Anharmonic interference effects in potassium

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Anharmonic interference effects in potassium

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Abstract. The contributions to the dynamic form factor \( S(Q, \omega) \) arising from interference between its one-phonon and multiphonon parts have been observed in the scattering of neutrons from potassium. Interference makes two qualitatively distinct contributions to \( S(Q, \omega) \). One is approximately proportional to the one-phonon part, \( S_1(Q, \omega) \), and as a result contributes scattering intensity largely within the one-phonon peak region which is symmetric about the one-phonon frequency. The other is asymmetric around the one-phonon frequency and for narrowly peaked phonon groups contributes intensity of opposite sign in the multiphonon region directly on each side of the one-phonon peak. Both contributions have been observed here, the second contribution apparently for the first time. Both contributions, and their dependence on wavevector \( Q \) and frequency \( \omega \), can be described by an anharmonic theory (Ambegaokar et al) which includes interference between the one- and two-phonon parts of \( S(Q, \omega) \) via the cubic anharmonic term.

1. Introduction

The purpose of the present paper is to investigate the contribution to the coherent inelastic scattering of neutrons from a crystal arising from interference between its one-phonon and multiphonon parts. Potassium is selected firstly since reliable descriptions of the interionic potential are available (Duesbury et al 1973, Geldart et al 1970) for computation of the interference effect, and secondly since the one-phonon scattering has already been studied extensively to determine both the 'harmonic' phonon frequencies at low temperatures (Cowley et al 1966) and the anharmonic contributions at high temperatures (Buyers and Cowley 1969).

The study of these interference phenomena is of importance because they arise purely from the anharmonic nature of a solid, and display a highly characteristic wavevector and temperature dependence which should (at least in principle) permit a rather direct investigation of the anharmonic contributions to the potential. It is also important to determine whether the interference is of sufficient magnitude to invalidate the usual interpretation of the dynamic form factor \( S(Q, \omega) \) as a simple

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sum of (i) a highly frequency-dependent, one-phonon part and (ii) a largely uniform and readily separable, frequency-independent, multiphonon part. This question arises since the interference term can make a frequency-dependent contribution to $S(Q, \omega)$ both inside and outside the one-phonon peak region. At least in simple cases, this contribution oscillates in sign with the sign of the reduced wave vector $q$ of the phonon under study. We define $q$ in terms of the momentum $hQ$ transferred to the crystal in the scattering event, by $hQ = h(q + T)$ where $T$ is the nearest vector of the reciprocal lattice. Interference can change the observed scattering intensity and line shape in the one-phonon region from their values expected in the absence of this anharmonic effect, in a sometimes confusing manner.

The nature of interference was first elucidated by Ambegaokar et al (1965) following a paper by Thompson (1963). However, an initial estimate of the distortion of $S(Q, \omega)$ in the one-phonon peak region caused by interference (Maradudin and Ambegaokar 1964) suggested interference contributions were small. The first experimental observation of interference effects was nevertheless made by Buyers and Smith (1966), as an unexpected variation with $Q$ of the intensity of the static form factor $S(Q)$ in an x ray thermal diffuse scattering study of NaCl. These results were initially interpreted in terms of a linear dependence of the form factor on the displacements of neighbouring atoms (Buyers et al 1968). Interference effects were subsequently observed, albeit with difficulty, in a neutron inelastic scattering study of KBr by Cowley et al (1969). A satisfactory interpretation of both sets of results in terms of interference was given by Cowley and Buyers (1969).

Following this early work, several x ray thermal diffuse scattering studies were made (see for example Pirie et al 1971, Hervet and Ober 1973, and other references cited therein). In these experiments, the anharmonic interference terms are seen to provide the dominant contributions to the observed intensity variations, although other effects arising from deformations of the electronic distributions around the ions were also present. Such electronic effects would not occur in the analogous neutron scattering experiments, so that a comparison of both x ray and neutron investigations of the same material should be helpful in separating these two contributions in the x ray experiments.

