Mode Grüneisen parameters in potassium: II

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Abstract. The mode Grüneisen parameters, \( \gamma \), in potassium have been computed employing the Dagens, Rasolt and Taylor description of the effective ion–ion interaction in metallic potassium. Comparison with the observed \( \gamma \) of Meyer et al in the preceding paper shows some significant discrepancies between theory and experiment. A comparison with previous calculations show these discrepancies are common to all calculation of \( \gamma \) employing the pseudopotential method. Particularly the discrepancy at low wavevector for the longitudinal mode along \([q, q, 0]\) suggests a possible contribution to \( \gamma(qL) \) depending explicitly on the volume which is not included in an effective ion–ion interaction.

1. Introduction

The purpose of this paper is to present calculations of the mode Grüneisen parameters, \( \gamma(qj) \), in potassium for comparison with the recent measurements of Meyer et al (1976). The observed \( \gamma \) provide additional new data on K that a fundamental description of the metal should correctly predict. To compute \( \gamma \), a potential \( \phi(r) \) describing the interaction between a pair of ions separated by a distance \( r \) in metallic potassium is required. Here we employ the effective ion–ion interaction \( \phi(r) \) derived by Dagens et al (1975) from the charge density induced by a single K ion in an electron gas. Thus the comparison between the observed and computed \( \gamma \) basically provides a further test of validity for this interaction and the ideas which underpin it. A quite detailed comparison with previous calculations of \( \gamma \) is also presented in order to discuss the pseudopotential method as a whole.

2. The Grüneisen parameter

The mode Grüneisen parameter describes the change in frequency, \( \omega(qj) \), of the phonon having wavevector \( q \) and branch index \( j \) with volume \( V \), and is defined as

\[
\gamma(qj) = -\frac{d \ln \omega(qj)}{d \ln V}. \tag{1}
\]

These \( \gamma(qj) \) were obtained here by computing the \( \omega(qj) \) at the crystal lattice constants, \( a \), corresponding to applied pressures \( p = 0 \) and \( p = 4.1 \) kbar (\( a = 5.233 \) Å and \( a = 5.06 \) Å, respectively) and using (1) as a finite difference equation. These pressures
are the experimental pressures and this method mimics that used to obtain \( \gamma(q_j) \) from the observed \( \omega(q_j) \).

The frequencies were observed in K at 4.5 K (Meyer et al 1976). At this temperature K is well described by a harmonic approximation so that

\[
\omega(q_j)^2 = \sum_{q_j} \epsilon(q_j) \left( \left( 1/M \right) \sum_{l} \left[ \exp(iq \cdot R_{0l}) - 1 \right] \phi_{q}(0l) \right) \epsilon(q_j)
\]

(2)

where \( \epsilon(q_j) \) is the polarization vector for phonon \( q_j \) and \( R_{0l} \) is the spacing of the \( l \)th ion from the origin. The \( \omega(q_j) \) change with volume for two reasons: (i) the second derivative \( \phi_{q}(R_{0l}) \) of the effective ion–ion interaction \( \phi(r) \) is evaluated at a different set of \( R_{0l} \) and (ii) the interaction \( \phi(r) \) itself changes with volume. Comparison of a calculation of \( \gamma \) with experiment therefore provides a test of \( \phi(r) \) and its volume dependence.

3. The effective ion–ion interaction

The Dagens, Rasolt and Taylor effective ion–ion interaction is obtained via the standard pseudopotential method (Harrison 1966) in which the electron–ion interaction is computed as a perturbation on a free electron gas up to second order only. The model pseudopotential describing this electron–ion interaction is an energy independent, non-local potential of the Heine and Abarenkov (1964) type. The parameters in this potential are, however, chosen in a novel manner as follows.

