1} q_{2} q_{3}} \sum_{\alpha \beta \gamma}\left(\frac{e_{\alpha} e_{\lambda}}{\omega_{1} j_{2}^{\prime} j_{3}^{\prime}+\dot{q}_{1}}\right)\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{\nu}}{\omega^{4}}\right)_{q_{3} j_{3}} \Delta\left(q_{1}+q_{2}+q_{3}\right) \\
& \times\left[2 F_{\alpha \beta \gamma}\left(\underline{q}_{1}\right) F_{\lambda \mu \nu}\left(\underline{q}_{1}\right)+2 F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\lambda \mu \nu}\left(q_{2}\right)\right. \\
& \left.+4 F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\lambda \mu \nu}\left(q_{3}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\mu_{\mu \nu}}\left(q_{3}\right)\right] \tag{5.24}
\end{align*}
$$

To factorize the Brillouin zone sums in Eq. (5.24), let us consider any of the four terms in the square bracket. For example, the first term is

$$
\begin{gathered}
N_{0}^{B(1)=} \frac{1}{3} \sum_{\substack{q_{1} q_{2} q_{3} \\
j_{1} j_{2} j_{3} \lambda \mu \nu}} \sum_{\alpha \mu \gamma}\left(\frac{e_{\alpha} e_{\lambda}}{\left.\omega^{2}\right)_{q_{j} j}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{\gamma} e_{2}}{\omega^{4}}\right)_{q_{3} j_{3}} \Delta\left(q_{1}+q_{2}+q_{3}\right)\right. \\
\\
\times 2 F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\lambda \mu \nu}\left(q_{1}\right)
\end{gathered}
$$

Representing the delta function $\Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right)$ by a plane wave following Eq. (5.1), and then factorizing the Brillouin zone sums, Eq. (5.25) can be written as

$$
\begin{aligned}
N_{0}^{B(1)}= & \frac{2}{3 N} \sum_{l} \sum_{\alpha \beta \gamma} \sum_{\lambda \mu}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2} j_{1}}\right)_{q_{1} j_{1}} F_{\alpha \beta \gamma}\left(\underline{q}_{1}\right) F_{\mu \nu}\left(\underline{q}_{1}\right) \cos \left(\underline{q}_{1} \cdot \underline{r}_{\lambda}\right) \\
& \times \sum_{q_{2 j 2}}\left(\frac{e_{\beta}-e_{\mu}}{\omega^{2}}\right)_{q_{2 j_{2}}} \cos \left(q_{2} \cdot \underline{r}_{l}\right) \sum_{q_{3} j_{3}}\left(\frac{e_{\gamma} e_{\nu}}{\omega^{4}}\right)_{q_{3} j_{3}} \cos \left(\underline{q}_{3} \cdot \underline{r}_{l}\right)
\end{aligned}
$$

Similarly, we can express the other three terms in Eq. (5.24).
These terms are

$$
\begin{aligned}
N_{0}^{B(2)} & =\frac{-2}{3 N} \sum_{\underline{l}} \sum_{\alpha \beta \gamma} \sum_{q_{i} j_{1}}\left(\frac{\left.e_{\alpha}^{2}\right)_{\lambda}}{\omega^{2}}\right)_{q_{1} j_{1}} F_{\alpha \beta \gamma}\left(q_{1}\right) \sin \left(q_{1} \cdot \underline{r}_{l}\right) \\
& \times \sum_{q_{2} i_{2}}\left(\frac{e_{\beta} e_{\mu}}{\left.\omega^{2}\right)_{q_{2} j_{2}}} F_{\lambda \mu \nu}\left(q_{2}\right) \sin \left(q_{2} \cdot r_{l}\right) \sum_{q_{3} j_{3}}\left(\frac{e_{\gamma} e_{\nu}}{\omega^{4}}\right)_{q_{3 j_{3}}} \cos \left(q_{3} \cdot \underline{r}_{l}\right)\right.
\end{aligned}
$$

$$
\begin{align*}
& N_{0}^{B(3)}=\frac{-4}{3 N} \sum_{\substack{\underline{\alpha} \\
\lambda \beta \gamma}} \sum_{q_{i j},}\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{\varepsilon_{j}, j_{1}} F_{\alpha \beta \gamma}(\underline{q}) \sin \left(\varepsilon_{1}, \underline{\varepsilon}_{\rho}\right) \\
& x \sum_{\underline{q}_{2} j_{2}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}} \cos \left(q_{2} \cdot \underline{r}_{2}\right) \\
& x \sum_{q_{3} j_{3}}\left(\frac{e_{\gamma} e_{\nu}}{\left.\omega^{4}\right)_{q_{3}}} F_{\lambda \mu \nu}\left(q_{3}\right) \sin \left(q_{3} \cdot r_{l}\right)\right. \\
& N_{0}^{B(4)}=\frac{1}{3 N} \sum_{\underline{l}} \sum_{\alpha \beta \gamma \nu} \sum_{\underline{q_{1}, 1}}\left(\frac{e_{\alpha} \varepsilon_{\lambda}}{\omega^{2}}\right)_{\varepsilon_{1}, 1} \cos \left(\varepsilon_{1}, \underline{\varepsilon}_{l}\right)  \tag{5.28}\\
& \times \sum_{q_{R} j_{2}}\left(\frac{e_{\beta} e_{\mu}}{\omega^{2}}\right)_{q_{2} j_{2}} \cos \left(q_{2}, \underline{r}_{1}\right) \\
& \times \sum_{q_{3} j_{3}}\left(\frac{e_{\gamma} \ell_{\nu}}{\left.\omega^{4}\right)_{q_{3} j_{3}}} F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\mu \nu}\left(q_{3}\right) \cos \left(q_{3} \cdot r_{l}\right)\right.
\end{align*}
$$

where

$$
\begin{equation*}
N_{0}^{B}=N_{0}^{B(1)}+N_{0}^{B(2)}+N_{0}^{B(3)}+N_{0}^{B(4)} \tag{5.30}
\end{equation*}
$$

Using Eqs. (5.2), (5.3), (5.5), (5.6), (5.7) and (5.8), Eqs. (5.26), (5.27), (5.28) and (5.29) can be written as

$$
\begin{align*}
N_{0}^{B(1)} & =\frac{2 N^{2}}{3} \sum_{\underline{l}} \sum_{\beta \gamma, \mu \nu} B_{\beta \gamma, \mu \nu}(\underline{l}) H_{\beta \mu}(l) T_{\gamma \nu}(\underline{l})  \tag{5.31}\\
N_{0}^{B(2)} & =\frac{-2 N^{2}}{3} \sum_{l} \sum_{\beta \gamma, \lambda \nu} D_{\lambda \beta \gamma}(l) D_{\beta \lambda \nu}(l) T_{\gamma \nu}(l) \tag{5.32}
\end{align*}
$$

$$
\begin{equation*}
N_{0}^{B(3)}=\frac{-4 N^{2}}{3} \sum_{!} \sum_{\beta \gamma, \lambda \mu} D_{\lambda \beta \gamma}(\underline{l}) H_{\beta \mu}(l) E_{\gamma \lambda \mu} \text { (l) } \tag{5.33}
\end{equation*}
$$

$$
N_{0}^{B(4)}=\frac{N^{2}}{3} \sum_{l} \sum_{\alpha \beta, \lambda \mu} H_{\alpha \lambda}(\underline{l}) H_{\beta \mu}(\underline{l}) C_{\alpha \beta, \lambda \mu}(\underline{l})
$$

Equation (5.30), combined with Eqs. (5.31), (5.32), (5.33) and (5.34), gives the required simplified expression for $N_{0}^{B}$.
5.4 SIMPLIFICATION OF $2 \mathrm{M}_{3}\left(\mathrm{q}_{0}\right)$

Equation (4.22) can be written as a sum of three terms as follows

$$
\begin{equation*}
N_{x x x x}^{c}=N_{x \times x x}^{c(1)}+N_{x \times x x}^{e(2)}+N_{x \times x}^{c} \text { (3) } \tag{5.35}
\end{equation*}
$$

where, separating the three terms in the square bracket in Eq. (4.22), expressions for $N_{x \times x \times}^{C}$ (1),$N_{x \times x x}^{C}$ (2) and $N_{x \times x x}^{C}$ (3) can be obtained. Thus, we can write

$$
\begin{aligned}
& N_{x \times x \times}^{c}=\sum_{\substack{\alpha \beta \gamma \delta \\
q_{1} q_{2} q_{3} q_{4}}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{i j}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{x} e_{\delta}}{\omega^{2}}\right)_{q_{4 j_{4}}} \\
& q_{1} q_{2} q_{3} q_{4} \\
& \bar{j}_{1} j_{2} \bar{j}_{3} j_{4} \\
& x \Delta\left(q_{1}+q_{2}+q_{3}+q_{4}\right) F_{\alpha \beta \gamma \delta} \text { (0) } \\
& =\frac{1}{N} \sum_{\alpha \beta \gamma \delta} \sum_{l} \sum_{\varepsilon_{1 j}, 1}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{\varepsilon_{1 j}} \cos \left(\underline{q}_{1} \cdot \underline{\varepsilon}_{1}\right) \sum_{\underline{q}_{2} j_{2}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{\underline{q}_{2} j_{2}} \cos \left(\underline{q}_{2} \cdot r_{1}\right)
\end{aligned}
$$

$$
\begin{aligned}
& =N^{3} \sum_{l} \sum_{\alpha \beta \gamma \delta} H_{x \alpha}(l) H_{x \beta}(l) H_{x \gamma}(\underline{l}) H_{x \delta}(l) F_{\alpha \beta \gamma \delta} \text { (0) }
\end{aligned}
$$

where, in obtaining Eq. (5.36) we have used Eqs. (5.1) and (5.2).

In a similar fashion we can obtain

$$
\begin{aligned}
N_{x x x x}^{e(2)}= & \frac{-4}{N} \sum_{\underline{l}} \sum_{\beta \gamma \delta} \sum_{q_{\alpha} j_{1}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{\underline{q}_{1} j_{1}} F_{\alpha \gamma \delta}\left(\underline{q}_{1}\right) \cos \left(\underline{q}_{1} \cdot \underline{r}_{l}\right) \\
& \times \sum_{q_{2 j 2}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2 j 2}} \cos \left(\underline{q}_{2} \cdot \underline{r}_{l}\right) \sum_{\underline{q}_{3} j_{3}}\left(\frac{e_{x}-e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}} \cos \left(\underline{q}_{3} \cdot \underline{r}_{l}\right) \\
& \times \sum_{q_{4} j_{4}}\left(\frac{e_{x} e_{\delta}}{\omega^{2}}\right)_{\underline{q}_{4} j_{4}} \cos \left(\underline{q}_{4} \cdot \underline{r}_{l}\right) \\
= & -4 N^{3} \sum_{\underline{\underline{l}}} \sum_{\beta \gamma \delta} G_{x \beta \gamma \delta}(\underline{l}) H_{x \beta}(\underline{l})_{x \gamma}(\underline{l}) H_{x \delta}(\underline{l})
\end{aligned}
$$

and

$$
\begin{aligned}
& N_{x \times x x}^{c(3)}=\frac{3}{N} \sum_{\underline{l}} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1}, q_{2}}\left(\frac{e_{x} e_{\alpha}}{j^{2}, j_{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{1}+\underline{q}_{2}\right) e^{i\left(\underline{q}_{1}+\underline{q}_{2}\right) \cdot \underline{r}_{l}} \\
& \times \sum_{\underline{q}_{3} j_{3}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{\underline{q}_{3} j_{3}} \cos \left(\underline{q}_{3} \cdot \underline{r}_{l}\right) \sum_{\underline{q}_{4} j_{4}}\left(\frac{e_{x} e_{\delta}}{\omega^{2}}\right)_{q_{4} j_{4}} \cos \left(\underline{q}_{4} \cdot \underline{r}_{l}\right) \\
& =3 N \sum \sum_{\underline{\underline{l}}} \sum_{\alpha \beta \gamma \delta} \sum_{\frac{q_{1} q_{2}}{j_{1}^{\prime}} j_{2}^{\prime}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{\underline{q}_{i_{1}}}\left(\frac{e_{x} e_{\beta}}{\left.\omega^{2}\right)}\right)_{\underline{q}_{2} j_{2}} F_{\alpha \gamma \delta}\left(\underline{q}_{1}+\underline{q}_{2}\right) e^{i\left(\underline{q}_{1}+\underline{q}_{2}\right) \underline{\underline{r}}_{l}} \\
& \times H_{x \gamma}(\underline{l}) H_{x \delta}(\underline{l})
\end{aligned}
$$

To separate the $q_{1}$ and $q_{2}$ sums in Eq. (5.38) we set
$q_{1}+q_{2}=\underline{q}_{n}$, or equivalently, introducing another delta function $\Delta\left(q_{1}+q_{2}-q_{n}\right)$, we have

$$
\begin{aligned}
N_{x x x x}^{c(3)} & =3 N \sum_{\underline{l}} \sum_{\alpha \beta \gamma \delta} \sum_{q_{i} \dot{j},} \sum_{q_{2} j_{2}} \sum_{q_{n}}\left(\frac{e_{x} e_{\alpha}}{w^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{w^{2}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \\
& x \Delta\left(\underline{q}_{1}+\underline{q}_{2}-\underline{q}_{n}\right) e^{i\left(\underline{q}_{1}+q_{2}\right) \cdot \underline{\tau}_{l}} H_{x \gamma}(\underline{l}) H_{x \delta}(\underline{l})
\end{aligned}
$$

which, with the help of Eqs. (5.1), (5.2) and (5.4), reduces to

$$
\begin{aligned}
& =\frac{3 N}{N} \sum_{\underline{l}} \sum_{m} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} j_{1}} \sum_{q_{2} j_{2}} \sum_{q_{n}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma \delta}\left(q_{n}\right) \\
& \times e^{i\left(q_{1}+\underline{q}_{2}-q_{n}\right) \cdot \underline{r}_{m}} e^{i\left(\underline{q}_{1}+\underline{q}_{2}\right) \cdot r_{l}} H_{x r}(\underline{l}) H_{x \delta} \text { (l) } \\
& =3 \sum_{\underline{l}} \sum_{m} \sum_{\alpha \beta \gamma \delta} \sum_{\underline{q}_{j} j_{1}}\left(\frac{e_{2 e_{\alpha}}}{\omega^{2}}\right)_{\underline{q}_{1} \dot{\eta}_{1}} \cos \left[\underline{\varepsilon}_{1} \cdot\left(\underline{r}_{l}+\underline{r}_{m}\right)\right] \\
& x \sum_{\underline{q}_{2} j_{2}}\left(\frac{e_{x} \underline{e}_{\beta}}{\omega^{2}}\right)_{\underline{q}_{2} j_{2}} \cos \left[\underline{q}_{2} \cdot\left(\underline{r}_{l}+\underline{r}_{m}\right)\right] \sum_{\underline{q}_{n}} F_{\alpha \beta \gamma \delta}\left(\underline{q}_{n}\right) \cos \left(\underline{q}_{n} \cdot \underline{r}_{m}\right) \\
& \times H_{x \times} \text { (l) } H_{x \&}(\underline{\ell}) \\
& =3 N^{3} \sum_{\underline{l}} \sum_{m} \sum_{\alpha \beta \gamma \delta} H_{x \alpha}(\underline{l}+\underline{m}) H_{x \beta}(\underline{l}+\underline{m}) \\
& \times A_{\alpha \beta \gamma \delta}(\mathrm{m}) H_{x \gamma}(\underline{l}) H_{x \delta} \text { (l) }
\end{aligned}
$$

The final simplified expression for $\quad N_{x \times x \times}^{c}$, which is most suitable for numerical work, is then given by Eqs. (5.35), (5.36), (5.37) and (5.39). To simplify the expression for $\left\{N_{x x y y}^{e}\right\}$ which appears in $2 M_{3}\left(\underline{q}_{0}\right)$, we first consider the expression for $N_{\text {xxyy }}^{c}$. From Eq. (4.23) we can write

$$
\begin{equation*}
N_{x x y y}^{c}=N_{x x y y}^{c}+N_{x x y y}^{c}+N_{x x y y}^{c} \tag{5.40}
\end{equation*}
$$

where, separating the three terms in the square bracket in Eq. (4.23), expressions for $N_{x x y y}^{e(1)}, N_{x x y y}^{c}(2)$ and $N_{x x y y}^{c}$ (3) can be obtained which are the following

$$
\begin{align*}
& N_{x x y y}^{e(1)}=\sum_{q_{1} \beta \gamma \delta}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} \dot{q}_{2}}\left(\frac{e_{y} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{y} e_{\delta}}{\omega^{2}}\right)_{q_{4} j_{4}} \\
& q_{1} \varepsilon_{2} q_{3} q_{4} \\
& \mathrm{JiO}_{2} \mathrm{O}_{3} \mathrm{O}_{4} \\
& \times \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right) \mathcal{F}_{\beta \gamma \delta}(0)  \tag{5.41}\\
& N_{x x y y}^{c(2)}=-4 \sum_{\substack{\alpha \beta \gamma \delta \\
q_{1} q_{2} q_{3} q_{4}}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1 j},}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2 j_{2}}}\left(\frac{e_{y} e_{y}}{\omega^{2}}\right)_{q_{3 j 3}}\left(\frac{e_{y} e_{\delta}}{\omega^{2}}\right)_{q_{4 j 4}} \\
& q_{1} q_{2} q_{3} q_{4} \\
& j_{1} j_{2} j_{3} \dot{j}_{4} \quad \times \Delta\left(q_{1}+q_{2}+q_{3}+q_{4}\right) F_{\beta \gamma \delta}\left(\underline{q}_{1}\right) \tag{5.42}
\end{align*}
$$

$$
\begin{array}{rl}
N_{x x y y}^{c(3)}= & =\frac{3}{\alpha \beta \gamma \delta} \\
& \left(\frac{e_{x} e_{\alpha}}{w^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{w^{2}}\right)_{q_{2} i_{2}}\left(\frac{e_{y} e_{\gamma}}{w^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{y} e_{\delta}}{w^{2}}\right)_{q_{4} j_{4}}  \tag{5.43}\\
j_{1} j_{2} j_{3} j_{4} & x \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}+\underline{q}_{4}\right) F_{\alpha \beta \gamma \delta}\left(q_{1}+\underline{q}_{2}\right)
\end{array}
$$

Now, as already explained in Eq. (4.18), the term $\left\{N_{x x y y}^{c}\right\}$ represents the sum of six tensors obtained by permuting the tensor indices $x, x, y, y$ in $N_{x x y y}^{c}$.