Interference phenomena have recently been observed in a most dramatic manner in neutron scattering experiments on the highly anharmonic crystal, solid helium (Minkiewicz et al 1968, 1973, Reese et al 1971, Osgood et al 1972, Horner 1972, Beck and Meier 1972, Werthamer 1972 and Glyde 1974). Interference makes a significant contribution to the scattering intensity in solid $^3$He (Nielsen 1972) and probably also in Ne (Skalyo et al 1972, Endoh et al 1975). A similar interference effect, though much more difficult to interpret clearly, appears in the neutron scattering from liquid $^4$He (Cowley and Woods 1971, Glyde 1974). In the context of these experiments, we investigate interference in potassium to see whether interference is observable and of importance in the case of a simple metal.

2. The nature of interference effects

As noted in the introduction, the dynamic form factor,

$$S(Q, \omega) = \int\sum_{e,e'} dt \exp(-i\omega t) (1/N) \sum_{e,e'} \left\langle \exp[-iQ \cdot r(e, t)] \exp[iQ \cdot r(e', 0)] \right\rangle \tag{1}$$
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is usually expanded as a sum representing scattering from a specific number of phonons,

\[ S(Q, \omega) = S_0(Q) + S_1(Q, \omega) + S_{\text{INT}}(Q, \omega) + S_2(Q, \omega) + \ldots \]

\[ \equiv S_0(Q) + S_p(Q, \omega) + S_2(Q, \omega) + \ldots . \]

Here \( S_0(Q) \) is the elastic, Bragg scattering not of interest here, \( S_1 \) represents scattering from one phonon, \( S_2 \) scattering from two phonons and so on. \( S_{\text{INT}} \) is the interference term between the one-phonon and multiphonon parts. This arises, for example, when an incoming neutron excites a single phonon and, before the neutron is emitted, the single phonon decays via anharmonic interactions into two or more phonons. The term \( S_p = S_1 + S_{\text{INT}} \) may be expressed as (Ambegaoker et al 1965)

\[ S_p(Q, \omega) = -2 [n(\omega) + 1] \text{Im} \{ R(Q, q\lambda, \omega) d(q\lambda, \omega) \}
\times R^*(Q, q\lambda, \omega) \sum_{\tau} \Delta(Q - q - \tau). \quad (2) \]

Here \( n(\omega) \) is the Bose function, \( R(Q, q\lambda, \omega) \) is a frequency-dependent structure factor and

\[ d(q\lambda, \omega) = \frac{2\omega_{q\lambda}}{-\omega^2 + \omega_{q\lambda}^2 + 2\omega_{q\lambda} \{ \Delta(q\lambda, \omega) + i\Gamma(q\lambda, \omega) \}} \]

is the one-phonon Green function. The \( \omega_{q\lambda} \) and \( \epsilon_{q\lambda} \) below, are the harmonic frequency and polarization vectors, respectively, of the one phonon having reduced wavevector \( q \) and branch index \( \lambda \) while \( \Delta(q\lambda, \omega) \) and \( \Gamma(q\lambda, \omega) \) are the anharmonic shift and inverse lifetime, respectively. When interference is absent, \( R \) reduces to the usual one-phonon structure factor for Bravais crystals,

\[ F(Q, q\lambda) = \left( \frac{\hbar}{2m\omega_{q\lambda}} \right)^{1/2} [Q, \epsilon_{q\lambda}] d(Q) \]

where \( m \) is the mass and \( d(Q) \) is the Debye–Waller factor. In this case \( S_p \) reduces to \( S_1 \) of form

\[ S_1(Q, \omega) = [n(\omega) + 1] \sum_{\lambda} F(Q, q\lambda)^2 A(q\lambda, \omega) \sum_{\tau} \Delta(Q - q - \tau) \quad (3) \]

where \( A(q\lambda, \omega) = -2 \text{Im} d(q\lambda, \omega) \) is the one-phonon response function and \( \Delta \) is the Kronecker delta function relating \( q \) to the scattering vector (or momentum transfer vector) \( Q \).