Firstly, a single ion represented by a full free ion potential is placed in an electron gas at the appropriate metallic density. The electron charge density attracted around the ion is calculated using the nonlinear self-consistent equations of Hohenberg and Kohn (1963) Kohn and Sham (1965) and Sham and Kohn (1966). The single ion is then represented by the non-local model potential noted above and the induced charge density is recalculated using linear response theory. The parameters of the model pseudopotential are then adjusted so that the linearly calculated charge density reproduces the full nonlinear result. In this way the nonlinear effects are simulated by adjusting the pseudopotential parameters.

The basic idea is that the charge density is of central importance in determining the properties of the metal and the pseudopotential should be chosen to reproduce this density. The resulting pseudopotential is then used in conjunction with the Geldart–Taylor (1970) electron gas screening function to compute form factors and \( \phi(r) \). No experimental information goes into the effective ion–ion interaction.

4. Results

The effective ion–ion interactions for \( a = 5.233 \) and \( a = 5.06 \) Å are shown in figure 1. From the upper portion of figure 1 we see that the effective ion–ion interaction changes little with volume. The main well depth is somewhat shallower at \( a = 5.06 \) Å but there is no significant shift in the position of the potential in compressing the electron gas from \( r_s = 4.860 \) to \( r_s = 4.708 \) (\( r_s = (3/8\pi)^{1/3} a/a_0 \approx 0.930 a_0 \), where \( a_0 \) is the Bohr radius). Particularly, the core does not become more repulsive at \( a = 5.06 \) Å. Most of the shift in \( \omega \) with volume is thus due to evaluating the derivatives in (2) at different positions in \( \phi \). This is shown in the lower portion of figure 1.
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Figure 1. The effective ion–ion interaction $\phi (r)$ (units $10^{-1} \text{ eV}$) in K for lattice constant $a = 5.233 \text{ Å} (p = 0 \text{ kbar})$, full curve and $a = 5.06 \text{ Å} (p = 4.1 \text{ kbar})$, broken curve. In the lower figure $r$ is in units of $a$ to display (arrows) where the first to fifth neighbours fall on the potential.

where $\phi(r)$ is plotted in units of $r/a$ in each case. The arrows indicate the locations of the first to fifth neighbours.

Figures 2 and 3 show the phonon frequency and Gr"uneisen $\gamma$ dispersion curves, respectively. As can be seen from figure 2, and as previously demonstrated by Dagens et al (1975), the phonon frequencies computed from $\phi$ at zero pressure agree very well with the observed values of Cowley et al (1966). In fact, these curves agree with experiment as well as do those generated from the Born–von K\'arm\'an force constant.

Figure 2. The phonon frequency dispersion curves in K, $a = 5.233 \text{ Å}$. The points $\triangle$ and $\bigcirc$ are observed frequencies from Cowley et al (1966).
model deduced by Cowley et al from the experimental frequencies themselves. However, from figure 3 we see that the computed \( \gamma \) are only in fair agreement with the observed \( \gamma \). There are particularly three points of disagreement. Firstly the two observed transverse, \( \gamma(qT) \), along \([0,0,q]\) and \([q,q,0]\) lie below the computed curves. Since \( q < 0.2 \) at these points, both points are largely fixed by the same elastic constant, \( c_{44} \). This discrepancy suggests that the computed volume dependence of \( c_{44} \) is somewhat too large. Secondly, the observed \( \gamma \) at the equivalent of \( D_4 \) (0.5, 0.5, 0.8), shown by the cross hatched point on the right hand side of figure 3, lies well below the computed \( D_4 \) branch. It is difficult to relate this point to an elastic constant since the reduced \( q \) is not small. Finally, the \( \gamma(qL) \) along \([q,q,0]\) lies significantly above the computed value and this is perhaps the chief disagreement between theory and experiment.