So, following Eq. (5.40) we can write

$$
\begin{equation*}
\left\{N_{x x y y}^{c}\right\}=\left\{N_{x x y y}^{e}\right\}+\left\{N_{x x y y}^{c}(1)\right\}+\left\{N_{x x y y}^{c}(3)\right\} \tag{5.44}
\end{equation*}
$$

By permuting the tensor indices $x, x, y$, $y$ in Eq. (5.41), and then relabelling the wave-vectors, it can be shown that

$$
N_{x x y y}^{e(1)}=N_{y y x x}^{e(1)}=N_{x y y x}^{c(1)}=N_{y x x y}^{c(1)}=N_{x y x y}^{c(1)}=N_{y x y x}^{c(1)}
$$

Similarly, it can be shown from Eqs. (5.42) and (5.43) that

$$
\begin{equation*}
N_{x x y y}^{c(2)}=N_{y y x x}^{c(2)}=N_{x y y x}^{c(2)}=N_{y x x y}^{c(2)}=N_{x y x y}^{c(2)}=N_{y x y x}^{c(2)} \tag{5.46}
\end{equation*}
$$

$$
\begin{equation*}
N_{x x y y}^{c}=N_{y y x x}^{c(3)} \tag{5.47}
\end{equation*}
$$

$$
N_{x y x y}^{e(3)}=N_{y x x y}^{e(3)}=N_{x y y x}^{e(3)}=N_{y x y x}^{c}
$$

Thus, Eq. (5.44) can be written as

$$
\begin{aligned}
\left\{N_{x x y y}^{c}\right\} & =6 N_{x x y y}^{c(1)}+6 N_{x x y y}^{c}(2) \\
& +2 N_{x x y y}^{c(3)}+4 N_{x y x y}^{e(3)}
\end{aligned}
$$

Using the plane wave representation of the delta function, Eq. (5.1), and then separating the $\underline{q}_{1}, q_{2}, \underline{q}_{3}$ and $\underline{q}_{4}$ sums, Eq. (5.41) can be written as

$$
\begin{aligned}
N_{x x y y}^{c} & =\frac{1}{N} \sum_{l} \sum_{\alpha \beta r \sigma} \sum_{q_{1 j} j_{1}}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{1} j_{1}} \cos \left(q_{1} \cdot r_{l}\right) \sum_{q_{2} j_{2}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} \cos \left(q_{2} \cdot r_{1}\right) \\
& \times \sum_{q_{3 j 3}}\left(\frac{e_{y} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}} \cos \left(q_{3} \cdot r_{1}\right) \sum_{q_{4 j 4}}\left(\frac{e_{y} e_{8}}{\omega^{2}}\right)_{q_{4} j_{4}} \cos \left(q_{4} \cdot r_{1}\right) \\
& \times F_{\alpha \beta \gamma \delta(0)}
\end{aligned}
$$

which, using Eq. (5.2), reduces to

$$
=N^{3} \sum_{\underline{L}} \sum_{\alpha \beta \gamma \delta} H_{x \alpha}(\underline{l}) H_{x \beta}(\underline{l}) H_{y \gamma}(\underline{l}) H_{y \delta}(\underline{l}) E_{\alpha \beta \gamma \delta}(0)
$$

Similarly, Eq. (5.42) can be simplified as

$$
\begin{align*}
& N_{x x y y}^{c(2)}=\frac{-4}{N} \sum_{\underline{l}} \sum_{\beta \gamma \delta} \frac{\sum_{\varepsilon_{i} j_{1}}}{}\left(\frac{e_{x} e_{\alpha}}{\omega^{2}}\right)_{q_{i} \dot{j}_{1}} F_{\alpha \beta \gamma \delta}\left(q_{1}\right) \cos \left(\underline{q}_{1}, \underline{r}_{\ell}\right) \\
& \times \sum_{q_{2} j_{2}}\left(\frac{\varepsilon_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} \cos \left(\underline{q}_{2} \cdot \underline{k}_{l}\right) \sum_{q_{3} j_{3}}\left(\frac{e_{y} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}} \cos \left(q_{3} \cdot \underline{r}_{l}\right) \\
& \times \sum_{\varepsilon_{4 j}}\left(\frac{e_{y} e_{\delta}}{\omega^{2}}\right)_{q_{4} j_{4}} \cos \left(q_{4} \cdot r_{\ell}\right) \\
& =-4 N^{3} \sum_{l} \sum_{\beta \gamma \delta} G_{x \beta \gamma \delta}(\underline{l}) H_{x \beta}(\underline{l}) H_{y \gamma}(\underline{l}) H_{y \delta}(\underline{l}) \tag{5.51}
\end{align*}
$$

Expressions for $N_{x x y y}^{c}$ (3) and $N_{x y x y}^{c}$ (3) can also be obtained in a similar manner from Eq. (5.43) and we obtain

$$
\begin{aligned}
N_{x x y y}^{c(3)} & =\frac{3}{N} \sum_{\underline{\varepsilon}} \sum_{\alpha \beta \gamma \delta} \sum_{q_{1} q_{2}}\left(\frac{e_{x} e_{\alpha}}{\left.\omega^{2}\right)_{q_{1} j 1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} F_{\beta r r}\left(\underline{q}_{1}+q_{2}\right)^{i\left(q_{1}+q_{2}\right) \cdot r_{1}}\right. \\
& \times \sum_{q_{3} j_{3}}\left(\frac{e_{y} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}} \cos \left(\underline{q}_{3} \cdot \underline{r}_{\lambda}\right) \sum_{q_{4} j_{4}}\left(\frac{e_{y} e_{\delta}}{\omega^{2}}\right)_{q_{4} j_{4}} \cos \left(q_{4} \cdot r_{2}\right)
\end{aligned}
$$

or, following the same procedure as used in the derivation of Eq. (5.39),

$$
\begin{gather*}
N_{x x y y}^{c(3)}=3 N^{3} \sum_{\underline{m}} \sum_{\underline{l}} \sum_{\alpha \beta \gamma \delta} A_{\alpha \beta \gamma \delta}(m) H_{x \alpha}(m+l) H_{x \beta}(m+l) \\
 \tag{5.52}\\
\times H_{y \gamma}(\underline{l}) H_{y \delta}(l)
\end{gather*}
$$

and, in an exactly similar manner, we get

$$
\begin{align*}
N_{x y x y}^{c(3)}=3 N^{3} \sum_{\underline{m}} \sum_{l} \sum_{\alpha \beta \gamma \delta} & A_{\alpha \beta \gamma \delta}(\underline{m}) H_{x \alpha}(m+l) H_{y \beta}(m+l) \\
& \times H_{x \gamma}(l) H_{y \delta}(l) \tag{5.53}
\end{align*}
$$

Eq. (5.49), combined with Eq. (5.50), (5.51), (5.52) and (5.53), gives the required simplified expressions for $\left\{N_{\text {xxyy }}^{e}\right\}$.
5.5 SIMPLIFICATION OF $2 \mathrm{M}_{4}\left(\mathrm{q}_{0}\right)$

Equation (4.24) can be written as

$$
\begin{align*}
& N_{x x \times x}^{D}=\sum_{\substack{q_{1} q_{2} q_{3} \\
j_{1}, \tilde{v}_{2} j_{3}^{\prime}}} \sum_{v_{5}^{\prime} q_{6}} \sum_{\substack{\alpha \beta \gamma \\
\alpha \beta \gamma \nu}} \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \Delta\left(-\underline{q}_{1}+\underline{q}_{5}+\underline{q}_{6}\right) \\
& x\left(\frac{e^{2} e_{1}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{x} e_{\mu}}{\omega^{2}}\right)_{q_{5 j} j_{6}}\left(\frac{e_{x} e_{\nu}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& \times\left[F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\mu \mu \nu}\left(\underline{q}_{5}\right)+\tilde{\alpha}_{\beta \gamma}\left(\underline{q}_{1}\right) F_{\mu \mu \nu}\left(\underline{q}_{6}\right)-F_{\beta \gamma \gamma}\left(\underline{q}_{1}\right) F_{\mu \nu}\left(\underline{q}_{1}\right)\right. \\
& +F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\mu \mu \nu}\left(\underline{q}_{5}\right)+F_{\alpha \beta \gamma}\left(\underline{q}_{2}\right) F_{\mu \nu \nu}\left(q_{6}\right)-F_{\beta \gamma \gamma}\left(q_{2}\right) F_{\mu \nu}\left(q_{1}\right) \\
& \left.+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\mu \nu}\left(q_{5}\right)+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{6}\right)-F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\mu \nu \nu}\left(q_{1}\right)\right] \tag{5.54}
\end{align*}
$$

By relabelling the wave-vectors it can be seen that, out of all the nine terms in the square bracket in Eq. (5.54), the first and the sixth and the second and the ninth terms cancel each other in pairs and the contributions of the fourth, fifth, seventh and eighth ones are equal to each other. Hence, Eq. (5.54) can be written as

$$
\begin{align*}
N_{x x x x}^{D} & =\sum_{\substack{q_{1} q_{2} q_{3} \\
j_{1}^{\prime} j_{2}^{\prime} j_{3}}} \sum_{q_{5} q_{6} j_{6}} \sum_{\alpha \beta \gamma} \Delta\left(\underline{q}_{1}+\underline{q}_{2}+\underline{q}_{3}\right) \Delta\left(-\underline{q}_{1}+\underline{q}_{5}+\underline{q}_{6}\right) \\
& \times\left(\frac{e_{\alpha} e_{1}}{\omega^{2}}\right)_{q_{1} j_{1}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{\underline{q}_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{x} e_{\mu}}{\omega^{2}}\right)_{q_{5} j_{6}}\left(\frac{e_{x} e_{\nu}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& \times\left[-F_{\alpha \beta \gamma}\left(\underline{q}_{1}\right) F_{\lambda \mu \nu}\left(\underline{q}_{1}\right)+4 F_{\alpha \beta \gamma}\left(\underline{q}_{2}\right) F_{\mu \mu \nu}\left(\underline{q}_{5}\right)\right] \tag{5.55}
\end{align*}
$$

The two terms in the square bracket in Eq. (5.55) can be written separately as

$$
\begin{equation*}
N_{x x x x}^{D}=N_{x \times x x}^{D}(1)+N_{x x x x}^{D} \tag{5.56}
\end{equation*}
$$

where,

$$
\begin{aligned}
& N_{x x_{x x}}^{D(1)}=\frac{-1}{N^{2}} \sum \sum \sum \sum_{i}\left(q_{\alpha} \sum_{1}\right) F_{\alpha \beta \gamma}\left(q_{1}\right) F_{\mu \nu}\left(q_{1}\right) e^{i\left[q_{1} \cdot\left(n_{1}+n_{m}\right)\right]} \\
& x \sum_{q_{2} j_{2}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} \cos \left(q_{2} \cdot r_{1}\right) \sum_{q_{3} j_{3}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}} \cos \left(q_{3} \cdot r_{1}\right) \\
& \times \sum_{\underline{q}_{5} j_{5}}\left(\frac{q_{x} e_{\mu}}{\omega^{2}}\right)_{q_{5} j_{5}} \cos \left(q_{5} \cdot r_{m}\right) \sum_{q_{6} j_{6}}\left(\frac{e_{x} e_{2}}{\left.\omega^{2}\right)_{q_{6} j_{6}}} \cos \left(\underline{q}_{6} \cdot r_{m}\right)\right.
\end{aligned}
$$

which, using Eq. (5.2), reduces to

$$
\begin{align*}
& N_{x \times x x}^{D}(1)  \tag{1}\\
& =-N^{2} \sum_{q_{1} j_{1}}\left[\sum_{\alpha \beta \gamma} \frac{F_{\alpha \beta \gamma}\left(q_{1}\right) e_{\alpha}\left(\underline{q}_{1} j_{1}\right)}{\omega\left(\varepsilon_{1} j_{1}\right)} \sum_{l} H_{x \beta}(\underline{l}) H_{x \gamma}(l) \cos \left(q_{1}, \underline{\tau}_{l}\right)\right]^{2}
\end{align*}
$$

and, following similar methods, the expression for $N_{x \times x \times}^{D}$ (2) can be written as

$$
\begin{aligned}
N_{x \times \times X}^{D(2)} & =4 N^{2} \sum_{q_{1} j_{1}}\left[\sum_{\alpha \beta \gamma} \sum_{\alpha\left(q_{1} j_{1}\right)} \frac{e_{\alpha}\left(q_{1} j_{1}\right)}{\omega\left(q_{1} \varepsilon_{l}\right.}\right. \\
& \left.\times \sum_{q_{2} j_{2}}\left(\frac{q_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}} F_{\alpha \beta \gamma}\left(q_{2}\right) e^{i q_{2} \cdot r_{l}} \sum_{q_{3} j_{3}}\left(\frac{e_{x} e_{2}}{\omega^{2}}\right)_{q_{3} j_{3}} e^{i q_{3} \cdot r_{1}}\right]^{2}
\end{aligned}
$$

or, using Eqs. (5.2) and (5.7) we can write the above expression in the following form

$$
\begin{align*}
& N_{x \times x \times}^{D(2)} \\
& \quad=4 N^{2} \sum_{q_{1} j_{1}}\left[\sum_{\alpha \gamma} \frac{e_{\alpha}\left(q_{1} j_{1}\right)}{\omega\left(q_{1} j_{1}\right)} \sum_{\underline{l}}^{D}{ }_{x \alpha \gamma}(\underline{l}) H_{x \gamma}(\underline{l}) \sin \left(q_{1} \cdot \underline{q}_{l}\right)\right]^{2} \tag{5.59}
\end{align*}
$$

Eq. (5.56), combined with Eqs. (5.58) and (5.59), gives the desired simplification of $N_{\times \times \times X}^{D}$.