Here we consider interference between the one- and two-phonon parts only. In addition, we link the one phonon \( (q\lambda) \) with another pair of phonons, labelled 1 and 2, only via the lowest order cubic anharmonic term, having coefficient \( V_3(q\lambda, q_{1\lambda_1}, q_{2\lambda_2}) \). In this case \( R \) is (Cowley and Buyers 1969, Glyde 1974)

\[ R(Q, q\lambda, \omega) = F(Q, q\lambda) - E(Q, q\lambda, \omega) \]

where

\[ E = \frac{1}{2\hbar N^{1/2}} \sum_{1,2} F_1 F_2 V_3(q, 1, 2) d_3(q, 1, 2, \omega) \Delta(q + q_1 + q_2). \]
Here \( d_2^2(1, 2, \omega + \varepsilon) \) is the harmonic two-phonon Green function having real and imaginary parts given, for example, in equation (25) of Glyde (1974), and \( F_1 \) and \( F_2 \) are one-phonon structure factors. Since \( V_3 \) is purely imaginary, \( R^* = -(F - E) \). Finally, to estimate the multiphonon background we include the two-phonon part

\[
S_2(Q, \omega) = \left[ n(\omega) + 1 \right] d^{-2}(Q) \sum_{1,2} F_1^2 F_2^2 \text{Im} d_2^2(1, 2, \omega) \sum_{\tau} \Delta[Q - (q_1 + q_2) - \tau].
\]

To compute \( S_1, S_p \) and \( S_2 \) we have used exactly the same effective ion–ion potential and self-consistent anharmonic theory employed by Duesbury et al (1973). The \( \omega_{q \lambda} \) are then the self-consistent harmonic frequencies with \( V_{3 \lambda}, \Delta(q \lambda, \omega) \) and \( \Gamma(q \lambda, \omega) \) obtained from a vibrationally averaged cubic anharmonic term. In order to simulate experiment, we have folded the resulting \( S(Q, \omega) \) with a gaussian function in \( \omega \), having a full width at half-maximum of \( W = 0.3 \text{ THz} \), a typical spectrometer resolution width.

The physical content of \( S_p(Q, \omega) \) may be clearly displayed by retaining the two lowest order interference contributions and writing \( S_p(Q, \omega) \) in equation (2) as

\[
S_p(Q, \omega) = S_1(Q, \omega) \left\{ 1 - 2 \left[ A + B \left( -\omega^2 + \Omega_{q \lambda}^2 \right) \right] \right\}
\]

where \( A \equiv \text{Re}(E/F), B \equiv \text{Im}(E/F) \) and \( \Omega_{q \lambda}^2 = \omega_{q \lambda}^2 + 2\omega_{q \lambda} \Delta \) is the one-phonon frequency including anharmonic contributions. Both \( A \) and \( B \) are proportional to \( Q \) and largely frequency-independent. Thus the interference has two contributions. The first \( S_{12}^1 \), where the subscript 12 denotes one-phonon–two-phonon interference, is proportional to \( S_1(Q, \omega) \) depending upon the sign of \( A \). The second, \( S_{12}^2 \), is zero at the one-phonon frequency and makes an asymmetric contribution, centred about \( \Omega_{q \lambda} \). If the one-phonon response is very sharply peaked, then the second term is very small within the one-phonon peak region, as sketched in figure 1, where the observed width of \( S_1 \) is governed mainly by instrumental resolution effects. Only if the one-phonon intrinsic width is relatively large can the asymmetric contribution distort the one-phonon peak shape or alter its peak position. However, the \( S_{12}^1 \) term can be significant outside the main peak of \( S_1(Q, \omega) \) if \( S_1 \) has tails extending outside its main peak region, as indicated in figure 1. (These tails can be seen in the actual calculations to be discussed below, see figure 2.) In this case \( S_{12}^1 \) has the effect of raising or lowering the apparent multiphonon background on each side of the main peak of \( S_1 \). The symmetric interference term, \( S_{12}^2 \), will always contribute intensity within the one-phonon peak region, however sharp the phonon group.

Examples of the calculated differences between \( S_1 \) and \( S_p \) are shown in figure 2. Since \( S_1 \propto Q^2 \) and \( (S_1 \times A) \propto Q^3 \), the interference grows relative to \( S_1 \) as \( Q \) increases. However, the multiphonon background scattering grows as \( Q^n \) where \( n \geq 4 \), so there will in practice be an optimum \( Q \) value for observing the interference effects.

