Toya's Electron-Phonon Interaction and Lattice Vibrations of Potassium

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The specific heat and elastic constants of potassium have been calculated by the use of Toya's expression. In order to improve the agreement, the argument of Bardeen's $g$ function has been multiplied by a constant multiplier 1.07. While there is considerable discrepancy between the theoretical and experimental values, by the use of original expressions, the modified expressions yield much better agreement with elastic as well as thermal data.

§1. Introduction

Recent experiments on neutron scattering by metallic crystals have shown that the standard theory of lattice dynamics based on elastic force models can be used to interpret the results only by the introduction of a large number of force constants used as independent parameters (Brockhouse and Iyenger,\cite{BrockhouseIyenger}) and\cite{Hermann}). These force constants cannot be given any detailed physical interpretation and do not bear any relationship to the actual interaction supposed to be present inside the metals. It is, therefore, increasingly being felt that the lattice dynamics should be directly linked to the modern theories of metals. For this purpose it is convenient to express each element of the dynamical matrix as the sum of three coupling coefficients $[xy]^c$, $[xy]^n$ and $[xy]^p$. The first two of these refer to the contributions of the coulomb and overlap ion-ion interactions respectively while the last term arises from the presence of the conduction electrons. Dayal and Tripathi,\cite{DayalTripathi} in their study of lattice vibrations of copper, calculated the first two terms as in the case of alkali halide crystals (Kellermann,\cite{Kellermann} Karo\cite{Karo}) and evaluated $[xy]^p$ phenomenologically by the use of methods developed by de Launay,\cite{deLaunay} and Bhatia.\cite{Bhatia} They obtained a fair agreement with the experimental data on specific heat and neutron diffraction results. Silver, for which neutron data are not available was studied by the present authors\cite{Silver} by the same methods and a very good agreement was obtained with the specific heat data.

Toya\cite{Toya} whose work was not known in this laboratory at the time, calculated $[xy]^p$ in a more rigorous manner. He has essentially followed the earlier work of Bardeen\cite{Bardeen} who has given a self consistent calculation of the scattering matrix on the basis of the first order perturbation theory. Bardeen, first determined a
potential energy $V_i$ at a given point arising from the displacements of all ions assuming the electronic charge distribution to be unchanged. He next calculated the change in the electronic energy distribution resulting from $V_i$ in terms of the one electron wave function $\Psi_k$ by the first order perturbation theory. From this a second contribution to the potential, $V_p$, was determined by the use of Poisson's equation, a contribution which is in opposite sense to $V_i$ and has a shielding effect on it. The self consistency is achieved by determining the wave function from the equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_i + V_p \right] \Psi_k = E_k \Psi_k \ldots,$$

in which $V_p$ contains the wave functions $\Psi_k$ explicitly.

Toya modified Bardeen's treatment by introducing an exchange potential in (1). This was done through the use of a simplified expression originally given by Slater. The potential of the ions was expanded in a power series of the normal coordinates. The second order terms gave rise to the coupling coefficient $4\pi/3 \cdot e^2 / v \cdot \delta_{xy}$ which is dimensionless in wave number and which according to Dayal and Tripathi is necessary for the vanishing of the frequency in the limit of the zero wave vector. Bardeen's procedure was then followed with the inclusion of the exchange term to obtain the perturbed wave function. The energy is worked out in the usual way and the $[xy]^n$ is calculated from it. The resulting expressions were subsequently corrected for the errors introduced through the use of Slater's exchange potential.

Toya calculated several vibrational frequencies for the waves propagated in the three principal symmetry directions of the alkali metals and copper. For copper the results were compared with the X-ray scattering data, and a good agreement was obtained. As far as this metal is concerned, the computation was based on certain arbitrarily assumed values of the constants occurring in the interionic exchange potential. Tripathi has shown that these are not consistent with Fuchs' calculations. It is, therefore, doubtful if Toya's results as such can be directly applied to this metal. In the case of sodium, results of Toya's computation have been compared by Woods et al. with the experimental data on neutron scattering. They report a good general agreement, except for $T_1$ branch of the [110] direction, where the experimentally observed limiting frequency is two and a half times the calculated value. The calculations made in this laboratory show that there is some arithmetical error in Toya's calculations for the $[xy]^n$ for this frequency; which reduces the discrepancy, but a large difference of about 33% still remains to be explained.