In order to obtain similar simplifications for $\left\{N_{x x y y}^{D}\right\}$, we first write the expression for $N_{x \times y y}^{D}$ from Eq. (4.25), which is

$$
\begin{align*}
& N_{x \times y Y}^{D}=\sum_{q_{1} q_{2} q_{3}} \sum_{q_{5} q_{6}} \sum_{\substack{\beta \gamma \\
j j_{2} j_{3} \\
j}} \Delta\left(q_{1}+q_{2}+q_{3}\right) \Delta\left(-q_{1}+q_{5}+q_{6}\right) \\
& \dot{j}_{1} j_{2} j_{3} j_{5} j_{6} \lambda \mu \nu \\
& \times\left(\frac{e_{\alpha} e_{\lambda}}{\omega^{2}}\right)_{q_{1 j}}\left(\frac{e_{x} e_{\beta}}{\omega^{2}}\right)_{q_{2} j_{2}}\left(\frac{e_{x} e_{\gamma}}{\omega^{2}}\right)_{q_{3} j_{3}}\left(\frac{e_{y} e_{\mu}}{\omega^{2}}\right)_{q_{5 j}}\left(\frac{e_{y} e_{y}}{\omega^{2}}\right)_{q_{6} j_{6}} \\
& x \sum_{\alpha_{\beta \gamma}}\left(q_{1}\right) F_{\lambda \mu \nu}\left(q_{5}\right)+F_{\alpha \beta \gamma}\left(\underline{q}_{1}\right) F_{\lambda \mu \nu}\left(\underline{q}_{6}\right)-F_{\beta \gamma}\left(q_{1}\right) F_{\mu \mu \nu}\left(\underline{q}_{1}\right) \\
& +F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\lambda \mu \nu}\left(q_{5}\right)+F_{\alpha \beta \gamma}\left(q_{2}\right) F_{i \mu \nu}\left(q_{6}\right)-F_{\alpha \beta \gamma}\left(q_{2}\right) F_{\mu \nu \nu}\left(q_{1}\right) \\
& \left.+F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{5}\right)+F_{\alpha \beta \gamma}\left(\underline{q}_{3}\right) F_{\lambda \mu \nu}\left(q_{6}\right)-F_{\alpha \beta \gamma}\left(q_{3}\right) F_{\lambda \mu \nu}\left(q_{1}\right)\right] \tag{5.60}
\end{align*}
$$

By permuting the cartesian indices $x, x, y, y$ in Eq. (5.60) and then relabelling the wave-vectors, it can be shown that

$$
\begin{equation*}
N_{x x y y}^{D}=N_{y y x x}^{D} \tag{5.61}
\end{equation*}
$$

and

$$
\begin{equation*}
N_{x y x y}^{D}=N_{y x y x}^{D}=N_{x y y x}^{D}=N_{y x x y}^{D} \tag{5.62}
\end{equation*}
$$

Following exactly similar procedures which have been used in the derivation of Eqs. (5.58) and (5.59), it can be shown from Eq. (5.60) that

$$
\begin{equation*}
\left[N_{x x y y}^{D}+N_{y y x x}^{D}\right]=2 N_{x \times x x}^{D} \tag{5.63}
\end{equation*}
$$

and

$$
\begin{align*}
& {\left[N_{x y x y}^{D}+N_{y x y x}^{D}+N_{x y y x}^{D}+N_{y x \times y}^{D}\right]} \\
& =-4 N^{2} \sum_{q_{1} j_{1}^{\prime}}\left[\sum_{\alpha \beta \gamma} \frac{F_{\alpha \beta \gamma}\left(q_{1}\right) e_{\alpha}\left(q_{1} j_{1}\right)}{\omega\left(q_{1} j_{1}\right)} \sum_{l} H_{x \beta}(l) H_{y \gamma}(l) \cos \left(q_{1} \cdot \underline{q}_{l}\right)\right]^{2} \\
& +16 N^{2} \sum_{q_{1} j_{1}}\left[\sum_{\alpha \gamma} \frac{e_{\alpha}\left(q_{1} j_{1}\right)}{\omega\left(q_{1} j_{1}\right)} \sum_{\underline{l}}^{D}{ }_{x \alpha \gamma}(l) H_{y \gamma}(l) \sin \left(q_{1} \cdot \underline{\pi}_{l}\right)\right]^{2} \tag{5.64}
\end{align*}
$$

> Eqs. (5.63) and (5.64) give the simplified expressions for $\left\{N_{x x y y}^{D}\right\}$.
6. INTERATOMIC POTENTIAL AND DIFFERENT WAVE-VECTOR DEPENDENT TENSORS

As we have seen in sections 3,4 and 5 , the numerical calculation of $2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(\underline{q}_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ is reduced to the calculation of $F_{\alpha \beta \gamma}(\underline{q}), F_{\alpha \beta \gamma \delta}(\underline{q})$ and the Brillouin zone sums through the functions $H_{\alpha \beta}(\underline{l}), T_{\alpha \beta}(\underline{l}), A_{\alpha \beta \gamma \delta}(\underline{l}), B_{\beta \gamma, \mu \nu}(\underline{l})$, $C_{\beta \gamma, \mu \nu}(\underline{l}), D_{\lambda \beta \gamma}(l), E_{\lambda \beta \gamma}(l)$ and $G_{\lambda \beta \gamma \gamma}(\underline{l})$ defined in Eqs. (5.2) to (5.9). Some of the Brillouin zone sums contain the eigenvalues $\omega(\underline{q} j)$ and eigenvectors $\underline{e}(\underline{q} j)$ obtained from the dynamical matrix elements ${\underset{\alpha}{\beta}}(\underline{q})$.

In this section we will outline the derivation of the expressions for the tensors $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ for a long range interatomic potential.

It is well known in lattice dynamics that, for a monatomic crystal, the dynamical matrix element $F_{\alpha \beta}(\underline{q})$ is defined as

$$
\begin{equation*}
F_{\alpha \beta}(\underline{q})=\frac{1}{M} \sum_{\underline{l}}^{\prime} \phi_{\alpha \beta}(\underline{l})\left[1-e^{-i \underline{q_{2}} \underline{r}_{s}}\right] \tag{6.1}
\end{equation*}
$$

Also from Eqs. (3.2), (3.3), (3.4) and (3.5), we can write

$$
\begin{array}{r}
F_{\alpha \beta \gamma}(\underline{q})=\sum_{l}^{\prime} \phi_{\alpha \beta \gamma}(\underline{l}) \sin \left(\underline{q}, r_{l}\right) \\
F_{\alpha \beta \gamma \delta}(\underline{q})=\sum_{\underline{l}}^{\prime} \phi_{\alpha \beta \gamma \delta}(\underline{l}) \cos \left(\underline{q} \cdot r_{l}\right) \tag{6.3}
\end{array}
$$

The two-body potential $\quad \phi(\underline{\ell})$ for a metallic crystal may be formally written as (Toya (1958))

$$
\begin{equation*}
\phi(l)=\phi^{c}(l)+\phi^{S}(l)+\phi^{E-I}(\ell) \tag{6.4}
\end{equation*}
$$

where
$\phi^{C}(l)$ is the direct coulomb interaction of the ion cores, $\phi^{S}(\ell)$ is the short range overlap interaction of the closed shells of the ions, and $\phi^{E-I}(\ell)$ is the electron-ion interaction as mediated by other electrons.

For small ion cores, which occupy a small portion of the atomic volume, the overlap term $\phi^{S}(\ell)$ is negligible. For sodium, Vosko (1964) has estimated the $\phi^{S}(l)$ for $\mathrm{Na}^{+}-\mathrm{Na}^{+}$interaction and has shown it to be small.

Analytically $\phi^{E-I}(1)$ is expressed in terms of the following integral (Cochran (1963)).

$$
\phi^{E-T}\left(\underline{\tau}^{l}\right)=\frac{-4 \pi Z_{0} e^{2}}{(2 \pi)^{3}} \int \frac{G(|Q|)}{|Q|^{2}} e^{2^{2} \underline{r_{l}}} d^{3} Q
$$

and, $\Phi^{C}(\ell)$ has the usual form,

$$
\phi^{c}(l)=\frac{z_{0} e^{2}}{\left|T_{2} l\right|}
$$

where,
$e$ is the electronic charge,
$Z_{0}$ is the valency of the metallic atom,
$Q$ is the wave-vector
and, from Shukla and Taylor (1974),

$$
\begin{equation*}
\left.G(|Q|)=\frac{1}{z_{0}^{2}} M\left(|Q|^{2}\right) Q_{0}(Q) /\left[Q^{2}+Q_{0}(Q)\right]\right] \tag{6.7}
\end{equation*}
$$

In Eq. (6.7), $M\left(|Q|^{2}\right)$ is the bare electron-ion matrix element, and $Q_{0}(\underset{\sim}{Q})$ is the static electron gas screening function which is related to the dielectric function $\in(\underset{\sim}{Q})$ through the equation

$$
\begin{equation*}
\epsilon(Q)=1+Q_{0}(Q) /\left(\left.\underline{Q}\right|^{2}\right. \tag{6.8}
\end{equation*}
$$

Now, for large values of $\ell, \phi(\ell)\left[=\phi^{C}(\ell)+\phi^{E-I}(\ell)\right]$ behaves as $\left\{\cos \left(2 k_{F} \pi_{l}\right) / \pi_{l}^{3}\right\} \quad$ where $k_{F}$ is Fermi wavevector (Harrison (1966)), and so, $\phi_{\alpha \beta}(l), \phi_{\alpha \beta \gamma}(l)$ and $\phi_{\alpha \beta \gamma \delta}(l)$ also behave as $\left\{\cos \left(2 k_{F} \pi_{l}\right) / r_{\ell}{ }^{3}\right\}$ for large $l$. Consequently, the values of $F_{\alpha \beta}(q), F_{\alpha \beta \gamma}(q)$ and $F_{\alpha \beta \gamma \delta}(q)$, obtained by performing the straightforward real lattice sum $\sum_{\underline{l}}^{\prime}$ in Eqs. (6.1), (6.2) and (6.3) respectively, also oscillates like $\left\{\cos \left(2 k_{F} r_{l}\right) / r_{l}^{3}\right\}$. Thus, for large distances, it becomes very difficult to obtain converged values of $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(q)$ when the summation
over $\underline{\ell}$ extends to a large number of neighbours. However, it is possible to overcome this difficulty. One such procedure is to differentiate first Eq. (6.6), and then differentiate under the integral sign and numerically integrate Eq. (6.5) to obtain contributions from $\phi^{\ell}(l)$ and $\phi^{E-I}\left(r_{l}\right)$ to $\phi^{\prime}(\ell), \phi^{\prime \prime}(l), \phi^{\prime \prime \prime}(l)$ and $\phi^{i v}(\ell)$, the first, second, third and fourth order radial derivatives of the potential $\phi(l)$ respectively. This then helps us to obtain values of $\phi_{\alpha \beta}(l), \phi_{\alpha \beta \gamma}(l)$ and $\phi_{\alpha \beta \gamma \delta}(l)$, and $F_{\alpha \beta}(q), F_{\alpha \beta \gamma}(q)$ and $F_{\alpha \beta \gamma \delta}(q)$ respectively by performing the sum $\sum_{\underline{l}}^{\prime}$ over a large number of neighbours. Then, beyond that neighbour, the potential is represented by an asymptotic form like $\left\{\cos \left(2 k_{F} \pi_{\ell}\right) / r_{l}^{3}\right\}$ and corrections to $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ are evaluated. This procedure has been employed by Gonenc (1977) in the calculation of quartic free energy $F_{4}$, mean square frequency $\left\langle\omega^{2}\right\rangle$ and the energy $U$ where he found that the correction to the above properties were small beyond the 23 rd neighbour in the case of sodium for the volume $90^{\circ} \mathrm{K}$.

An alternative procedure is to evaluate the contributions to $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta(\underline{q}) \text { directly from the two terms }}$ $\phi^{c}(l)$ and $\phi^{E-I}\left(\mathscr{I}_{\ell}\right)$ of the potential $\phi(l)$. This is done by evaluating the contributions to $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ from $\phi^{e}(\ell)$ by the Ewald procedure and the other contribution from $\phi^{E-I}\left(\varkappa_{1}\right)$ is evaluated exactly. In this thesis we will follow this procedure.

The complete expressions for the tensors $\phi_{\alpha \beta}(l)$, $\phi_{\alpha \beta \gamma}(\ell)$ and $\Phi_{\alpha \beta \gamma \delta}(\ell)$ obtained from a central force two-body potential $\phi(\ell)$ are

$$
\begin{align*}
\phi_{\alpha \beta}(l) & =\left.\frac{\partial^{2} \phi\left(1 r_{l}+\underline{u}_{l}^{l}\right)}{\partial u_{\alpha}^{l} \partial u_{\beta}^{l}}\right|_{\underline{u}_{l}^{l}=0}  \tag{6.9a}\\
& =\frac{x_{\alpha}^{l} x_{\beta}^{l}}{r_{l}^{2}}\left[\phi^{\prime \prime}(l)-\frac{1}{r_{l}} \phi^{\prime}(l)\right]+\frac{\partial_{\alpha \beta}}{r_{l}} \phi^{\prime}(l)  \tag{6.9b}\\
\phi_{\alpha \beta \gamma}(l) & =\left.\frac{\partial^{3} \phi\left(1 r_{l}+\underline{u}^{l} 1\right)}{\partial u_{\alpha}^{l} \partial u_{\beta}^{l} \partial u_{\gamma}^{l}}\right|_{u^{l}}=0  \tag{6.10a}\\
& =\frac{x_{\alpha}^{l} x_{\beta}^{l} x_{\gamma}^{l}}{r_{l}^{3}}\left[\phi^{\prime \prime \prime}(l)-3 \frac{\phi^{\prime \prime}(l)}{r_{l}}+3 \frac{\phi^{\prime}(l)}{r_{l}^{2}}\right] \\
& +\frac{x_{\alpha}^{l} \delta_{\beta \gamma}+x_{\beta}^{l} \delta_{\alpha \gamma}+x_{\gamma}^{l} \delta_{\alpha \beta}}{r_{l}^{2}}\left[\phi^{\prime \prime}(l)-\frac{1}{r_{l}} \phi^{\prime}(l)\right]  \tag{6.10b}\\
\phi_{\alpha \beta \gamma \delta}(l) & =\left.\frac{\partial^{4} \phi\left(1 r_{l}+u^{l} l\right)}{\partial u_{\alpha}^{l} \partial u_{\beta}^{l} \partial u_{\gamma}^{l} \partial u_{\delta}^{l}}\right|_{(6.10 \mathrm{~b})}  \tag{6.11a}\\
& =\frac{x_{\alpha}^{l} x_{\beta}^{l} x_{\gamma}^{l} x_{\delta}^{l}}{r_{l}^{4}}\left[\phi^{i v}(l)-\frac{6 \phi^{\prime \prime \prime}(l)}{r_{l}}+\frac{15 \phi^{\prime \prime}(l)}{r_{l}^{2}}-\frac{15 \phi^{\prime}(l)}{r_{l}^{3}}\right] \\
& +\left[x_{\alpha}^{l} x_{\beta}^{l} \delta_{\gamma \delta}+x_{\alpha}^{l} x_{\gamma}^{l} \delta_{\beta \delta}+x_{\alpha}^{l} x_{\delta}^{l} \delta_{\beta \gamma}+x_{\beta}^{l} x_{\gamma}^{l} \delta_{\alpha \delta}\right. \\
+ & \left.x_{\beta}^{l} x_{\delta}^{l} \delta_{\alpha \gamma}+x_{\gamma}^{l} x_{\delta}^{l} \delta_{\alpha \beta}\right] \times \frac{1}{r_{l}^{3}}\left[\phi^{\prime \prime \prime}(l)-\frac{3 \phi^{\prime \prime}(l)}{r_{l}}+\frac{3 \phi^{\prime}(l)}{r_{l}^{2}}\right] \\
+ & {\left[\delta_{\alpha \beta} \delta_{\gamma \delta}+\delta_{\alpha \gamma} \delta_{\beta \delta}+\delta_{\alpha \delta} \delta_{\beta \gamma}\right] \times \frac{1}{r_{l}^{2}}\left[\phi^{\prime \prime}(l)-\frac{1}{r_{l}} \phi^{\prime}(l)\right] } \tag{6.11b}
\end{align*}
$$

where $x_{\alpha}^{\ell}$ refers to the cartesian $\alpha$-component of the equilibrium lattice vector $\underline{I}_{\ell}$.

We first derive expressions for the contributions from $\phi^{E-I}\left(\underline{r}_{\ell}\right)$ to $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q}) \quad$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ which may be denoted by $F_{\alpha \beta}^{E-I}(\underline{q}), F_{\alpha \beta \gamma}^{E-I}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}^{E-I}(\underline{q})$ respectively.

From Eqs. (6.1), (6.5) and (6.9), we can write

$$
\begin{equation*}
F_{\alpha \beta}^{E-I}(q)=\frac{4 \pi Z_{0} e^{2}}{(2 \pi)^{3}} \sum_{l}^{1} \int_{Q} \frac{G(|Q|)}{|Q|^{2} Q_{\alpha} Q_{\beta} d^{3} Q e^{i Q \cdot \underline{q}_{l}}\left[1-e^{-i \varepsilon^{2} \cdot \tau_{l}}\right]} \tag{6.12}
\end{equation*}
$$

Since $\sum_{l}^{\prime}$ is a discrete lattice sum, upon changing the order of integration and summation in Eq. (6.12) we obtain
$F_{\alpha \beta}^{E-I}(q)=\frac{4 \pi Z_{0} e^{2}}{(2 \pi)^{3}} \int_{Q}^{G\left(Q Q_{1}\right)} Q_{\alpha}^{2} Q_{\beta} d^{3} Q \sum_{l}^{1}\left[e^{i Q \cdot r_{l}}-e^{i(Q-q) \cdot r_{l}}\right]$

Now, we recall the well-known relation which transforms the sum over the direct lattice vector $\boldsymbol{\ell}$ into a sum over the reciprocal lattice vector ? ,

$$
\sum_{\underline{s}} e^{i \underline{q_{2}} \underline{\sigma}_{s}}=\frac{(2 \pi)^{3}}{v_{a}} \sum_{\tau} \delta(\underline{q}-\tau)
$$

or, $\sum_{\underline{l}}^{\prime} e^{i q \cdot r_{l}}=\frac{(2 \pi)^{3}}{v_{a}} \sum_{I} \delta(q-\tau)-1$,
where $\mathcal{V}_{\boldsymbol{a}}$ is the unit cell volume and the prime over the $\underset{\sim}{\boldsymbol{\ell}}$ summation indicates that $\ell=0$ is excluded.