Finally, the cubic coefficient \( V_3 \) in \( E \) is zero if the reduced wavevector, \( q = Q - \tau \), is zero. Thus the interference effect is zero at all reciprocal lattice points \( \tau \).

A particularly simple case is that in which \( q, Q \) and \( \tau \) are all parallel. Then \( q \) is positive (negative) when \( Q \) is greater (less) than \( \tau \). Since \( V_3 \) is an odd function of \( q \), the interference changes sign with the sign of \( q \), figure 1. An additional consequence of symmetry is that the interference effect is zero at points half-way between two reciprocal lattice points. The oscillatory nature of the effect is shown in figure 3,
Figure 1. Schematic illustration of interference contributions to $S(Q, \omega)$ in potassium. $S_1(Q, \omega)$ (full curve) is the one-phonon part and $S_{12}(Q, \omega)$ is the one–two phonon interference. $S_{12}$ (-----) is symmetric about the one-phonon peak and $S_{12}$ (----) is asymmetric about the peak. The change of sign of $S_{12}(Q, \omega)$ as $q$ changes sign is clearly shown.

in a particularly straightforward way for the [110] direction. Along the [100] and [111] directions there are accidental zeros, depending on the detailed nature of $V_3$, in addition to the symmetry zeros mentioned above. There are also certain specific experimental difficulties with making the required measurements along the [100] and [111] directions. We therefore selected modes propagating along [110] for detailed study.

Ambegaokar et al showed that $S_1(Q, \omega)$ and $S_2(Q, \omega)$ both satisfy the same first moment sum rule

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega \left\{ \frac{S_2(Q, \omega)}{S_1(Q, \omega)} \right\} = \frac{\hbar Q^2}{2m} d^2(Q).$$

This holds because the two types of interference contribution, (a) and (b), cancel exactly in equation (6). The cancellation is no longer exact if the integration over $\omega$ is over a restricted range, say $\omega_{q_1} - \delta < \omega < \omega_{q_1} + \delta$, around the one-phonon frequency $\omega_{q_1}$. When the integration is restricted to frequencies near the one-phonon region, the symmetric term (a) contributes most to equation (6). In practice $S_2(Q, \omega)$ can be separated from the observed $S(Q, \omega)$ in the one-phonon peak region only. In this case apparent deviations of the sum rule can be obtained which depend sensitively on the choice of $\delta$.

There is, however, an important and well-defined difference between form factors with and without interference

$$S_p(Q) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_p(Q, \omega)$$

and

$$S_1(Q) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_1(Q, \omega)$$
respectively. Although again $S_p(Q, \omega)$ (or $S_1(Q, \omega)$) can be separated from $S(Q, \omega)$ only over a restricted frequency interval, in practice and in calculations (Glyde 1974) the ratio $S_p(Q)/S_1(Q)$ is not very sensitive to reasonable choice of $\delta$. Thus to identify the symmetric interference contribution corresponding to $S_{12}^*$, we will compare observed and computed values of $S_p(Q)/S_1(Q)$.

In summary, we look for two contributions arising from interference: (i) a contribution to the intensity within the one-phonon peak region and (ii) an asymmetric contribution to the multiphonon background on each side of that region. To identify these contributions, we take advantage of their expected $Q$-dependence for a given reduced wavevector $q$ with respect to several reciprocal lattice vectors, and also of its expected temperature dependence. No other effects having such specific properties are believed to exist in the present neutron scattering experiments.

3. Experimental

The experiments were performed with a large ($\sim 15 \text{ cm}^3$) single crystal of potassium metal in a sealed, thin-walled aluminum can, mounted inside a variable-temperature
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Figure 3. The percentage difference between the one-phonon static form factor when the one–two phonon interference contribution is included ($S_2$) and when it is not ($S_1$) for longitudinal phonons along the three symmetry directions in $K$ at 220 K.