As a further check on the validity of Toya's theory, a computation of the specific heats of sodium and potassium on its basis was undertaken in this laboratory by P.L. Srivastava and R.S. Srivastava. These calculations showed that the calculated $C_v$ are considerably higher than the experimental values.
General considerations showed that the contribution of the Umklapp process to the numerical values of the frequencies is somewhat exaggerated and causes large errors whenever the contribution of the other terms becomes relatively smaller. Toya's expression for electronic coupling coefficient $[xy]^E$ contains two functions $G$ and $F$ which involve a number of electronic parameters of rather uncertain values. In addition to this the $G$ function contains another function $g(2k_Fpl\cdot st)$ which largely controls the contribution of Umklapp processes. This was originally derived by Bardeen and is the overlap integral or the interference factor for the incident and scattered electron wave functions inside a single Wigner and Seitz cell. In the derivation the atomic polyhedron is replaced by a sphere for the purpose of integration. According to Ziman, Bardeen’s expression for this function is reasonable but not exact. It was, therefore, felt that disagreement with Toya's theory was largely due to inherent errors in the $G$, $F$ and $g$ functions. Since it is not desirable to make changes in a great many parameters, Dayal and P.L. Srivastava introduced the simplest possible modification in Toya's expression for $[xy]^E$ by multiplying the argument of the $g$ function with a constant $\alpha$ nearly equal to unity. There is an advantage in this modification. The $G$ function should vanish for the Umklapp processes connected with the zero phonon vector otherwise it yeilds a non zero frequency for waves of infinite length. This is not so in the case of Toya's expression, though the value of $G$ functions does become very small in this case. The modification given above makes it a zero of higher order. Dayal and P.L. Srivastava studied the case of sodium by taking $\alpha=1.04$, and found that there was a considerable improvement in the degree of agreement both with the specific heat and the neutron diffraction data of the metal.

In this paper the present authors have studied the case of potassium by Toya's method, with the same type of modification as given above. Unfortunately neutron data are not available for this metal. We are, however, able to get a fair agreement with the experimental data on specific heats if the constant $\alpha$ is given a value of 1.07. As a proof of the correctness of this modification the elastic constants have also been calculated and it is found that the modified expression gives a better agreement with the experimental values.

§ 2. Elements of the secular determinant

Proceeding in the usual way the determinant for the determination of the vibration frequencies can be written as

$$|M-m\omega^2 I|=0,$$

where $I$ is the unit matrix of order 3. The elements $[xy]$ of the dynamical matrix $M$ can be represented as the sum of three terms $[xy]^c$, $[xy]^R$ and $[xy]^E$. The first two terms represent the contribution of the coulomb and non-coulomb
ion-ion interactions respectively while the third owes its origin to the conduction electrons.

The electrostatic coupling coefficients \([xy]^{\nu}\)

The expressions for these have been derived by Kellermann.\(^5\) The numerical values for body centered cubic crystals for 47 wave vectors have been calculated by P.L. Srivastava and R.S. Srivastava.\(^6\)

The non-coulomb ion-ion interaction term \([xy]^{\nu}\)

As already mentioned the contributions due to this part are small but they affect the lower vibration frequencies considerably. Following Fuchs, Toya determined the effect of this interaction in the alkali metals by using Born and Mayer's\(^{18}\) expression.

\[
v_{\nu}(r) = C_{11} b \exp \left\{ \frac{(2\nu_{\nu} - r)}{\rho} \right\},
\]

where \(b = 10^{-12}\) ergs, \(\rho = 3.45 \times 10^{-8}\) cm, \(C_{11} = 1.25\) and \(\nu_{\nu} = 1.185 \times 10^{-8}\) cm.