5. Discussion

5.1. Comparison with previous theories

In the preceding section we saw that the present calculations of \( \gamma \) did not agree particularly well with the observed values. This was disappointing given the excellent agreement of the phonon frequencies in figure 2 with experiment at the zero pressure volume. In table 1 is a compilation of some previous calculations of \( \gamma \) listing the form of pseudopotential and electron gas screening employed, the quality of agreement of the zero-pressure phonon frequencies with experiment, and finally the goodness of fit of the resulting \( \gamma \)'s with experiment taken from the preceding paper. From table 1 we see that, while the fit of previously calculated \( \gamma \)'s to experiment is comparable to the present ones, the agreement is always worse. Thus, given the generally good agreement with experiment of the phonon frequencies in table 1, the agreement of all calculations of \( \gamma \) with experiment obtained using the pseudopotential method can be said to be disappointing.
Table 1. Calculations of Grüneisen Parameters

<table>
<thead>
<tr>
<th>Author</th>
<th>Type of bare pseudopotential</th>
<th>Local or non-local</th>
<th>Type of screening</th>
<th>Number of free parameters</th>
<th>Data fitted$^1$</th>
<th>Agreement with observed $\omega$</th>
<th>$F$ fit of $\gamma$ to experiment$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>Heine-Abarenkov</td>
<td>Non-local</td>
<td>Geldart-Taylor (1970)</td>
<td>0</td>
<td>Excellent</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>Toya (1961)</td>
<td>Bardeen matrix element</td>
<td>Non-local</td>
<td>Slater exchange</td>
<td>0</td>
<td></td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>Kushwaha and Rajput (1975)</td>
<td>Modified point-ion</td>
<td>Local</td>
<td>Hartree</td>
<td>2</td>
<td>$a_0, B_0$</td>
<td>Reasonable</td>
<td>2.15</td>
</tr>
<tr>
<td>Wallace (1968)</td>
<td>Modified point-ion</td>
<td>Local</td>
<td>Hubbard (1957)</td>
<td>3</td>
<td>$E_0, a_0, B_0$</td>
<td>Excellent</td>
<td>2.21</td>
</tr>
<tr>
<td>Shimada (1974)</td>
<td>Shimada special</td>
<td>Local</td>
<td>Kleinman (1967)-Langreth (1969)</td>
<td>3</td>
<td>$E_0, a_0.c$</td>
<td>Reasonable</td>
<td>3.62</td>
</tr>
</tbody>
</table>

$^1$ Symbols denoting data used to fix free parameters are: $E_0$ = ground state energy, $a_0$ = zero pressure lattice constant, $B_0$ = bulk modulus, $c$ = elastic constants and $\langle \omega^2 \rangle$ = average of phonon frequencies squared. All theories use as an input parameter the observed electron density.

$^2$ $F$ is the root standard deviation of the calculated and observed $\gamma$ (see Meyer et al 1976).
For the purposes of discussion, the treatments of the pseudopotential method outlined in Table 1 may be separated into two categories: those which employ a bare electron–ion pseudopotential having free parameters which are fixed by fits to metallic properties, and those which have no free parameters. The last three approaches in Table 1 fall into the first category while the first two have no free parameters to be determined by solid properties. The difference is important for the following reason.

When there is no prior fitting to experiment, comparison of the calculated $\omega$ with experiment is a stringent test of the theory. However, in the fitted cases, when the model is fitted to the elastic constants or the bulk modulus, the initial slope of the $\omega(qj)$ dispersion curves must be correct. Since the basic shape of the dispersion curves is largely fixed by symmetry, this gives the $\omega(qj)$ a good chance of being correct in many regions of $q$ space. Yet, in the fitted cases, if we now change the crystal volume, by applying pressure, we would not necessarily expect to get reliable values for the frequencies at the new volume. Thus, in the first category, good agreement with experiment of the $\omega$ at one volume would not suggest good agreement of the $\gamma$. In the second category, since there is nothing special about the zero pressure volume, good agreement with experiment at one volume suggests good agreement at any volume. Although this is generally borne out by the results for $\gamma$ in Table 1, we are surprised, given the excellent agreement of the $\omega$ in Figure 2, that the present $\gamma$ in Figure 3 are not in better agreement with experiment.