Substituting Eq. (6.14) into Eq. (6.13), we obtain

$$
\begin{align*}
F_{\alpha \beta}^{E-I}(q) & =\frac{(2 \pi)^{3}}{v_{a}} \frac{4 \pi z_{0} e^{2}}{(2 \pi)^{3}} \int_{Q} \frac{G(Q Q 1)}{Q^{2}} Q_{\alpha} Q_{\beta} d^{3} Q \sum_{\tau} \delta(Q-\tau) \\
& -\frac{(2 \pi)^{3}}{v_{a}} \frac{4 \pi z_{0} e^{2}}{(2 \pi)^{3}} \int_{Q} \frac{G(1 Q 1)}{Q^{2}} Q_{\alpha} Q_{\beta} d^{3} \sum_{\tau} \delta(Q-q-\tau) \tag{6.15}
\end{align*}
$$

In both the integrals on the right hand side of Eq. (6.15), we interchange once again the order of the integration and the summation, which is permissible because $\sum_{\boldsymbol{I}}$ is a discrete sum. Then we carry out the trivial delta function integration and obtain

$$
\begin{aligned}
& \tilde{\alpha}_{\alpha}^{E-I}(\underline{q})=\frac{4 \pi z_{0} e^{2}}{v_{\alpha}} \sum_{\tau}\left[\frac{G(\tau T)}{\tau^{2}} \tau \tau_{\beta}-\frac{G(I \tau+\underline{q})}{(\tau+\underline{q})^{2}}\left(\underline{T}+\underline{q}_{\alpha}\left(\tau+\underline{q}_{\beta}\right]\right.\right. \\
& =\frac{4 \pi z_{0} e^{2}}{v_{a}} \frac{\sum_{g}}{\underline{g}}\left[\frac{G(\underline{g} \mid}{g^{2}} \underline{g}_{2} g_{\beta}-\frac{G(\underline{g}+\underline{P})}{(\underline{g}+\underline{P})^{2}}(\underline{g}+\underline{P})_{\alpha}\left(\underline{g}+\underline{P}_{\beta}\right]\right.
\end{aligned}
$$

where $\underline{g}$ and $\underline{P}$ are related to $T$ and $\underline{q}$ via

$$
I=(2 \pi / a) \underline{g} \text { and } \underline{q}=(2 \pi / a) \underline{p}, \quad \text { 'a' }
$$

being the lattice parameter.
Similarly, from Eqs. (6.2), (6.5) and (6.10a) we can write

$$
\begin{align*}
F_{\alpha \beta \gamma}^{E-I}(\underline{\varepsilon})= & \frac{4 \pi Z_{0} e^{2}}{(2 \pi)^{3}} \sum_{l}^{1} \int_{Q} \frac{G\left(1 Q_{1}\right)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} i^{3} d^{3} Q \\
& \times e^{i Q \cdot \pi_{l}}\left[e^{i \underline{q} \cdot \underline{q}_{l}}-e^{-i \underline{q} \cdot \underline{r}_{l}}\right] / 2 i \tag{6.17}
\end{align*}
$$

In Eq. (6.17) we have made the following substitution,

$$
\sin \left(\underline{q} \cdot \underline{\underline{g}}_{l}\right)=\frac{1}{2 i}\left[e^{i \underline{q} \cdot \underline{q}_{l}}-e^{-i^{i q} \cdot \underline{q}_{l}}\right]
$$

Now, interchanging the order of integration and summation in Eq. (6.17), we can write

$$
\begin{aligned}
F_{\alpha \beta \gamma}^{E-I}(\underline{q}) & =\frac{4 \pi Z_{0} e^{2}}{2(2 \pi)^{3}} \int_{Q} d^{3} Q \frac{G(1 Q 1)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} \sum_{l}^{\prime} e^{i(Q-q) \cdot \xi_{l}} \\
& -\frac{4 \pi Z_{0} e^{2}}{2(2 \pi)^{3}} \int_{Q} d^{3} Q \frac{G(1 Q 1)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} \sum_{l}^{1} e^{i(Q+q) \cdot r_{l}}
\end{aligned}
$$

or, using Eq. (6.14), the above equation becomes

$$
\begin{align*}
F_{\alpha \beta \gamma}^{E-I}(q) & =\frac{4 \pi Z_{0} e^{2}}{2 v_{a}} \int_{Q} d^{3} Q \frac{G\left(1 Q_{1}\right)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} \sum_{T} \delta(Q-\underline{q}-T) \\
& -\frac{4 \pi Z_{0} e^{2}}{2 v_{a}} \int_{Q} d^{3} Q \frac{G(\underline{Q})}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} \sum_{T} \delta(Q+q-T) \tag{6.18}
\end{align*}
$$

In each term on the right hand side of Eq. (6.18) we change the order of integration and summation, and then perform the trivial delta function integration. All these operations yield

$$
\begin{align*}
\tilde{K}_{\alpha \gamma}^{\varepsilon-I}(\underline{\varepsilon}) & =\frac{2 \pi z_{0} e^{2}}{v_{a}} \sum_{\tau} \frac{G(I T+\underline{q})}{(\tau+\underline{q})^{2}}(\tau+\underline{q})_{\alpha}(\tau+\underline{q})_{\beta}(\tau+\underline{q})_{\gamma} \\
& -\frac{2 \pi z_{0} e^{2}}{v_{a}} \sum_{\tau} \frac{G(1 \tau+\underline{q})}{(\tau-\underline{q})^{2}}(\tau-\underline{q})_{\alpha}(\tau-\underline{q})_{\beta}(\tau-\underline{q})_{\gamma} \tag{6.19}
\end{align*}
$$

In the second term on the right hand side of Eq. (6.19), we replace $\mathcal{T}$ by $-\mathcal{T}$, which is permissible because in ${\underset{\mathcal{T}}{ }, \quad \mathcal{T} \text { runs }, ~}_{\mathcal{T}}$, over all + and - values. Then, remembering that $G(|-\tau \underline{q}-\underline{q}|)=G(|\underline{\tau}+\underline{q}|)$, we can write Eq. (6.19) as

$$
F_{\alpha \beta \gamma}^{E-I}(\underline{q})=\frac{4 \pi Z_{0} e^{2}}{v_{a}} \sum_{\tau} \frac{G(|\tau+q|)}{(\tau+q)^{2}}(\tau+q)_{\alpha}(\tau+q)_{\beta}(\tau+q)_{\gamma}
$$

which in terms of $g$ and $\underline{P}$, reduces to

Finally, using Eqs. (6.3), (6.5) and (6.11a), we can write

$$
\begin{align*}
& F_{\alpha \beta \gamma \delta}^{E-I}(\underline{q})=\frac{4 \pi Z_{0} e^{2}}{(2 \pi)^{3} \sum_{l}^{1} \int_{Q} \frac{G\left(1 Q_{1}\right)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} Q_{\gamma} d^{3} Q_{\gamma}, ~ Q^{2}} \\
& \times e^{i Q \cdot \xi_{l}} e^{-i q_{1} \cdot \tau_{2}} \tag{6.21}
\end{align*}
$$

Interchanging the order of integration and summation in Eq. (6.21), we get

$$
F_{\alpha \beta \gamma \delta}^{E-I}(\underline{q})=\frac{4 \pi z_{0} e^{2}}{(2 \pi)^{3}} \int_{Q} \frac{G(I Q Q)}{Q^{2}} Q_{\alpha} Q_{\beta} Q Q_{\gamma} \alpha^{3} Q \sum_{\underline{l}} e^{i(Q-\underline{q}) \cdot r_{x}}
$$

or, using Eq. (6.14)

$$
\begin{aligned}
&{\underset{\alpha \beta \gamma \delta}{E-I}(\underline{q})}_{E}^{E}=\frac{4 \pi z_{0} e^{2}}{v_{a}} \int_{-} \frac{G(1 Q 1)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} Q_{\delta} d^{3} Q_{\tau} \delta(Q-q-I) \\
&-\frac{4 \pi z_{0} e^{2}}{(2 \pi)^{3}} \int_{\mathcal{Q}} \frac{G(|Q|)}{Q^{2}} Q_{\alpha} Q_{\beta} Q_{\gamma} Q_{\delta} \alpha^{3} Q
\end{aligned}
$$

The second term on the right hand side of Eq. (6.22) can be dropped, because it is independent of $\mathcal{T}$ and is essentially a constant which comes in several times in the expressions of $2 \mathcal{M}_{1}\left(\underline{\varepsilon}_{0}\right)$ and $2 M_{3}\left(\underline{q}_{0}\right)$ and exactly cancels each other as can be seen in Eqs. (3.13) and (3.15), respectively.

Also, in the first term on the right hand side of Eq. (6.22) we can interchange the order of the integration and summation and then, performing the trivial delta function integration, we get

$$
F_{\alpha \beta \gamma \delta}^{E-I}(\underline{q})=\frac{4 \pi z_{0} e^{2}}{v_{a}} \sum_{T} \frac{G(T+q 1)}{(T+q)^{2}}(T+\underline{q})_{\alpha}(T+q)_{\beta}(T+q)_{\gamma}(\tau+q)_{\delta}
$$

which, in terms of $\underline{g}$ and $\underset{\sim}{P}$, reduces to

$$
\begin{equation*}
F_{\alpha \beta \gamma \delta}^{E-I}(\underline{q})=\frac{16 \pi^{3} z_{0} e^{2}}{a^{2} v_{a}} \sum_{g} \frac{G(1 \underline{g}+\underline{p})}{(g+\underline{p})^{2}}(g+p)_{\alpha}(\underline{g}+\underline{p})_{\beta}(\underline{g}+\underline{p})_{\gamma}(\underline{g}+\underline{p})_{\delta} \tag{6.23}
\end{equation*}
$$

In Eqs. $(6.16),(6.20)$ and (6.23) we have derived expressions for the contributions from $\phi^{E-I}\left(\pi_{l}\right)$ to $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ which are defined in terms of reciprocal lattice vector sums.

We now describe the derivations of the contributions to $\mathcal{F}_{\alpha \beta}(\underline{q})$, $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ from $\phi^{c}(l)$.

For a coulomb potential defined in Eq. (6.6), the expressions for the derivatives $\phi^{\prime}(l), \phi^{\prime \prime}(l), \phi^{\prime \prime \prime}(l)$ and $\phi^{i v}(l)$ are :

$$
\begin{align*}
\phi^{\prime}(l) & =\frac{-z_{0}^{2} e^{2}}{r_{l}^{2}}  \tag{6.24}\\
\phi^{\prime \prime}(l) & =\frac{2 z_{0}^{2} e^{2}}{r_{l}^{3}}  \tag{6.25}\\
\phi^{\prime \prime \prime}(l) & =\frac{-6 z_{0} e^{2}}{r_{l}^{4}}  \tag{6.26}\\
\phi^{i v}(l) & =\frac{24 z_{0}^{2} e^{2}}{r_{l}^{5}} \tag{6.27}
\end{align*}
$$

When Eqs. (6.24) to (6.27) are substituted in Eqs. (6.9b), (6.10b)
and (6.11b) which, in turn, are then substituted in Eqs. (6.1), (6.2) and (6.13), we can see that the expressions of $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ involve the tensors of the various ranks of the following type :

$$
\begin{aligned}
& S_{0}^{n}(\underline{q})=\sum_{\underline{l}}^{\prime} \frac{\cos \left(\underline{q} \cdot \underline{r}_{l}\right)}{r_{l}^{n}} \\
& S_{\alpha}^{n}(\underline{q})=\sum_{l}^{\prime} \frac{x_{\alpha}^{l}}{r_{l}^{n}} \sin \left(\underline{q} \cdot \underline{r}_{l}\right) \quad(6.28 a)
\end{aligned}
$$

$$
\begin{aligned}
& S_{\alpha \beta}^{n}(q)=\sum_{l}^{1} \frac{x_{\alpha}^{l} x_{\beta}^{l}}{r_{l}^{n}} \cos \left(\underline{q} \cdot \underline{r}_{l}\right) \\
& S_{\alpha \beta \gamma}^{n}(\underline{q})=\sum_{l}^{1} \frac{x_{\alpha}^{l} x_{\beta}^{l} x_{\gamma}^{l}}{r_{l}^{n}} \sin \left(\underline{q}_{l} \underline{r}_{l}\right) \quad(6.28 c) \\
& S_{\alpha \beta \gamma \delta}^{n}(\underline{q})=\sum_{l}^{1} \frac{x_{\alpha}^{l} x_{\beta}^{l} x_{r}^{l} x_{\delta}^{l}}{r_{l}^{n}} \cos \left(\underline{q} \cdot \underline{r}_{l}\right) \quad(6.28 \alpha)
\end{aligned}
$$

In fact, all these real lattice sums defined by tensors $S_{0}^{n}(\underline{q})$, $S_{\alpha}^{n}(\underline{q}), S_{\alpha \beta}^{n}(q), S_{\alpha \beta \gamma}^{n}(\underline{q})$ and $S_{\alpha \beta \gamma \delta}^{n}(\underline{q})$ can be obtained from the differentiation of the basic sum $S_{0}^{n}(\varepsilon)=\sum_{\underline{L}}^{\prime} \cos \left(\varepsilon_{l} \mu_{l}\right) / r_{l}^{n}$ with respect to $q_{x}$, $q_{y}$ and $q_{z}$ as follows:

$$
\begin{align*}
& S_{\alpha}^{n}(q)=-\frac{\partial}{\partial q_{\alpha}} S_{0}^{n}(\underline{q})  \tag{6.29}\\
& S_{\alpha \beta}^{n}(\underline{q})=-\frac{\partial^{2}}{\partial q_{\alpha} \partial q_{\beta}} S_{0}^{n}(q)  \tag{6.30}\\
& S_{\alpha \beta \gamma}^{n}(\underline{q})=\frac{\partial^{3}}{\partial q_{\alpha} \partial q_{\beta} \partial q_{\gamma}} S_{0}^{n}(\underline{q})  \tag{6.31}\\
& S_{\alpha \beta \gamma \delta}^{n}(\underline{q})=\frac{\partial^{4}}{\partial q_{\alpha} \partial q_{\beta} \partial q_{\gamma} \partial q_{\gamma}} S_{0}^{n}(\underline{q}) \tag{6.32}
\end{align*}
$$

Now we sketch the evaluation of the sum $S_{0}^{n}(\underline{q})$ by the Ewald procedure. In this method, at first the following integral transformation is used to write $\frac{1}{\pi_{l}^{n}}$ as an integral,

$$
\begin{equation*}
\frac{1}{r_{l}^{n}}=\frac{2}{\Gamma(n / 2)} \int_{0}^{\infty} y^{n-1} e^{-r_{l}^{2} y^{2}} d y \tag{6.33}
\end{equation*}
$$

Substituting for $1 / r_{l}^{n}$ from Eq. (6.33) into Eq. (6.28a )we get

$$
\begin{equation*}
S_{0}^{n}(q)=\frac{2}{\Gamma(n / 2)} \sum_{l}^{1} e^{i \underline{q} \cdot \tau_{l}} \int_{0}^{\infty} y^{n-1} e^{-r_{l}^{2} y^{2}} d y \tag{6.34}
\end{equation*}
$$

Since $\sum_{\underline{e}}^{\prime}$ is a discrete sum, in Eq. (6.34) we can interchange the order of the summation and the integration. Then Eq. (6.34) becomes

$$
\begin{equation*}
S_{0}^{n}(q)=\frac{2}{\Gamma(n / 2)} \int_{0}^{\infty} d y y^{n-1} \sum_{l}^{1} e^{-r_{l}^{2} y^{2}+i \underline{q} \cdot \varepsilon_{l}} \tag{6.35}
\end{equation*}
$$

The advantage of using the integral transformation, defined in Eq. (6.33), is that a Gaussian function in the sum $S_{0}^{2}(\underline{q})$ in Eq. (6.35) converges better than a function of the form $\frac{1}{\pi_{l}^{n}}$. But, for small $y$, the influence of the Gaussian becomes small and so, the sum $\sum_{\underline{\underline{I}}}^{\prime}$ in Eq. (6.35) has a convergence problem.