helium cryostat so that the $[1\overline{1}0]$ crystallographic axis was vertical, i.e. perpendicular to the plane containing the incident and scattered neutron beams. The triple-axis crystal spectrometer IN2 at the High Flux Reactor, Institute Laue–Langevin, was employed in its 'constant-$Q$' mode of operation with neutron energy loss (Brockhouse 1961) for all of the measurements. The variable energy incident neutron beam was obtained from a double monochromator, the $(220)$ reflecting planes of two copper crystals, while the energy of the scattered neutrons was determined with the help of the $(220)$ planes of a germanium crystal, set to accept a fixed neutron energy $E_F = 22.5$ meV (wavevector $k_F = 3.30$ Å$^{-1}$). The great advantage of a fixed scattered neutron energy for accurate intensity measurements is that the analyser crystal reflectivity and overall detection efficiency remain constant during all scans. A fission counter, whose (low) efficiency is proportional to $1/k_i$, is used to monitor the incident beam just before the sample, and each scattered neutron count is normalized with respect to a preselected total number of monitor counts. To a first approximation, this method of neutron counting automatically eliminates the trivial $(1/k_i)$ factor in the one-phonon scattering cross section. Unfortunately, the ratio of higher order to first-order neutrons present in the incident beam varies with $k_i$; thus the fission monitor counting rate is distorted by the higher order incident neutrons to an extent which also varies with $k_i$. All scans over the same frequency or energy range are of course correctly normalized to each other but a correction factor (of the order of 15% in the present experiments) is necessary when one compares scattered neutron intensities over different energy ranges.

In figure 4 we show the (quasi-harmonic) cross section $S_1(Q, \omega)$, equation (3), calculated for a 1.37 THz mode in $K$ assuming an effective Debye temperature $\theta_D = 90$ K, which, as we shall see later, represents fairly closely the mean-square atomic displacement $\langle u^2 \rangle$. At low temperatures, the $Q^2$ term dominates the exponential over a wide range of $Q$, so that the scattered neutron intensity is highest for
Figure 4. The quasiharmonic scattering cross section \( S_1(Q, \omega) \) in K at \( T = 99, 150, 220 \) and 300 K, assuming an effective \( \theta_0 = 90 \) K. The full sections of the curves show the regions of \( Q \) chosen to study interference.

large \( Q \). At 300 K, however, the intensity at high \( Q \) is greatly reduced by the exponential factor, so that it becomes extremely difficult to make accurate intensity measurements even at medium \( Q \) values. The anharmonic interference effects under investigation when expressed as percentages of \( S_1 \), are largest for high \( T \) and high \( Q \). A compromise is therefore necessary between the conflicting requirements of high neutron cross section (i.e. high \( Q \)–low \( T \), or high \( T \)–low \( Q \)) and a large interference effect. It would also be advantageous to study normal modes of low frequency, and hence high intensity, but we see from figure 3 that the interference effect tends to zero as \( q \) (and hence \( \omega \)) tends to zero. Taking all these factors into account, we find that the optimum series of measurements consists of \((aQ/2\pi) = (0.2, 0.2, 0)\), \((aQ/2\pi) = (1.8, 1.8, 0); (2.2, 2.2, 0); (2.8, 2.8, 0)\) and \((3.2, 3.2, 0)\); the optimum temperature range is 100–150 K, with \( T = 4.5 \) K also necessary as a standard, in order to verify that the interference effects are completely absent at very low \( T \). The neutron groups observed at 4.5 K are particularly well defined since the multiphonon background is very low. These measurements also serve therefore as a check on the absence of any spurious scattering effects. As a further check, \((aQ/2\pi) = (2.5, 2.5, 0)\) was also studied, since interference effects should be absent by symmetry at such a zone boundary point. The low temperature scans are particularly important in order to assess accurately the well known focusing effects of a triple-axis spectrometer, which would normally vary considerably over the range of \( Q \) values mentioned above. Resolution function calculations were carried out in order to choose the spectrometer configuration which minimizes the variation in focusing conditions from one \( Q \) value to another. Conditions of extremely good focusing were thereby avoided, in order that all observed peaks would be of comparable energy width. Since the scattering cross...
sections for both one-phonon and multiphonon processes vary considerably with $Q$ and $T$; it was found necessary to employ total neutron counting times varying between 20 and 110 min per point, in order to obtain roughly comparable statistical accuracy for all peaks. At each $(Q, T)$, many independent scans were made, each corresponding to 10 min per point or less, and these were added together (after checking for consistency) to obtain the final results to be discussed below.