The disagreement is all the more puzzling given the recent calculations of the ideal resistivity, $\rho$, of Shukla and Taylor (1976). The ideal resistivity is another measure of the phonon spectrum and is quite sensitive to the phonon frequencies. Dugdale and Gugan (1962) measured $\rho(p, T)$ as a function of temperature and pressure (up to 3 kbar) and from their data were able to deduce values of not only the constant pressure resistivity but also the constant volume resistivity. Using the same model potential and electron gas screening as outlined in §3 here (and no experimental input), Shukla and Taylor obtained good agreement with both the observed constant pressure and constant volume resistivities. Also most of their calculated values of $\partial \ln \rho(T)/\partial \ln V$ fell within the experimental error bars. This suggests that the volume derivatives of $\omega(qj)$, on which the calculation is based, should be quite reliable.

5.2. The discrepancies

An important part of the present discrepancy in Figure 3 is that the calculated difference between $\gamma(qT)$ and $\gamma(qL)$ (along $[q, q, 0]$) is not large enough. Particularly, the calculated $\gamma(qL)$ at low $q$ along $[q, q, 0]$ is too small. If $\gamma(qL)$ along $[q, q, 0]$ at low $|q|$ did not decrease substantially with $q$, but rather remained at the value $\gamma_L(0.5, 0.5, 0)$, reasonable agreement with experiment would have been obtained. For the calculations employing fitted pseudopotentials, particularly those of Shimada and Wallace, it is interesting that the $\gamma(qL)$ did not decrease substantially with $q$ but were nearly constant, independent of $q$ along all symmetry directions. Shimada employed a bare pseudopotential having repulsion which stiffens as pressure is applied and Wallace incorporated Born–Mayer repulsion between the ions which could increase the stiffness of the ion–ion interaction as the volume decreases. While we believe it is unlikely that these features have a physical basis, they may simulate an important factor which is omitted from all the calculations of $\gamma$. (For example, if Born–Mayer repulsion is completely negligible at $p = 0$, it will almost certainly
remain unimportant after an inter-ion spacing decrease of only \( \sim 4\% \). Shimada's \( \gamma(q) \) have a particularly good spread between the \( \gamma(q_L) \) and \( \gamma(q_T) \) and his disagreement with experiment arises from \( \gamma \)'s which are generally too small at all \( q \) values.

5.3. Areas for future work

All the theories in table 1 employ an effective ion-ion interaction, and the possible volume dependence of this interaction, to calculate \( \gamma \). There are, however, terms in the expression for the total energy of the crystal which depend only upon the crystal volume \( (r_i) \) which are not included in the effective ion-ion interaction. These terms contribute to the bulk modulus and may be quite important for the volume derivative of the bulk modulus. Since the \( \gamma(q_L) \) and low \( q \) should be consistent with the volume derivative of the bulk modulus, these strictly volume terms may be important for \( \gamma(q_L) \). Finnis (1974) has discussed the importance of these terms at \( p = 0 \) and an explicit numerical estimate of these contributions at higher pressures would be most interesting as a possible answer to the existing discrepancies in \( \gamma \).

Finally, the present discussion hinges on mode Gr"uneisen parameters observed at a few points. The Gr"uneisen parameters obtained by Smith and Smith (1965) from sound velocity measurements in K at room temperature yield \( \gamma_L(q, q, 0) = 1.46 \) and \( \gamma_T(q, q, 0) = 1.13 \) as \( q \to 0 \). While there are almost certainly anharmonic contributions at room temperature, these results suggest the spread between \( \gamma(L) \) and \( \gamma(T_2) \) along \( [q, q, 0] \) at low \( q \) may not be so large as that observed by neutron scattering. For this reason, additional measurements of \( \gamma \) would also be most worthwhile.

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