To tackle this situation, the integration in Eq. (6.35) is divided into two parts by dividing the range of $y$ at an arbitrary value, say, $y=\alpha$. Eq. (6.35) then can be written as

$$
\begin{align*}
s_{0}^{n}(\underline{\varepsilon}) & =\frac{2}{\Gamma(n / 2)} \int_{0}^{\alpha} y^{n-1} d y \sum_{\underline{l}}^{1} e^{-r_{l}^{2} y^{2}+i \underline{z} \cdot r_{l}} \\
& +\frac{2}{\Gamma(n / 2)} \int_{\alpha}^{\infty} y^{n-1} d y \sum_{!}^{1} e^{-r_{l}^{2} y^{2}+i \underline{r} \cdot r_{l}}
\end{align*}
$$

On the right hand side of Eq. (6.36), we represent the first integral by $J_{1}$ and the second integral by $J_{2}$, and then formally write Eq. (6.36) as

$$
\begin{equation*}
S_{0}^{n}(q)=J_{1}+J_{2} \tag{6.37}
\end{equation*}
$$

Obviously, if $\alpha$ is not too small, only the first integral has the convergence problem. In order to overcome this problem, Ewald's method suggests a transformation which changes the variable of integration $y$ to a new variable proportional to $\frac{1}{y}$, so that a small value of $y$ gives a large value for $\frac{1}{y}$, and then, the integral $J_{1}$ converges as quickly as the second integral $J_{2}$.

The required transformation from $y$ to $\frac{1}{y}$ is easily obtained from Born and Huang (1954). The transformation changes the sum in direct lattice $\underline{\ell}$ to a sum in the reciprocal lattice $\boldsymbol{\sim}$. Explicitly, the transformation is

$$
\sum_{l} e^{-r_{l}^{2} y^{2}+i q \cdot r_{l}}=\frac{\pi^{3 / 2}}{v_{a}} \sum_{I} \frac{e^{-(\underline{q}+\tau)^{2} / 4 y^{2}}}{y^{3}}
$$

or,

$$
\begin{align*}
& \sum_{\underline{l}}^{\prime} e^{-r_{l}^{2} y^{2}+i \underline{q} \cdot r_{l}} \\
&=\frac{\pi^{3 / 2}}{v_{a}} \sum_{\tau} \frac{e^{-(\underline{q}+\tau)^{2} / 4 y^{2}}}{y^{3}}-1 \tag{6.38}
\end{align*}
$$

Substituting Eq. (6.38) into the first integral on the right hand side of Eq. (6.36), we get

$$
\begin{equation*}
J_{1}=\frac{2 \pi^{3 / 2}}{2 \Gamma \Gamma(n / 2)}\left[\int_{0}^{\alpha} y^{n-1} d y \sum_{\tau} \frac{e^{-(\underline{q}+\tau)^{2} / 4 y^{2}}}{y^{3}}-\frac{\alpha^{n} v_{a}}{n \pi^{3 / 2}}\right] \tag{6.39}
\end{equation*}
$$

Changing the order of integration and summation in Eq. (6.39), which is permissible since $\sum_{I}$ is a discrete sum, we obtain

$$
\begin{equation*}
J_{1}=\frac{2 \pi^{3 / 2}}{v_{a} \Gamma(n / 2)}\left[\sum_{\tau} \int_{0}^{a} y^{n-4} e^{-(q+I)^{2 / 4} y^{2}} d y-\frac{v_{a} \alpha^{n}}{\pi^{3 / 2} n}\right] \tag{6.40}
\end{equation*}
$$

Putting $y=\frac{\alpha}{t}$ and $d y=\frac{-\alpha}{t^{2}} d t$ in the integral

$$
T=\int_{0}^{\alpha} y^{n-4} e^{-(\underline{q}+\tau)^{2} / 4 y^{2}} d y
$$

we obtain

$$
T=\int_{1}^{\infty} \alpha^{n-3} t^{-n+2} e^{-(\underline{q}+\tau)^{2} t^{2} / 4 \alpha^{2}} d t
$$

which, putting $t^{2}=\beta$ and $2 t d t=\alpha \beta$, reduces to

$$
\begin{align*}
& =\frac{1}{2} \int_{1}^{\infty} \alpha^{n-3} \beta^{-\frac{n}{2}+\frac{1}{2}} \exp \left[-\frac{(q+\tau)^{2} \beta}{4 \alpha^{2}}\right] d \beta \\
& =\frac{1}{2} \alpha^{n-3} \int_{1}^{\infty} \beta^{-\frac{n}{2}+\frac{1}{2}} \exp \left[\frac{-\pi^{2}(P+q)^{2} \beta}{a^{2} \alpha^{2}}\right] d \beta \tag{6.41}
\end{align*}
$$

Substituting Eq. (6.41) into Eq. (6.40), we obtain

$$
\begin{align*}
& J_{1}=\frac{\pi^{3 / 2} \alpha^{n-3}}{\Gamma(n / 2) v_{a}}\left[\sum_{g} \int_{1}^{\infty} \beta^{-\frac{n}{2}+\frac{1}{2}} \exp \left[\frac{-\pi^{2}(\underline{p}+g)^{2} \beta}{a^{2} \alpha^{2}}\right] \alpha \beta\right. \\
&\left.-\frac{2 v_{a} \alpha^{3}}{\pi^{3 / 2} n}\right] \tag{6.42}
\end{align*}
$$

In Eq. (6.42), putting $\alpha=\frac{c}{a}$ on dimensional grounds where $c$ is a constant parameter known as Ewald's parameter, and $v_{a}=\frac{a^{3}}{m}$ where $m=2$ for bcc lattices and $m=4$ for fcc lattices, we get

$$
\begin{align*}
J_{1}=\frac{m \pi^{3 / 2} c^{n-3}}{\Gamma(n / 2) a^{n}}\left[\sum_{g} \int_{1}^{\infty} \beta^{-\frac{n}{2}+\frac{1}{2}}\right. & \exp \left[\frac{-\pi^{2}(\underline{P}+g)^{2} \beta}{c^{2}}\right] d \beta \\
& \left.-\frac{2 c^{3}}{m n \pi^{3 / 2}}\right] \tag{6.43}
\end{align*}
$$

Eq. (6.43) gives the final expression for $J_{1}$ suitable for numerical work. To obtain a similar expression for $\boldsymbol{J}_{\mathbf{2}}$, in the second term on the right hand side of Eq. (6.36) we interchange the
order of integration and summation which is permissible since $\sum_{l}^{\prime}$ is a discrete sum. Then we get

$$
\begin{equation*}
J_{2}=\frac{2}{\Gamma(n / 2)} \sum_{\underline{l}}^{1} \cos \left(\underline{\varepsilon} \cdot \underline{r}_{2}\right) \int_{\alpha}^{\infty} y^{n-1} e^{-r_{l}^{2} y^{2}} d y \tag{6.44}
\end{equation*}
$$

In the integral

$$
T=\int_{\alpha}^{\infty} y^{n-1} e^{-r_{l}^{2} y^{2}} d y .
$$

we put $y^{2}=\alpha^{2} \xi, 2 y d y=\alpha^{2} d \xi$ and $\quad y=\alpha \xi^{1 / 2} \quad$, and then we can write

$$
T=\frac{\alpha^{2}}{2} \int_{1}^{\infty} \alpha^{n-2} \xi^{\frac{n-2}{2}} e^{-r_{l}^{2} \alpha^{2} \xi} d \xi
$$

and so, Eq. (6.44) can be written as

$$
J_{2}=\frac{2}{\Gamma(n / 2)} \sum_{\underline{l}}^{\prime} \cos \left(\underline{q} \cdot \underline{r}_{l}\right) \frac{\alpha^{n}}{2} \int_{1}^{\infty} \xi \frac{n-2}{2} e^{-r_{l}^{2} \alpha^{2} \xi} d \xi
$$

Once again, we put $\alpha=\frac{c}{a}$ in Eq. (6.45) and obtain

$$
J_{2}=\frac{c^{n}}{a^{n} \Gamma(n / 2)} \sum_{\underline{l}}^{\prime} \cos \left(\varepsilon \cdot r_{l}\right) \int_{1}^{\infty} \xi^{\frac{n-2}{2}} e^{-r_{l}^{2} \frac{c^{2}}{a^{2}} \xi} d \xi
$$

or

$$
\begin{equation*}
J_{2}=\frac{e^{n}}{\Gamma(n / 2) a^{n}} \sum_{\underline{l}}^{1} \cos (\pi P \cdot l) \int_{1}^{\infty} \xi^{\frac{n-2}{2}} e^{-\left(e^{2} e^{2} \xi / 4\right)} d \xi \tag{6.46}
\end{equation*}
$$

Eq. (6.46) gives the final expression for $J_{2}$ suitable for numerical work.

Substituting Eqs. (6.43) and (6.46) into Eq. (6.37), an expression for the sum $S_{0}^{n}(\underline{q})$ can be obtained. From the sum $S_{0}^{n}(\underline{\varepsilon})$, expressions for other tensors defined in Eqs. (6.286) to (6.32) also can be obtained, which, to avoid repetition, we will not describe here.

Combining the contributions coming from $\phi^{C}(\ell)$ and $\phi^{E-I}(\ell)$ to $F_{\alpha \beta}(q), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$, we can obtain the final expressions for $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$.

In fact, out of the nine components of $F_{\alpha \beta}(\underline{q})$, the following six are independent:

$$
F_{x x}(\underline{q}), F_{y y}(\underline{q}), F_{z z}(\underline{q}), F_{x y}(\underline{q}), F_{x z}(\underline{q}) \text { and } F_{y z}(\underline{q})
$$

Expressions for two of them are

$$
\begin{align*}
& \left.F_{x x}(\underline{q})=\left(4 \pi e^{2} / M v_{a}\right) \sum_{g}^{\prime}\left(g_{x}^{2} / g^{2}\right) E \exp \left(-\pi^{2} g^{2} / c^{2}\right)+G(1 g 1)\right] \\
& +\left(4 \pi e^{2} / M v_{a}\right) \sum_{g}^{-}\left[\left(p_{x}+g_{x}\right)^{2} /(p+g)^{2}\right]\left[\exp \left(-\pi^{2}(\underline{p}+g)^{2} / c^{2}\right)-G(1 \underline{P}+g)\right] \\
& +\left(e^{2} c^{5} / 2 M v_{a} \sqrt{\pi}\right) \sum_{\underline{l}}^{-}\left[\int_{1}^{\psi} \xi^{3 / 2} \exp \left[-l^{2} e^{2} \xi / 4\right] d \xi l_{x}^{2}(1-\cos (\pi P \cdot \underline{Q}))\right] \\
& -\left(e^{2} c^{3} / M \cup \Omega \sqrt{\pi}\right) \sum_{l}^{1}\left[\int_{1}^{\infty} \xi^{1 / 2} \exp \left[-\underline{l}^{2} c^{2} \xi / 4\right] d \xi\left[1-\cos \left(\pi \pi_{n} \cdot l\right)\right]\right]  \tag{6.47}\\
& F_{x y}(q)=\left(4 \pi e^{2} / M v_{a}\right) \sum_{\underline{g}} \frac{\left(p_{x}+g_{x}\right)\left(p_{y}+g_{y}\right)}{(\underline{p}+\underline{g})^{2}}\left[\exp \left(-\frac{\pi^{2}}{c^{2}}(\underline{p}+\underline{g})^{2}\right)-G(|\underline{p}+\underline{g}|)\right] \\
& +\frac{e^{2} c^{5}}{2 M v_{a} \sqrt{\pi}} \sum_{l}^{\prime}\left[\int_{1}^{\infty} \xi^{3 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi l_{x} l_{y}(1-\cos (\pi P \cdot \underline{l}))\right] \tag{6.48}
\end{align*}
$$

By changing the indices $x, y$ and $z$, expressions for $F_{y y}$ (q) and $F_{\mathcal{Z}}(\underline{\mathscr{E}})$ can be obtained from Eq. (6.47), and expressions for $F_{x_{z}}(\underline{\varepsilon})$ and $F_{y_{z}}(\underline{\varepsilon})$ can be obtained from Eq. (6.48).

Out of the twenty-seven components of $F_{\alpha \beta \gamma}(\underline{q})$, only ten are independent. They are

$$
\begin{aligned}
& F_{x x x}(\underline{q}), F_{y y y}(\underline{q}), F_{z z z}(\underline{q}), F_{x y z}(\underline{q}), F_{x x y}(\underline{q}), \\
& F_{x x z}(\underline{q}), F_{y y x}(\underline{q}), F_{y y z}(\underline{q}), F_{z z x}(\underline{q}) \text { and } F_{z z y}(\underline{q})
\end{aligned}
$$

Expressions for three of them are

$$
\begin{align*}
F_{x x x}(\underline{q}) & =\frac{8 \pi^{2} e^{2}}{a v_{a}} \sum_{g} \frac{\left(P_{x}+g_{x}\right)^{3}}{(\underline{P}+g)^{2}}\left[\exp \left(-\frac{\pi^{2}}{c^{2}}(\underline{P}+g)^{2}\right)-G(|\underline{P}+g|)\right. \\
& +\frac{3 e^{2} c^{5}}{a v_{a} \sqrt{\pi}} \sum_{l}^{1}\left[l_{x} \sin (\pi \underline{P} \cdot \underline{l}) \int_{1}^{q} \xi^{3 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right] \\
& -\frac{e^{2} c^{7}}{2 v_{a} a \sqrt{\pi}} \sum_{l}^{1}\left[l_{x}^{3} \sin (\pi P \cdot l) \int_{\xi}^{\infty} \xi^{5 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi\right] \tag{6.49}
\end{align*}
$$

$$
\begin{align*}
& F_{x x y}(q)=\frac{8 \pi^{2} e^{2}}{a v_{a}} \sum_{g} \frac{\left(P_{x}+g_{x}\right)^{2}\left(P_{y}+g_{y}\right)}{(\underline{P}+g)^{2}}\left[\exp \left(-\frac{\pi^{2}}{c^{2}}(\underline{P}+g)^{2}\right)-G(|P+g|)\right] \\
& +\frac{e^{2} c^{5}}{v_{a} a \sqrt{\pi}} \sum_{l}^{\prime}\left[l_{y} \sin (\pi P \cdot l) \int_{1}^{\infty} \xi^{3 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi\right] \\
& -\frac{e^{2} e^{7}}{2 v_{a} a \sqrt{\pi}} \sum_{l}^{1}\left[\sin (\pi P \cdot l)\left(l_{x}^{2} l y\right) \int_{l}^{b} \xi^{5 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right] \\
& F_{x y z}(q)=\frac{8 \pi^{2} e^{2}}{a v_{a}} \sum_{\underline{g}} \frac{\left(p_{x}+g_{x}\right)\left(p_{y}+g_{y}\right)\left(p_{z}+g_{z}\right)}{(\underline{P}+g)^{2}}\left[\exp \left(-\frac{\pi^{2}}{e^{2}}(\underline{p}+g)^{2}\right)-G(|p+g|)\right.  \tag{6.50}\\
& -\frac{e^{2} c^{7}}{2 v_{a} a \sqrt{\pi}} \sum_{l}^{1}\left[l_{x} l_{y} l_{z} \sin (\pi P \cdot \underline{\varepsilon}) \int_{j}^{4 / 2} e^{-\ell^{2} e^{2} \xi / 4} d \xi\right] \tag{6.51}
\end{align*}
$$

By changing the indices $x, y$ and $z$, expressions for $F_{y y y}(\underline{q})$ and $\quad F_{Z Z Z}(\underline{q})$ can be obtained from Eq. (6.49), expressions for $F_{X X Z}(\underline{\varepsilon})$, $F_{y y x}(\underline{q}), F_{y y z}(\underline{\varepsilon}), \quad F_{z z x}(\underline{\varepsilon})$ and $F_{z z y}(\underline{q})$ can be obtained from $E q$. (6.50).