4. Results and interpretation

4.1. Data analysis

Figure 5 shows the observed $S(Q, \omega)$ for longitudinal phonons propagating along the $[110]$ direction for $(aQ/2\pi) = (2.2, 2.2, 0), (2.8, 2.8, 0)$ and $(3.2, 3.2, 0)$ in K at 4.5, 99 and 150 K. These phonon groups are typical of those observed at the other wavevectors and show the variation of $S(Q, \omega)$ with temperature. This variation is used to identify the interference contributions entering $S(Q, \omega)$ as the crystal becomes more anharmonic at higher temperature.

To describe $S(Q, \omega)$ more quantitatively, a Gaussian function $G$ times a polynomial, $G(I, \omega_0, \omega, w) \times [1 + a_2(\omega - \omega_0) + ...]$, plus a linear background (flat or sloping), $L = a_0 + a_1\omega$, was fitted to the data by the method of least squares. Here $I$ is the intensity (area) under the Gaussian function, $\omega_0$ is the position of the central peak and $w$ is the full width at half height. The values obtained for these parameters...
Table 1. Parameters obtained by fitting observed one-phonon peaks and multiphonon backgrounds to a gaussian function $G$ (area $I$) plus a linear function $L=a_0+a_1\omega$. All results are normalized to the same integrated intensity incident on the specimen. The width $w$ and centre frequency $\omega_0$ (in THz) of the Gaussian are included for completeness as is the total counting time $t$ (in min) per point of the neutron groups.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$(aQ/2\pi)$</th>
<th>Peak intensity $I$</th>
<th>Background slope $a_1$</th>
<th>Centre frequency $\omega_0$</th>
<th>Peak width $w$</th>
<th>Total counting time per point $t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>1.8</td>
<td>6.01 ± 0.62</td>
<td>-1.6 ± 1.0</td>
<td>1.396</td>
<td>0.295</td>
<td>70</td>
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<tr>
<td></td>
<td>2.2</td>
<td>9.15 ± 0.55</td>
<td>+1.6 ± 1.1</td>
<td>1.387</td>
<td>0.211</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>13.60 ± 0.90</td>
<td>+0.8 ± 1.7</td>
<td>1.419</td>
<td>0.228</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>17.50 ± 1.35</td>
<td>+3.5 ± 2.3</td>
<td>1.392</td>
<td>0.265</td>
<td>20</td>
</tr>
<tr>
<td>99.0</td>
<td>1.8</td>
<td>9.28 ± 0.56</td>
<td>-5.5 ± 1.1</td>
<td>1.357</td>
<td>0.266</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>12.40 ± 0.57</td>
<td>-7.8 ± 0.9</td>
<td>1.368</td>
<td>0.247</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
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<td>-5.2 ± 1.3</td>
<td>1.385</td>
<td>0.252</td>
<td>40</td>
</tr>
<tr>
<td></td>
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<td>-8.5 ± 1.5</td>
<td>1.369</td>
<td>0.369</td>
<td>60</td>
</tr>
<tr>
<td>150.0</td>
<td>1.8</td>
<td>8.62 ± 0.68</td>
<td>-9.9 ± 1.3</td>
<td>1.337</td>
<td>0.267</td>
<td>50</td>
</tr>
<tr>
<td></td>
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<td>11.52 ± 0.60</td>
<td>-11.2 ± 1.2</td>
<td>1.346</td>
<td>0.253</td>
<td>50</td>
</tr>
<tr>
<td></td>
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<td>-5.7 ± 1.0</td>
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<td>0.282</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
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<td>-13.0 ± 1.2</td>
<td>1.345</td>
<td>0.339</td>
<td>110</td>
</tr>
</tbody>
</table>

are listed in table 1. Good fits to the observed points could equally well be obtained with the polynomial chosen to be $1 + a_2(\omega - \omega_0)$. In the latter case $a_2$ was often not well determined and showed no significant variation with $Q$ or temperature. This suggests that any asymmetries in the one-phonon peaks themselves were too small to be measured. The width of the intrinsic one-phonon peaks themselves were too small to be measured. The width of the intrinsic one phonon group at 150 K is expected to be 0.03 THz (Buyers and Cowley 1969). Thus the observed widths here are governed almost entirely by the spectrometer resolution. Furthermore, $w$ does not show any marked variation with $Q$, which might, for example, have arisen from focusing effects. To identify interference effects we focus on the intensity $I$ under the Gaussian peak and on the values of $a_1$ describing the slope of the ‘multiphonon background line’.

4.2. The symmetric interference term

To identify the symmetric interference contribution, which is approximately proportional to $S_1(Q, \omega)$, the observed intensity $I$ under the one-phonon peak region is plotted as the logarithm $\ln \{I/[S_1(Q)/d^2(Q)]\}$ against $Q^2$ in figure 6. Here $S_1(Q)$ is the intensity expected for a purely harmonic crystal. If the crystal were indeed harmonic, then this plot would be simply a plot of $d^2(Q)$, a straight line having slope $<u^2>$ at each temperature. The common intercept of the straight lines would then correspond to the common proportionality factor between the observed intensities and the theoretically calculated $S_1(Q)$. This plot is useful since the Debye–Waller factors are not accurately known and the results are presented in their most direct form.
Anharmonic interference effects in potassium

Figure 6. The integrated intensity \( I \) under the one-phonon peak region at the observed \( S(Q, \omega) \), plotted as \( \ln(1/[S(Q)/d^2(Q)]) \) against \( Q^2 \) (points with error bars). \( S(Q) \) is the expected value for \( I \) if the crystal is harmonic and the broken line shows the integrated intensity for this case. The full curves show \( \ln[S(Q)/[S(Q)/d^2(Q)] \), the computed integrated intensity including the one-phonon–two-phonon interference contributions.

To obtain the Debye–Waller factors shown by the three broken lines in figure 6, the observed results were fitted to straight lines on the assumption of harmonic behaviour. The three slopes correspond to fixed effective \( \theta_D \) values of 96, 91 and 88 K at temperatures of 4.5, 99 and 150 K respectively. These values are entirely reasonable for K showing that the scattered intensity corresponds, on average, to the expected harmonic values. The fits are not very sensitive to the chosen \( \theta_D \), but the restriction that all the lines pass through a common intercept at \( Q = 0 \) is quite a severe test of the overall consistency of the data. (We believe that anharmonic corrections to the Debye–Waller factor are negligible at these temperatures.) The triangular points correspond to the intensity at \( aQ/2\pi = (2.5, 2.5, 0) \). These points include a constant, temperature-independent correction to the intensity of \(-17.7\%\) to account for the additional intensity arising from second-order neutrons (see §3). In theory these points should fall directly on the harmonic lines since the interference contributions are zero at such a zone boundary point.

The full curves in figure 6 show the computed values of \( \ln[S(Q)/[S(Q)/d^2(Q)] \) where \( S(Q) \) includes the interference contributions discussed in §2. At 4.5 K all the observed intensities fall on the straight line within the experimental error. At higher temperatures, on the other hand, the observed intensities clearly oscillate about the
Figure 7. Normalized peak intensities $I/S_1(Q)$, at 99 K ($\circ$) and 150 K ($\Delta$). Purely harmonic behaviour corresponds to the horizontal straight line, while the computed anharmonic terms at these two temperatures are shown as the full and broken curves respectively.

harmonic lines with an amplitude and sign in qualitative agreement with the anharmonic curves including interference.