Out of the eighty-one components of $F_{\alpha \beta \gamma \delta}(\underline{q})$, only fifteen are independent. They are

$$
\begin{aligned}
& F_{x x x x}(\underline{q}), F_{y y y y}(q), F_{z z z z}(\underline{q}), F_{x x x y}(\underline{q}), F_{x x x z}(\underline{q}), \\
& F_{y y y x}(\underline{q}), F_{y y y z}(\underline{q}), F_{z z z x}(\underline{q}), F_{z z z y}(\underline{q}), F_{x x y z}(\underline{q}), \\
& F_{y y x z}(\underline{q}), F_{z z x y}(\underline{q}), F_{x x y y}(\underline{q}), F_{x x z z}(\underline{q}) \text { and } F_{y y z z}(\underline{q}),
\end{aligned}
$$

Expressions for four of them are

$$
\begin{align*}
& F_{x \times x x}(\underline{q})=\frac{16 \pi^{3} e^{2}}{v_{a} a^{2}} \sum_{g} \frac{\left(P_{x}+g_{x}\right)^{4}}{(\underline{p}+\underline{g})^{2}}\left[\exp \left(-\frac{\pi^{2}}{e^{2}}(\underline{p}+\underline{g})^{2}\right)-G(|\underline{p}+\underline{g}|)\right] \\
& -\frac{12}{5} \frac{e^{2} c^{5}}{2 a^{2} \sqrt{\pi}} \\
& +\frac{e^{2} c^{9}}{2 v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{\prime}\left[l^{4} \cos (\pi P \cdot l) \int_{1}^{\infty} \xi / 2 e^{-l^{2} e^{2} \xi / 4} d \xi\right] \\
& -\frac{6 e^{2} c^{7}}{v_{a} a^{2} \sqrt{\pi}} \sum_{\underline{l}}^{\prime}\left[l_{x}^{2} \cos (\pi P \cdot \underline{l}) \int_{1}^{\infty} \xi^{5 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right] \\
& +\frac{6 e^{2} e^{5}}{\vartheta_{a} a^{2} \sqrt{\pi}} \sum_{l}^{\prime}\left[\cos (\pi P \cdot \underline{l}) \int_{1}^{\infty} \xi^{3 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi\right] \tag{6.52}
\end{align*}
$$

$$
\begin{aligned}
& F_{x x x y}(\underline{q})=\frac{16 e^{2} \pi^{3}}{v_{a} a^{2}} \sum_{\underline{g}} \frac{\left(p_{x}+g_{x}\right)^{3}\left(P_{y}+g_{y}\right)}{(\underline{P}+\underline{g})^{2}}\left[\exp \left(-\frac{\pi^{2}}{c^{2}}(\underline{p}+\underline{g})^{2}\right)-G(|\underline{P}+\underline{g}|)\right] \\
& +\frac{e^{2} c^{9}}{2 v a a^{2} \sqrt{\pi}} \sum_{l}^{\prime}\left[l_{x}^{3} l_{y} \cos (\pi P \cdot \underline{l}) \xi^{\infty} 7 / 2 e^{-l^{2} e^{2} \xi / 4} d \xi\right] \\
& -\frac{3 e^{2} c^{7}}{v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{\prime}\left[l_{x} l_{y} \cos (\pi P \cdot l) \int_{1}^{8} \xi^{5 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right]
\end{aligned}
$$

$$
\begin{aligned}
& F_{x x y z}(\underline{q})=\frac{16 e^{2} \pi^{3}}{v_{a} a^{2}} \sum_{g} \frac{\left(P_{x}+g_{x}\right)^{2}\left(P_{y}+g_{y}\right)\left(P_{z}+g_{z}\right)}{(\underline{P}+\underline{g})^{2}}\left[\operatorname { e x p } \left(-\frac{\pi^{2}}{c^{2}}(\underline{P}+\underline{g})^{2}\right.\right. \\
& -G(|\underline{p}+\underline{g}|)] \\
& +\frac{e^{2} c^{9}}{2 v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{1}\left[l_{x}^{2} l_{y} l z \cos (\pi P \cdot l) \int_{1}^{\infty} \xi^{7 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi\right] \\
& -\frac{e^{2} e^{7}}{v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{1}\left[l_{y} l \cos (\pi P \cdot l) \int_{\xi}^{\infty} \xi^{5 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right]
\end{aligned}
$$

$$
\begin{align*}
& -\frac{4}{5} \frac{e^{2} c^{5}}{v_{a} a^{2} \sqrt{\pi}} \\
& +\frac{e^{2} c^{9}}{2 v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{1}\left[l^{2} l^{2} \cos (\pi P \cdot \underline{l}) \int_{\xi}^{\infty} 7 / 2 e^{-l^{2} c^{2} \xi / 4} d \xi\right] \\
& -\frac{e^{2} c^{7}}{v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{\prime}\left[\left(l_{x}^{2}+l_{y}^{2}\right) \cos (\pi P \cdot l) \int_{l}^{\infty} \xi^{5 / 2} e^{-l^{2} c^{2} \xi / 4} d \xi\right] \\
& \left.+\frac{2 e^{2} e^{5}}{v_{a} a^{2} \sqrt{\pi}} \sum_{l}^{\prime}[\cos (\pi P \cdot l))^{4} \xi^{3 / 2} e^{-l^{2} e^{2} \xi / 4} d \xi\right] \tag{6.55}
\end{align*}
$$

By changing the indices $x, y$ and $z$, expressions for $F_{y y y y}(\underline{q})$ and $\quad F_{\mathbb{Z} Z \mathbf{Z}}(\underline{q})$ can be obtained from Eq. (6.52), expressions for $F_{x x x z}(\underline{q}), F_{y y y x}(\underline{q}), F_{y y y z}(\underline{q}), F_{z z z x}(\underline{q})$ and $F_{z z z y}(\underline{q})$ can be obtained from Eq. (6.53), expressions for $F_{y y x z}$ ( $\underline{q}$ ) and $F_{\mathbf{Z z} \times \boldsymbol{y}}(\underline{\boldsymbol{\varepsilon}})$ can be obtained from Eq. (6.54), and expressions for $F_{x x z z}(\underline{q})$ and $\quad F_{y y z z}(\underline{q})$ can be obtained from Eq. (6.55).

All these expressions in Eqs. (6.47) to (6.55) hold for a monovalent metallic crystal. The integral $\int_{1}^{\infty} \xi^{n / 2} e^{-s^{2} c^{2} \xi / 4} d \xi$, which arises in these equations, has been introduced by Misra (1940), and later used by Cohen and Refer (1955).

In fact, if

$$
\theta_{m}(x)=\int_{1}^{\infty} \beta^{m} e^{-\beta x} d \beta
$$

then,

$$
\theta_{m}(x)=\theta_{0}(x)+(m / x) \theta_{m-1}(x)
$$

where

$$
\begin{aligned}
& \theta_{0}(x)=e^{-x} / x \\
& \theta_{-1}(x)=-E_{i}(-x),
\end{aligned}
$$

and

$$
\theta_{-\frac{1}{2}}(x)=(\pi / x)^{1 / 2}\left[1-\theta\left(x^{1 / 2}\right)\right]
$$

$E_{i}(-x)$ is the exponential integral, and $\theta(x)$ is the error function.

## 7. NUMERICAL CALCULATION AND RESULTS

From what has been explicitly stated in the previous sections, it is obvious that the calculation of $2 M\left(\underline{q}_{0}\right)$ requires the calculation of the tensors $F_{\alpha \beta \gamma}(\underline{q}), F_{\alpha \beta \gamma \delta}(\underline{q}), H_{\alpha \beta}(\underline{l})$ and $T_{\alpha \beta}(\underline{l})$. Also we see from Eqs. (5.2) and (5.3) that the calculation of $H_{\alpha \beta}(\underline{l})$ and $T_{\alpha \beta}(\ell)$ requires the eigenvalues $\omega(\underline{\xi})$ and the associated eigenvectors $\underline{e}(\underline{q})$ obtained from the tensor $F_{\alpha \beta}(\underline{q})$.

In order to calculate the tensors $F_{\alpha \beta}(\underline{q}), F_{\alpha \beta \gamma}(\underline{q})$
and $F_{\alpha \beta \gamma \delta}(\underline{q})$ from Eqs. (6.47) to (6.55), we first generate the wave-vectors in the first Brillouin zone. This is done by using a step-1ength $Z=32$ which yields 240 odd wave-vectors in the $1 / 48^{\text {th }}$ portion of the first Brillouin zone. Then we select a value for the Ewald parameter ' $c$ ' in such a way that each of the real sum $\sum_{\underline{!}}^{\prime \prime}$ and the reciprocal sum $\sum_{2}$ converges quickly. Following Cohen and Keffer (1955), we choosē $c=\sqrt{\pi}$. We found that for convergence up to at least six significant figures, the real lattice sum $\sum_{\underline{l}}^{\prime}$ requires 25 shells and the reciprocal lattice sum $\sum_{g}$ requires the individual vectors up to the $25^{\text {th }}$ shell.

To check our calculation of $F_{\alpha \beta}(\underline{q})$, we calculated frequencies $\left.\nu\left(q_{j}\right) E \omega\left(\xi_{j}\right) / 2 \pi\right]$ along the three principal symmetry directions $[111],[110]$ and $[100]$ in q-space. To obtain $\omega(\underline{q})$ we diagonalised the matrix of $\mathcal{F}_{\beta}(\underline{q})$ by using the Jacobi method. Our calculated values of $\nu(\ell j)$ along $[111],[110]$ and $[100]$ directions, and the experimental values of them measured by Wood et al (1962) are presented in Tables (1a), (1b) and (1c).

The coulombic contributions to the tensors $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ satisfy a number of identities which serve a useful check on our numerical work.

From Eqs. (6.49), (6.50) and (6.51), we can derive the following identities or sum rules for $F_{\alpha \beta \gamma}^{e}(\underline{q})$.

$$
\begin{equation*}
F_{x x x}^{c}(\underline{q})+F_{y y x}^{c}(\underline{q})+F_{z z x}^{c}(\underline{q})=0 \tag{7.1}
\end{equation*}
$$

$$
\begin{equation*}
F_{X X y}^{c}(\underline{q})+F_{y Y y}^{c}(\underline{q})+F_{z Z y}^{c}(\underline{q})=0 \tag{7.2}
\end{equation*}
$$

$$
\begin{equation*}
F_{x \times z}^{c}(\underline{q})+F_{y y z}^{c}(\underline{q})+F_{z z z}^{e}(\underline{q})=0 \tag{7.3}
\end{equation*}
$$

$$
\text { Similarly, from Eqs. }(6.52),(6.53),(6.54) \text { and }(6.55) \text {, we can }
$$

show that the identities or sum rules satisfied by the components of

$$
F_{\alpha \beta \gamma \sigma}^{c}(q) \text { are : }
$$

$$
\begin{equation*}
F_{x x x x}^{c}(\underline{q})+F_{x x y y}^{c}(\underline{q})+F_{x x z z}^{c}(\underline{q})=0 \tag{7.4}
\end{equation*}
$$

$$
\begin{equation*}
F_{y y y y}^{c}(\underline{q})+F_{y y z z}^{c}(\underline{q})+F_{x x y y}^{c}(\underline{q})=0 \tag{7.5}
\end{equation*}
$$

$$
\begin{equation*}
F_{z z z z}^{c}(\underline{q})+F_{x x z z}^{c}(\underline{q})+F_{y y z z}^{c}(\underline{q})=0 \tag{7.6}
\end{equation*}
$$

$$
\begin{align*}
& F_{x x x y}^{c}(\underline{q})+F_{y y y x}^{c}(\underline{q})+F_{z z x y}^{c}(\underline{\varepsilon})=0  \tag{7.7}\\
& F_{x x y z}^{c}(\underline{\varepsilon})+F_{y y y z}^{c}(\underline{\varepsilon})+F_{z z z y}^{c}(\underline{\varepsilon})=0  \tag{7.8}\\
& F_{x x x z}^{c}(\underline{\varepsilon})+F_{y y x z}^{c}(\underline{\varepsilon})+F_{z z z x}^{c}(\underline{\varepsilon})=0 \tag{7.9}
\end{align*}
$$

For any wave-vector $q$, these sum rules are satisfied to an accuracy of at least 1 part in $10^{6}$ in our calculations. This indicates that all the components of the third and fourth rank tensors $F_{\alpha \beta \gamma}^{c}(\underline{\varepsilon})$ and $F_{\alpha \beta \gamma \delta}^{C}(\varepsilon)$ are accurate to the same order.

As a further check on these tensors, we calculated $\phi_{\alpha \beta \gamma}(l)$ and $\phi_{\alpha \beta \gamma \delta}(l)$ from our calculated values of $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}$ (q) following the relations

$$
\begin{align*}
& \phi_{\alpha \beta \gamma}(\underline{l})=\sum_{\underline{q}} F_{\alpha \beta \gamma}(\underline{q}) \sin \left(\underline{q} \cdot \underline{r}_{l}\right)  \tag{7.10}\\
& \phi_{\alpha \beta \gamma \delta}(l)=\sum_{\underline{q}} F_{\alpha \beta \gamma \delta}(\underline{q}) \cos \left(\underline{q} \cdot \underline{r}_{l}\right) \tag{7.11}
\end{align*}
$$

Our calculated values of $\phi_{\alpha \beta \gamma}(l)$ and $\phi_{\alpha \beta \gamma \delta}(l)$ agreed up to at least four significant figures with those calculated independently by numerical integration (obtained from R.C. Shukla, through private communication).

Thus, having assured ourselves of the correctness of our calculated values of $F_{\alpha \beta}(\underline{\varepsilon}), F_{\alpha \beta \gamma}(\underline{\varepsilon})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$, we entered into the second phase of our numerical work. We calculated eigenvalues and eigenvectors, $\boldsymbol{\omega}(\underline{\xi})$ and $\boldsymbol{\ell}(\underline{\xi})$ respectively, by diagonalising the matrix of $F_{\alpha \beta}(\underline{\varepsilon})$ where $F_{\alpha \beta}(\underline{\varepsilon})$ is calculated for a given volume implying thereby the volume dependence of $\omega(q j)$ and $\underline{e}(q \dot{j}) \cdot F_{\alpha \boldsymbol{\beta}}(\underline{q})$ is volume dependent because they are calculated from a potential function $\phi(\ell)$ the coulomb part of which is volume dependent through the lattice parameter ' $a$ ' and the electronion part is volume dependent through $G\left(\mid Q_{1}\right)$. These eigenvalues and eigenvectors are utilized in the various tensors in performing the Brillouin zone summations defined in Eqs. (5.2) to (5.9). All of these tensors are also volume dependent. The volume dependence of the tensors $H_{\alpha \beta}(l)$ and $T_{\alpha \beta}(l)$ arises from the frequencies and eigenvectors, $\omega(\varepsilon j)$ and $\underline{\underline{q}}(\underline{q})$. The other tensors, $A_{\alpha \beta \gamma \delta}(l)$, $B_{\beta \gamma, \mu \nu}(\underline{l}), C_{\beta \gamma, \mu \nu}(!), D_{\lambda \beta \gamma}(l), E_{\lambda \beta \gamma}(l) \quad$ and $G_{\lambda \beta \gamma r}(l)$, depend on volume also through $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$ which are volume dependent because their calculation is carried out from the potentials given in Eqs. (6.5) and (6.6). Considerable reduction in computer time can be achieved if each of these whole Brillouin zone summations defined in EqS. (5.2) to (5.9) can be reduced to a summation over the $1 / 48^{\text {th }}$ portion of the Brillouin zone by writing their invariant forms. This has been done for the second and fourth rank tensor Brillouin zone sums by Shukla and Wilk (1974) and we have followed essentially the same procedure here. To obtain the invariant form expressions for the Brillouin zone summations involving the third
rank tensors, we have followed essentially the same procedure as has been suggested by Shukla and Taylor (1974) for real space summations $\sum_{\underline{\ell}}^{\prime}$. In fact, the invariant form expressions in $\underset{\sim}{q}$-space and
$\underline{\ell}$ space are exactly similar, only the cartesian components of $\ell$ and $q$ interchanges. So, to avoid repetition, we will not describe those transformations here.

In our calculations, we have replaced the frequency $\omega(\underline{q})$ by a dimensionless frequency $\lambda(\underline{q})$ by writing $\lambda(\underline{q} j)=\omega(\varepsilon j) \frac{M}{A_{11}}$ where $M$ is the atomic mass and $A_{11}$ is a force constant. At the end of our calculations, we have multiplied $\lambda(\underline{q} j)$ by only $A_{11}$, thus the M's arising in the definitions of $2 M_{0}\left(\underline{q}_{0}\right), 2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(\underline{q}_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\xi_{0}\right)$, in Eqs. (2.2), (3.14), (3.16), (3.12) and (3.18), exactly cancel.