To put the comparison on a more quantitative basis, we divide the observed intensities $I(Q)$ by $d^2(Q)$. For harmonic behaviour, the broken lines of figure 6 then coincide with a single horizontal straight line. The observed intensities $(I/S_1)$, normalized so that the mean value is unity, are plotted along with $(S_p/S_1)$ in this form in figure 7. The general oscillatory behaviour can be made more quantitative by first noticing that the mean deviations from unity of the 4 observed values of $(I/S_1)$ are $0.00 \pm 0.03$ and $0.00 \pm 0.035$ at 99 and 150 K respectively. If we now multiply these $(I/S_1)$ values at the 4 successive wavevectors by $(-1, +1, -1, +1)$ we find new mean deviations of $+0.06 \pm 0.03$ and $+0.125 \pm 0.035$ at 99 and 150 K, respectively. These new deviations should, of course, be zero if the observed $(I/S_1)$ in figure 7 were randomly scattered about the horizontal line. If we perform the same operation on the deviations from units of the calculated $(S_p/S_1)$ at the same $Q$ values, we obtain mean deviations of $+0.11$ and $+0.18$ at 99 and 150 K, respectively. This suggests that the anharmonic theory of §2 overestimates the actual oscillation. Given that the calculations include only one–two phonon interference contributions, and in addition only the interaction via the cubic anharmonic term, the agreement is quite reasonable. It is interesting, however, that with the cubic term alone the interference effect seems to be over-estimated while the phonon lifetimes calculated with this term alone are much longer than the observed ones (Duesbury et al 1973, Buyers and Cowley 1969).

4.3. The asymmetric interference contribution

In §4.1 we saw that the observed one-phonon group could be well fitted by an undistorted Gaussian function, that is to say, the asymmetric interference term does
not distort the one-phonon lineshape to an observable degree. This is almost certainly because the intrinsic one-phonon linewidth is very narrow (≤0.03 THz). However, the asymmetric interference contribution can act outside the one-phonon peak to alter the shape of the background on either side of the one-phonon peak. For example, in figures 1 and 2 we see that the asymmetric term reduces $S(Q, \omega)$ just below the one-phonon peak region for $(aQ/2\pi) = (2.8, 2.8, 0)$ but increases $S(Q, \omega)$ there for $(aQ/2\pi) = (3.2, 3.2, 0)$ for $T \gtrsim 150$ K. This effect will manifest itself as a change in slope of the background 'line' described by the fitting parameter $a_1$.

In figure 5 the asymmetric interference contribution to the background can be seen in the observed $S(Q, \omega)$ at 99 and 150 K. It appears as a substantially reduced background on the low frequency side of the $(aQ/2\pi) = (2.8, 2.8, 0)$ phonon compared with the $(aQ/2\pi) = (2.2, 2.2, 0)$ and $(3.2, 3.2, 0)$ phonons. The contribution can also be seen in table 1 as an oscillation in the slope of the background given by parameter $a_1$ between $Q = 1.8$ and 3.2 at 99 and 150 K.

5. Summary and conclusions

In the preceding sections we saw that there are two distinct contributions to the dynamic form factor, $S(Q, \omega)$ arising from interference between its one- and multi-phonon parts. The first, often referred to as the 'off-shell' contribution, distorts the shape of $S(Q, \omega)$ near the one-phonon peak region. As noted by Maradudin and Ambegaokar (1964), this term is generally quite small; the one-phonon peak is usually too narrow for this distortion to alter one-phonon peak itself. However, we have been able to observe this off-shell contribution to the multiphonon background at each side of the one-phonon peak. The off-shell contribution tilts the background around the one-phonon peak and this tilting changes sign, as expected from interference, for wavevectors on opposite sides of a reciprocal lattice point. This appears to be the first observation of this term, aside from the highly anharmonic crystal, solid helium.

The second contribution, often referred to as 'on-shell' interference has approximately the same frequency dependence as $S_1(Q, \omega)$ and simply contributes intensity to the one-phonon peak. This was observed here as an additional contribution to the integrated intensity in the one-phonon peak region, which changed sign as the sign of the wavevector $q$ changed with respect to various reciprocal lattice points. The magnitude of the contribution is in qualitative agreement with calculations which take into account interference between the one- and two-phonon parts of $S(Q, \omega)$ only. Higher order contributions can in principle be included, but the magnitude of the interference here is sufficiently small to suggest that this is not worthwhile.

To conclude, we have observed both types of interference contributions between the one- and multiphonon parts, of $S(Q, \omega)$ in the simple metal potassium at intermediate temperatures. This interference should be readily observable in other metals, and perhaps more strongly in molecular crystals where anharmonic effects are large.

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