The expressions for $2 M_{0}\left(\underline{q}_{0}\right), 2 M_{1}\left(\underline{q}_{0}\right), 2 M_{2}\left(\underline{q}_{0}\right), 2 M_{3}\left(\underline{q}_{0}\right)$ and $2 M_{4}\left(\underline{q}_{0}\right)$ then can be written from Eqs. (5.11a), (4.9), (4.10), (4.20) and (4.21) as

$$
\begin{equation*}
2 M_{0}\left(\varepsilon_{0}\right)=\left(K_{B} T\right) \varepsilon_{0}^{2} a_{0}(v) \tag{7.12}
\end{equation*}
$$

$$
\begin{equation*}
2 M_{1}\left(\underline{q}_{0}\right)=-\left(K_{B} T\right)^{2} \varepsilon_{0}^{2} a_{1}(v) \tag{7.13}
\end{equation*}
$$

$$
\begin{equation*}
2 M_{2}\left(q_{0}\right)=\left(k_{B} T\right)^{2} q_{0}^{2} a_{2}(v) \tag{7.14}
\end{equation*}
$$

$$
\begin{align*}
& 2 m_{3}\left(q_{0}\right)=\left(k_{B} T\right)^{3}\left[a_{3}^{(1)}(v)\left(q_{0}^{4}+q_{0 y}^{4}+q_{0}^{4}\right)\right. \\
& \left.+a_{3}^{(2)}(v)\left(q_{o_{x}}^{2} q_{y}^{2}+q_{o_{x}}^{2} q_{o_{z}}^{2}+q_{o y}^{2} q_{o_{z}}^{2}\right)\right]  \tag{7.15}\\
& 2 m_{4}\left(\varepsilon_{0}\right)=-\left(k_{B} T\right)^{3}\left[a_{4}^{(1)}(v)\left(q_{0_{x}}^{4}+q_{0}^{4}+\varepsilon_{0}^{4}\right)\right. \\
& \left.+a_{4}^{(2)}(v)\left(\varepsilon_{0}^{2} q_{0}^{2}+q_{0_{x}}^{2} \varepsilon_{0_{z}}^{2}+\varepsilon_{0_{y}}^{2} \varepsilon_{0_{z}}^{2}\right)\right] \tag{7.16}
\end{align*}
$$

where the volume dependent quantities $a_{0}(v), a_{1}(v), a_{2}(v), a_{3}^{(1)}(v)$, $a_{3}^{(2)}(v), a_{4}^{(1)}(v)$ and $a_{4}^{(2)}(v)$ are given by

$$
\begin{align*}
& a_{0}(v)=N_{H}(v)  \tag{7.17}\\
& a_{1}(v)=N_{0}^{A}(v) / N^{2}  \tag{7.18}\\
& a_{2}(v)=N_{0}^{B}(v) / 2 N^{2} \tag{7.19}
\end{align*}
$$

$$
\begin{align*}
& a_{3}^{(1)}(v)=N_{x x x x}^{c}(v) / 12 N^{3}  \tag{7.20}\\
& a_{3}^{(2)}(v)=\left\{N_{x x y y}^{c}(v)\right\} / 12 N^{3} \tag{7.21}
\end{align*}
$$

$$
\begin{equation*}
a_{4}^{(1)}(v)=N_{x x x x}^{D} \text { (v) } / 4 N^{3} \tag{7.22}
\end{equation*}
$$

$$
\begin{equation*}
a_{4}^{(2)}(v)=\left\{N_{x x y y}^{D}(v)\right\} / 4 N^{3} \tag{7.23}
\end{equation*}
$$

and the terms
$N_{H}(v), N_{0}^{A}(v), N_{0}^{B}(v)$, $N_{x x x_{x}}^{c}(v),\left\{N_{x x y y}^{C}(v)\right\}, N_{x x x_{x}}^{D}(v)$ and $\left\{N_{x x_{y y}}^{D}(v)\right\}$ are defined in Eqs. (5.11b), (4.15), (4.16), (4.22), (4.23), (4.24) and (4.25), respectively, and their simplified expressions given in section 5 . The explicit volume and temperature dependence of $2 \boldsymbol{M}\left(\underline{q}_{0}\right)$ is shown in Eqs. (7.12) to (7.23). We note that the volume itself is again a temperature dependent quantity.

Since the inharmonic terms in $2 \boldsymbol{M}\left(\underline{q}_{0}\right)$, given by Eqs. (7.18) to (7.23) are already of $O\left(\lambda^{2}\right)$, there is no need to examine the variation of these quantities with volume as the increase in volume simply produces the effect of higher order inharmonic terms in $\boldsymbol{\lambda}$. Thus, to take care of the volume dependence of $2 \mathrm{M}\left(\underline{q}_{0}\right)$, it is sufficient at least to $O\left(\lambda^{2}\right)$ to consider the volume dependence of the harmonic contributions to $2 \mathbb{M}\left(\underline{\varepsilon}_{0}\right)$. We have done this by calculating the eigenvalues $\omega(\underline{q} j)$ and the eigenvectors $\boldsymbol{\ell}(\underline{\varepsilon} j)$ at five different volumes by using five values of the lattice parameter " $a$ " and the corresponding five values of the electron-ion term $G(1 Q 1)$ which correspond to the temperatures $\mathrm{T}=5^{\circ} \mathrm{K}, 111^{\circ} \mathrm{K}, 160^{\circ} \mathrm{K}, 293^{\circ} \mathrm{K}$ and $361^{\circ} \mathrm{K}$. The values of ' $a$ ' and $G\left(\mid Q_{1}\right)$ were obtained from R.C. Shukla (through private communication).

On the other hand to calculate the anharmonic terms in $2 M\left(\underline{q}_{0}\right)$, given by Eq. (7.18) to (7.23), we used the lattice parameter ' $a$ ' and $G\left(1 Q_{1}\right)$ for only one volume corresponding to temperature $\mathrm{T}=5^{\circ} \mathrm{K}$ which is very close to $0^{\circ} \mathrm{K}$.

Since experimental results related to the Debye-Waller factor are available at temperatures $\mathrm{T}=117^{\circ} \mathrm{K}, 180^{\circ} \mathrm{K}, 291^{\circ} \mathrm{K}$ and $368^{\circ} \mathrm{K}$, our calculations of $2 \mathrm{M}\left(\underline{q}_{0}\right)$ were performed at these temperatures. In order to calculate $2 \mathrm{M}\left(\varepsilon_{0}\right)$, we regrouped various anharmonic terms as follows

$$
\begin{align*}
2 m_{1+2}\left(\underline{q}_{0}\right) & =2 m_{1}\left(\underline{q}_{0}\right)+2 m_{2}\left(\underline{q}_{0}\right) \\
& =\left(K_{B} T\right)^{2} q_{0}^{2}\left[a_{2}(v)-a_{1}(v)\right] \tag{7.24}
\end{align*}
$$

$$
\begin{equation*}
2 m_{3+4}^{(1)}\left(q_{0}\right)=\left(k_{B} T\right)^{3}\left(\varepsilon_{0}^{4}+q_{0}^{4}+q_{0_{z}}^{4}\right)\left[a_{3}^{(1)}(v)-a_{4}^{(1)}(v)\right] \tag{7.25}
\end{equation*}
$$

$$
2 M_{3+4}^{(2)}\left(\varepsilon_{0}\right)=\left(k_{B} T\right)^{3}\left(\varepsilon_{0}^{2} q_{0}^{2}+\varepsilon_{0_{x}}^{2} \varepsilon_{0}^{2}+q_{0_{y}}^{2} \varepsilon_{0}^{2}\right)
$$

$$
\begin{equation*}
x\left[a_{3}^{(2)}(v)-a_{4}^{(2)}(v)\right] \tag{7.26}
\end{equation*}
$$

Calculated values of $a_{0}(v), a_{1}(v), a_{2}(v), a_{3}^{(1)}(v)$, $a_{3}^{(2)}(v), \quad a_{4}^{(1)}(v)$ and $a_{4}^{(2)}(v)$ are given in Table 2 (inC.G.S. unit).
 five lowest order reflections (110), (200), (220), (310) and (400), are given in Tables (3a.), (3b), (3c) and (3d).

In order to compare our results with those of experiments of Dawton (1937) from our calculated values of the harmonic and anharmonic contributions to $2 M\left(\underline{q}_{0}\right)$, we calculated the values of $\left(\rho_{T_{0}} / \rho_{T}\right)$ by using the following relation

$$
\begin{equation*}
\frac{\rho_{T_{0}}}{\rho_{T}}=\frac{\exp \left[-2 M\left(q_{0}\right)\right]_{T_{0}}}{\exp \left[-2 M\left(q_{0}\right)\right]_{T}} \tag{7.27}
\end{equation*}
$$

where $\rho_{T_{0}}$ is the intensity of reflection at some standard temperature $T_{0}$ and $\boldsymbol{P}_{\boldsymbol{T}}$ is the intensity of reflection at some other temperature $T$. Values of temperatures used by us are $T_{0}=117^{\circ} \mathrm{K}$ and $\mathrm{T}=180^{\circ} \mathrm{K}, 291^{\circ} \mathrm{K}$ and $368^{\circ} \mathrm{K}$.

We have calculated the values of $\left(\rho_{T_{0}} / \rho_{T}\right)$ in the following three ways :
(1) by using only the harmonic contribution to $2 M\left(\varepsilon_{0}\right)$
(2) by using the harmonic and anharmonic contributions to $2 M\left(\underline{q}_{0}\right)$ but excluding the anomalous part of it, and
(3) by using the harmonic and anharmonic contributions (normal and anomalous) to $2 M\left(\underline{q}_{0}\right)$.
Values of $\left(\rho_{117} / \rho_{180}\right),\left(\rho_{117} / \rho_{291}\right)$ and $\left(\rho_{117} / \rho_{368}\right)$, calculated by us for reflections (110), (200), (220), (310) and (400) are produced in Table 4.

## 8. DISCUSSION OF NUMERICAL RESULTS

From the previous sections, we have seen that the basic quantities which enter into our calculation of $2 M\left(q_{0}\right)$ are the tensors $F_{\alpha \beta \gamma}(\underline{q})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$, and the eigenvalues $\omega(\underline{j})$ and the eigenvectors $\underline{e}(\varepsilon j)$ of the matrix of $F_{\alpha \beta}(\underline{q})$. From Tables $1 \mathrm{a}, 1 \mathrm{~b}$ and 1 c , we see that our calculated values of $\nu(\underline{\varepsilon} j)[=\omega(\underline{\xi}) / 2 \pi]$ are in excellent agreement with the experimental values. This provides confidence in our calculation of the tensors $F_{\alpha \beta}(\underline{q})$ and the eigenvalues and eigenvectors obtained from it. Consequently the tensors $H_{\alpha \beta}(\underline{\ell})$ and $T_{\alpha \beta}(\underline{\ell})$ which are defined in terms of $\omega(\underline{j})$ and $\underline{e}(\underline{q} \boldsymbol{j})$ are also reliable. Also, we have given in section 7 the assessment of the accuracy of our calculated values of $F_{\alpha \beta \gamma}(\underline{\varepsilon})$ and $F_{\alpha \beta \gamma \delta}(\underline{q})$.

In section 7 , we have described the calculation of the harmonic and the inharmonic (normal and anomalous) contributions to $2 M\left(q_{0}\right)$ which are given in Tables $3 \mathrm{a}, 3 \mathrm{~b}, 3 \mathrm{c}$ and 3 d . The calculated ratio of intensities $\left(\rho_{T_{0}} / \rho_{\boldsymbol{T}}\right)$ for the reflections (110), (200), (220), (310) and (400) at $T_{0}=117^{\circ} \mathrm{K}$ and $\mathrm{T}=180^{\circ} \mathrm{K}, 291^{\circ} \mathrm{K}$ and $368^{\circ} \mathrm{K}$ respectively, along with the experimental values obtained by Dawton (1937), are given in Table 4. At this point we note that, for the harmonic part of the calculation, we have taken into account the volume change (quasiharmonic calculation). For the quasi-harmonic calculations of $2 M_{0}\left(\underline{q}_{0}\right)$ at the temperatures $117^{\circ} \mathrm{K}, 180^{\circ} \mathrm{K}, 291^{\circ} \mathrm{K}$ and $368^{\circ} \mathrm{K}$, we have used slightly different volumes corresponding to the temperatures $111^{\circ} \mathrm{K}, 160^{\circ} \mathrm{K}, 293^{\circ} \mathrm{K}$ and $361^{\circ} \mathrm{K}$ respectively, because the first principle potential was available at these volumes. For the reasons explained in section 7, we
have performed the calculation of the anharmonic contributions to $2 M\left(\underline{q}_{0}\right)$ at the $5^{\circ} \mathrm{K}$ volume.

From Table 4, the difference between our calculated and the experimental values of $\left(\rho_{\tau_{0}} / \rho_{T}\right)$ can be expressed as the percentage difference from the experimental values. We call this percentage difference $P_{n}\left(T_{0} / T\right)$ in general. When this percentage difference is referred to our quasi-harmonic calculations, we call it $P_{1}\left(T_{0} / T\right)$, and similarly $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ refer to our (quasiharmonic + normal anharmonic) and (quasi-harmonic + total anharmonic) results respectively. Values of $P_{1}\left(T_{0} / T\right), P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ are given in Table 5 for all the reflections.

From Table 5 , we note that the values of $P_{1}(117 / 180)$ remain within +5.2 to -3.5 for all reflections, which indicates that our quasiharmonic values of $\left(\rho_{117} / \rho_{180}\right)$ can mostly account for the experimental values. But the values of $P_{1}(117 / 291)$ lie within +3.5 to -22.9 and the values of $P_{1}(117 / 368)$ lie within -20.0 to -44.1 . From these results we can infer that our quasi-harmonic results are inadequate to explain the experimental results at $\mathrm{T}=368^{\circ} \mathrm{K}$ whereas at $\mathrm{T}=291^{\circ} \mathrm{K}$ the quasi-harmonic results are adequate for the reflections (400), (310) and (220), and inadequate for the reflections (110) and (200).

A careful observation of Table reveals mainly two types of behaviour of the quantities $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ for various reflections. The first kind may be called the "converging type" where the anharmonic contributions bring the quasi-harmonic results closer to the experimental values. For example, we note that, for the reflection (110),

$$
\left|P_{3}(117 / 180)\right| \leqslant\left|P_{2}(117 / 180)\right| \leqslant\left|P_{1}(117 / 180)\right|
$$

The physical significance of this may be as follows. For the reflection (110) and $T=180^{\circ} \mathrm{K}$, the addition of the normal and the anomalous anharmonic terms to the quasi-harmonic one improves the agreement with the experimental result. Similar behaviour is exhibited by $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ for the reflections (110) and (200) for all valuesof $T$.

The second kind of behaviour of the quantities $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ may be called the 'diverging type' where the enharmonic contributions are in the opposite direction and their addition to the quasi-harmonic results produces poor agreement with the experimental values. For example, we note that for the reflection (220)

$$
\left|P_{3}(117 / 180)\right|>\left|P_{2}(117 / 180)\right|>\left|P_{1}(117 / 180)\right|
$$

With the exception of $P_{2}(117 / 368)$ and $P_{3}(117 / 368)$ for the reflection (400), all other percentages, viz. $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ for the reflections (220), (310) and (400) are of the divergent type.
$P_{2}(117 / 368)$ and $P_{3}(117 / 368)$, for the reflection (400) are exceptions because $P_{3}(117 / 368)$ indicates almost a complete agreement with the experimental result, whereas if the anomalous terms are left out the agreement is within $12 \%$.

In order to explain all these behaviour of our calculated values of the Debye-Waller factor, we would like to mention that the expressions of the inharmonic contributions to the Debye-Waller factor, as given by Maradudin and Fin, are not complete. These expressions contain anharmonic contributions only up to $O\left(\lambda^{2}\right)$ and do not contain any term of $O\left(\lambda^{4}\right)$. But anharmonic terms of $O\left(\lambda^{4}\right)$ may be quite
significant too. For example, Shukla and Cowley (1971) and Shukla and Wilk (1974) have calculated the Helmholtz free energy of an anharmonic crystal to $O\left(\lambda^{4}\right)$, and found that the contributions from terms of $O\left(\lambda^{4}\right)$ are not negligible. So, for the case of the anharmonic contributions to the Debye-Waller factor also, we expect the anharmonic terms of $O\left(\lambda^{4}\right)$ to be quite important. All these facts suggest that if the terms of $O\left(\lambda^{4}\right)$ are added to terms of $O\left(\lambda^{2}\right)$, the values of the Debye-Waller factor may converge in a better way.

Keeping all these facts in mind, and noting the values of $P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$ for all the reflections in Table $\mathcal{F}$, we can reasonably say that the agreement between our calculated results and the experimental results is satisfactory.

In order to establish the relative importance of the normal and the anomalous anharmonic terms in $2 M\left(\underline{q}_{0}\right)$, we examine the Table 6 which gives our calculated values of $\left[2 M_{1+2}\left(q_{0}\right) / 2 M_{0}\left(q_{0}\right)\right] \times 100$, $\left[2 m_{3+4}^{(1)}\left(q_{0}\right) / 2 M_{0}\left(q_{0}\right)\right] \times 100$, and $\left[2 m_{3+4}^{(2)}\left(q_{0}\right) / 2 m_{0}\left(q_{0}\right)\right] \times 100$. We denote them by $R_{1+2}, R_{3+4}^{(1)}$ and $R_{3+4}^{(2)}$, respectively. From this table it is seen that, for all the reflections, $R_{1+2}$ increases with temperature and remains practically constant for different reflections. $R_{1+2}$ varies from $4.2 \%$ at $117^{\circ} \mathrm{K}$ to $12.5 \%$ at $368^{\circ} \mathrm{K}$. Noting that the Debye temperature $\theta_{\mathcal{D}}$ of sodium is $\sim 151^{\circ} \mathrm{K}$ and its melting temperature $T_{m}$ is $\sim 371^{\circ} \mathrm{K}$, we find that the normal anharmonic contribution to $2 M\left(q_{0}\right)$ is not negligible even at $T<\theta_{D}$, and it becomes quite significant at $T \sim T_{m}$.
(2) On the other hand, we find from Table 6 that $R_{3+4}^{(1)}$ and
$R_{3+4}^{(1)}$ do not remain constant for different reflections. $R_{3+4}^{(2)}$ increases with the order of reflection whereas $R_{3+4}$ varies in a different way. But both $R_{3+4}^{(1)}$ and $R_{3+4}^{(2)}$ increase with the increase of temperature. Combining $R_{3+4}^{(1)}$ and $R_{3+4}^{(2)}$, we find that the total contribution of the anomalous terms to $2 M\left(q_{0}\right)$ becomes of the order of $1 \%$ at the lowest temperature $T=117^{\circ} \mathrm{K}$ for reflections (220) and (310), whereas at the highest temperature $T=368^{\circ} \mathrm{K}$ the total anomalous contribution becomes $2.8 \%, 1.4 \%, 9.3 \%, 5.5 \%$ and $2.8 \%$ for the reflections (110), (200), (220), (310) and (400) respectively. Thus, the anomalous terms are found not to be negligible for certain reflections even at $T \sim \theta_{\mathcal{D}}$ and they become quite significant at $T \sim T_{m}$ for most of the reflections.

## 9. CONCLUSION

We have derived the anharmonic contribution to $2 M\left(q_{0}\right)$, for a cubic metal with small ion core, in terms of $F_{\alpha \beta \gamma}(\underline{\varepsilon})$ $F_{\alpha \beta \gamma \delta}(\underline{q})$, and the eigenvalues $\omega(\underline{q})$ and the eigenvectors $\underline{e}(\underline{q})$ of the tensor $F_{\alpha \beta}(\underline{q})$. We have introduce methods for an accurate calculation of the tensors $F_{\alpha \beta}(\underline{q})$,

$$
F_{\alpha \beta \gamma}(\underline{q}) \text { and } F_{\alpha \beta \gamma \delta}(\underline{q}) \text {. All the restricted multiple }
$$ whole Brillouin zone sums have been reduced to single whole Brillouin zone sums using the plane wave representation of the delta function. Thus, the first two objectives of this thesis, as mentioned in the introduction, have been achieved.

We have calculated $2 M\left(q_{0}\right)$ for sodium and compared the calculated results with the experimental results of Dawson (1937). From our calculations, we found that the anomalous terms in $2 M\left(q_{0}\right)$ are significant for certain reflections and become important at temperatures of the order of the melting temperature.

This completes the remaining two objectives of this thesis.

Table (la ) Calculated and experimental values of phonon frequencies $v(\underset{\sim}{q})$ (in units of $10^{12} \mathrm{cps}$ ) along $\underset{\sim}{q}=\frac{2 \pi}{a}[\zeta, 0,0]$ direction, for sodium at $90^{\circ} \mathrm{K}$

| $\zeta$ | Calculated | Experimenta 1 |
| :---: | :---: | :---: |
| (Longitudinal, L) |  |  |
| 0.20 | 1.296 | $1.43 \pm 0.07$ |
| 0.30 | 1.869 | $1.94 \pm 0.06$ |
| 0.40 | 2.322 | $2.44 \pm 0.05$ |
| 0.50 | 2.689 | $2.78 \pm 0.06$ |
| 0.60 | 2.965 | $3.01 \pm 0.07$ |
| 0.70 | 3.202 | $3.24 \pm 0.06$ |
| 0.80 | 3.406 | $3.44 \pm 0.05$ |
| 0.85 | 3.489 | $3.53 \pm 0.06$ |
| 0.90 | 3.562 | $3.55 \pm 0.05$ |
| 1.00 | 3.614 | $3.58 \pm 0.04$ |
| (Transverse, T) |  |  |
| 0.20 | 1.131 | $1.09 \pm 0.04$ |
| 0.30 | 1.675 | $1.64 \pm 0.03$ |
| 0.40 | 2.169 | $2.17 \pm 0.04$ |
| 0.50 | 2.607 | $2.59 \pm 0.05$ |
| 0.60 | 2.970 | $2.96 \pm 0.03$ |
| 0.70 | 3.246 | $3.23 \pm 0.04$ |
| 0.75 | 3.358 | $3.35 \pm 0.04$ |
| 0.80 | 3.450 | $3.45 \pm 0.05$ |
| 0.90 | 3.574 | $3.57 \pm 0.06$ |
| 1.00 | 3.614 | $3.58 \pm 0.04$ |

Table (lb ) Calculated and experimental values of phonon frequencies $\nu(q j)$ (in units of $10^{12} \mathrm{cps}$ ) along $q=\frac{2 \pi}{a}[\zeta, \zeta, 0]$ direction, for sodium at $90^{\circ} \mathrm{K}$
$\zeta$ Calculated Experimenta 1
(Longitudinal, L)

| 0.10 | 1.222 | $1.25 \pm 0.04$ |
| :--- | :--- | :--- |
| 0.20 | 2.308 | $2.32 \pm 0.03$ |
| 0.25 | 2.762 | $2.77 \pm 0.05$ |
| 0.30 | 3.130 | $3.17 \pm 0.05$ |
| 0.35 | 3.408 | $3.46 \pm 0.06$ |
| 0.40 | 3.607 | $3.67 \pm 0.05$ |
| 0.45 | 3.725 | $3.75 \pm 0.09$ |
| 0.50 | 3.763 | $3.82 \pm 0.07$ |

(Transverse, $\mathrm{T}_{1}$ )

| 0.14 | .364 | $0.43 \pm 0.03$ |
| :--- | :--- | :--- |
| 0.21 | .522 | $0.61 \pm 0.03$ |
| 0.28 | .664 | $0.76 \pm 0.03$ |
| 0.35 | .777 | $0.87 \pm 0.03$ |
| 0.42 | .837 | $0.92 \pm 0.04$ |
| 0.50 | .856 | $0.93 \pm 0.02$ |

(Transverse, $T_{2}$ )

| 0.15 | 1.168 | $1.16 \pm 0.04$ |
| :--- | :--- | :--- |
| 0.20 | 1.513 | $1.52 \pm 0.04$ |
| 0.25 | 1.815 | $1.81 \pm 0.03$ |
| 0.28 | 1.976 | $1.97 \pm 0.03$ |
| 0.30 | 2.074 | $2.09 \pm 0.03$ |
| 0.35 | 2.282 | $2.27 \pm 0.04$ |
| 0.40 | 2.431 | $2.47 \pm 0.04$ |
| 0.45 | 2.523 | $2.52 \pm 0.06$ |
| 0.50 | 2.554 | $2.56 \pm 0.05$ |

Table (lc ) Calculated and experimental values of phonon frequencies $v(\underset{\sim}{q})$ (in units of $10^{12} \mathrm{cps}$ ) along $\underset{\sim}{q}=\frac{2 \pi}{a}[\zeta, \zeta, \zeta]$ direction, for sodium at $90^{\circ} \mathrm{K}$ $\zeta$ Calculated Experimental
(Longitudinal, L)

| 0.10 | 1.545 | $1.53 \pm 0.05$ |
| :--- | :--- | :--- |
| 0.20 | 2.760 | $2.72 \pm 0.06$ |
| 0.25 | 3.169 | $3.16 \pm 0.06$ |
| 0.30 | 3.385 | $3.38 \pm 0.06$ |
| 0.35 | 3.451 | $3.44 \pm 0.05$ |
| 0.40 | 3.386 | $3.42 \pm 0.06$ |
| 0.45 | 3.177 | $3.22 \pm 0.06$ |
| 0.50 | 2.858 | $2.88 \pm 0.04$ |

(Transverse, T)

| 0.20 | 1.326 | $1.28 \pm 0.06$ |
| :--- | :--- | :--- |
| 0.30 | 1.941 | $1.92 \pm 0.06$ |
| 0.40 | 2.452 | $2.47 \pm 0.05$ |
| 0.50 | 2.858 | $2.88 \pm 0.04$ |

Table 2. Calculated values of the coefficients $a_{0}(v), a_{1}(v), a_{2}(v)$, $a_{3}{ }^{(1)}(v), a_{3}^{(2)}(v), a_{4}^{(1)}(v)$ and $a_{4}^{(2)}(v)$ in Eqs. (7.17) to (7.23).

Volumes or the corresponding
Coefficients lattice parameter
Values

| $a_{0}(v)$ | $\mathrm{a}=4.2247 \mathrm{~A}^{\circ}\left(\mathrm{T}=5^{\circ} \mathrm{K}\right)$ | $0.227010 \times 10^{-3}$ |
| :---: | :---: | :---: |
|  | $\mathrm{a}=4.244 \mathrm{~A}^{\circ}\left(\mathrm{T}=111^{\circ} \mathrm{K}\right)$ | $0.224117 \times 10^{-3}$ |
|  | $\mathrm{a}=4.251 \mathrm{~A}^{\circ}\left(\mathrm{T}=160^{\circ} \mathrm{K}\right)$ | $0.225378 \times 10^{-3}$ |
|  | $\mathrm{a}=4.288 \mathrm{~A}^{\circ}\left(\mathrm{T}=293^{\circ} \mathrm{K}\right)$ | $0.249097 \times 10^{-3}$ |
|  | $\mathrm{a}=4.309 \mathrm{~A}^{\circ}\left(\mathrm{T}=361^{\circ} \mathrm{K}\right)$ | $0.237456 \times 10^{-3}$ |
| $a_{1}(v)$ | [all these anharmonic | $0.370073 \times 10^{10}$ |
| $\mathrm{a}_{2}(\mathrm{v})$ | coefficients are calculated | $0.42833 \times 10^{10}$ |
| $a_{3}^{(1)}(v)$ | at the same volume which | $0.147430 \times 10^{5}$ |
| $a_{3}^{(2)}(v)$ | refers to the lattice parameter | $-0.115742 \times 10^{6}$ |
| $a_{4}^{(1)}(v)$ | at $\left.5^{\circ} \mathrm{K}\right]$ | $-0.159900 \times 10^{5}$ |
| $\mathrm{a}_{4}{ }^{(2)}(\mathrm{v})$ |  | $-0.285015 \times 10^{6}$ |

$a_{0}(v)$ is expressed in units of $\mathrm{erg}^{-1} \mathrm{~cm}^{2}$.
$a_{1}(v)$ and $a_{2}(v)$ are expressed in units of $\operatorname{erg}^{-2} \mathrm{~cm}^{2}$.
$a_{3}{ }^{(1)}(v), a_{3}^{(2)}(v), a_{4}^{(1)}(v)$, and $a_{4}^{(2)}(v)$ are in units of $\mathrm{erg}^{-3} \mathrm{~cm}^{4}$.

Table 3a. Calculated values of $2 \mathrm{M}_{\mathrm{o}}\left(\mathrm{q}_{\sim}\right)$

| Reflection | $117^{\circ} \mathrm{K}$ | $180^{\circ} \mathrm{K}$ | $291^{\circ} \mathrm{K}$ | $368^{\circ} \mathrm{K}$ |
| :---: | :---: | :---: | :---: | :---: |
| 110 | 0.1587 | 0.2447 | 0.4894 | 0.4298 |
| 200 | 0.3174 | 0.9789 | 0.8595 | 1.0261 |
| 220 | 0.6348 | 1.2236 | 2.7190 | 2.0521 |
| 310 | 0.7935 | 1.9578 | 3.4380 | 2.5651 |
| 400 | 1.2696 |  | 4.1042 |  |

$$
\text { Table 3b. Calculated values of } 2 M_{1+2}\left(q_{0}\right)
$$

| Reflection | $117^{\circ} \mathrm{K}$ | $180^{\circ} \mathrm{K}$ | $291^{\circ} \mathrm{K}$ | $368^{\circ} \mathrm{K}$ |
| :--- | :--- | ---: | :--- | :--- |
| 110 | 0.0067 | 0.0157 | 0.0404 | 0.0639 |
| 200 | 0.0133 | 0.0314 | 0.0808 | 0.1279 |
| 220 | 0.0267 | 0.0629 | 0.1615 | 0.2558 |
| 310 | 0.0333 | 0.0786 | 0.2019 | 0.3197 |
| 400 | 0.0533 | 0.1258 | 0.3230 | 0.5116 |

Table 3c. Calculated values of $2 \mathrm{M}(1)\left(\mathrm{q}_{3}\right)$

| Reflection | $117^{\circ} \mathrm{K}$ | $180^{\circ} \mathrm{K}$ | $291^{\circ} \mathrm{K}$ | $368^{\circ} \mathrm{K}$ |
| :---: | :---: | :---: | :---: | :---: |
| 110 | 0.0001 | 0.0005 | 0.0018 | 0.0036 |
| 200 | 0.0005 | 0.0018 | 0.0074 | 0.0146 |
| 220 | 0.0010 | 0.0036 | 0.0147 | 0.0292 |
| 310 | 0.0017 | 0.0063 | 0.0257 | 0.0510 |
| 400 | 0.0040 | 0.0744 | 0.0588 | 0.1166 |

Table 3d. Calculated values of $2 M_{3+4}^{(2)}\left(q_{0}\right)$

| Reflection | $117^{\circ} \mathrm{K}$ | $180^{\circ} \mathrm{K}$ | $291^{\circ} \mathrm{K}$ | $368^{\circ} \mathrm{K}$ |
| :--- | ---: | ---: | ---: | ---: |
| 110 | 0.0003 | 0.0012 | 0.0051 | 0.0100 |
| 200 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 220 | 0.0055 | 0.0198 | 0.0810 | 0.1606 |
| 310 | .0031 | 0.0112 | 0.0455 | 0.0903 |
| 400 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4. Calculated and experimental values of $\rho_{T_{0}} / \rho_{T}$

Quasiharmonic

Quasi-
harmonic + normal anharmonic

Reflection (110)
$\rho_{117} / \rho_{180}$
$\rho_{117} / \rho_{291}$
$\rho_{117} / \rho_{368}$
$\rho_{117} / \rho_{180} \quad 1.188$
$\rho_{117} / \rho_{291}$
$\rho_{117} / \rho_{368}$
1.720
2.031
$\rho_{117} / \rho_{180}$
$\rho_{117} / \rho_{291}$
$\rho_{117} / \rho_{368}$
4.126
1.537
$\rho_{117} / \rho_{180}$
$\rho_{117} / \rho_{291}$
$\rho_{117} / \rho_{368}$
5.881
$\rho_{117} / \rho_{180}$
$\rho_{117} / \rho_{291}$
$\rho_{117} / \rho_{368}$
1.090
1.311
1.425
1.100
1.356
1.509

Reflection (200)
1.209
1.840
2.278

Reflection (220)
1.463
3.384
5.189

Reflection (310)
. 53
3.878
1.609
4.590
7.831

Reflection (400)
2.140
11.452
26.921
1.101
1.13
1.365
1.7
1.529
1.9
1.211
1.23
1.852
2.0
2.310
2.5
1.488
1.34
3.700
2.9
6.232
5.3
1.629
1.50
4.905
4.0
8.976
8.3
2.162
1.96
12.097
8.8
30.131
30.4

Table 5. Values of $P_{1}\left(T_{0} / T\right), P_{2}\left(T_{0} / T\right)$ and $P_{3}\left(T_{0} / T\right)$

|  |  | $P_{3}\left(T T_{0} / T\right)$ |
| :--- | :--- | :--- |
|  |  | $P_{2}\left(T_{0} / T\right)$ |
| $P_{n}\left(T_{0} / T\right)$ | $P_{1}\left(T_{0} / T\right)$ | Quasi- |
|  | Quasi- | harmonic + |
| harmonic | normal | normal |
|  |  | anharmonic |
|  |  | Reflection (110) |


| $P_{n}(117 / 180)$ | -3.5 |
| :--- | :--- |
| $P_{n}(117 / 291)$ | -22.9 |
| $P_{n}(117 / 368)$ | -24.7 |

-2.7
-20.0
-20.5
$-2.7$
$-19.4$
-20.5
$-19.5$
Reflection (200)

| $P_{n}(117 / 180)$ | -3.3 |
| :--- | :--- |
| $P_{n}(117 / 291$ | -14.0 |
| $P_{n}(117 / 368)$ | -20.0 |

$$
-1.6
$$

$$
-1.6
$$

$-8.0$
$-7.5$
$-8.8$
$-6.6$
Reflection (220)

| $P_{n}(117 / 180)$ | 5.2 |
| :--- | :--- |
| $P_{n}(117 / 291)$ | 3.5 |
| $P_{n}(117 / 368)$ | -22.1 |

9.0
11.2
16.6
27.6
$-2.1$
17.5

Reflection (310)

| $P_{n}(117 / 180)$ | 2.7 |
| :--- | :--- |
| $P_{n}(117 / 291$ | -3.0 |
| $P_{n}(117 / 368$ | -28.9 |


| 7.3 | 8.7 |
| :--- | :--- |
| 14.8 | 22.8 |
| -5.7 | 8.2 |

Reflection (400)

| $P_{n}(117 / 180)$ | 1.5 |
| :--- | :--- |
| $P_{n}(117 / 291$ | -1.1 |
| $P_{n}(117 / 368)$ | -44.1 |

Table 6. Calculated values of $R_{1+2}, R_{3+4}^{(1)}$, and $R_{3+4}^{(2)}$.


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