Only the contributions from the nearest and next nearest ions have been taken into account. These can be easily expressed as

\[
[x y]^{\nu}_{x=y} = \frac{8}{3} \left( \phi_2'' + 2\phi_4' \right) \left( 1 - C_1 C_3 \right) + 4\phi_2'' S_1^2 + 4\phi_4' (S_2^2 + S_3^2)
\]

and

\[
[x y]^{\nu}_{x\neq y} = \frac{8}{3} \left( \phi_2'' - \phi_4' \right) S_1 S_3 C_3,
\]

where

\[
C_i = \cos(q_i a), S_i = \sin(q_i a), \\
\phi'' = \frac{d^2 v_{\nu}(r)}{dr^2}, \phi' = \frac{1}{r} \frac{dv_{\nu}(r)}{dr},
\]

\(q_x = q_1, q_2 = q_2, q_3 = q_3\) and \(q_y = q_4\) are the components of the wave number vector \(q\) of the lattice vibration, and \(a\) is the half of the lattice constant. The derivatives are evaluated for the equilibrium position of the ions. The suffixes 1 and 2 of \(\phi'\) or \(\phi''\) refer to the nearest and next nearest neighbours respectively.

The electronic interaction term \([xy]^{k}\)

Toya has given the following expressions for \([xy]^{k}\)

\[
[x y]^{k} = e^2 v \left[ \frac{4\pi}{3} \sum_{q} \frac{(q_1 + K_h)(q_2 + K_h)}{|q + K_h|^2} G^2(t) F^{-1}(t) f(t) \right],
\]

where \(K_h\) is the reciprocal lattice vector, \(k_F\) the wave number vector of an electron at the Fermi surface, and \(t = |q + K_h|/2k_F\). The functions \(G(t), F(t)\) and \(f(t)\) are defined as
Toya's Electron-Phonon Interaction and Lattice Vibrations of Potassium

\[ G(t) = \left[ 1 + \gamma (V(r_s) - E_0) \frac{3}{\beta \zeta_0} t^2 \right] g(\alpha \cdot 2k_F r_s t), \]

\[ F(t) = \frac{D_o}{D} \frac{2}{\beta} t^2 + (1 - B t^2) f(t) \text{ for } 1 > B t^2, \]

\[ = \frac{D_o}{D} \frac{2}{\beta} t^2 \text{ for } 1 \leq B t^2, \]

\[ f(t) = \frac{1}{2} + \frac{1-t^2}{4t} \ln \left| \frac{1+t}{1-t} \right|, \]

\[ g(\alpha \cdot 2k_F r_s t) = g(x) = \frac{3(\sin x - x \cos x)}{x^3}, \]

where \( \alpha \) is an empirical constant introduced in this paper. Toya's form is obtained by putting it equal to 1.

\[ \gamma = u_0^2(r_s) = 1; \beta = \frac{e^2 k_F}{\pi \zeta_0}; \zeta_0 = \frac{\hbar^2 k_F^2}{2m} \]

is the Fermi energy.

\( V(r_s) \) is the Hartree-Fock potential energy at the surface of atomic sphere of radius \( r_s \). \( D \) and \( D_o \) are the densities of states with and without the exchange and correlation energies taken into account, \( B \) is a constant introduced to take into account the effect of exchange and correlation interaction on the screening field. It is assumed to be independent of \( |q + K_h| \).

In our calculation \( \alpha \) has been taken as 1.07.

§ 3. The elastic constants of potassium

The validity of introducing a parameter \( \alpha = 1.07 \) in Toya's expression for interference factor \( G \) can be examined by calculating the elastic constants \( C_{11} \) and \( C_{11}^{\#} \) from the modified and unmodified expressions and comparing the results with the experimental values. The elastic constants can be obtained by expanding the coupling coefficients in terms of the phonon wave vectors in the long wave length limit and comparing the expressions with the corresponding elastic expressions.

We divide the contributions to \( C_{11} \) into three parts, i.e. \( \frac{\alpha}{v} C_{11} \), \( \frac{\alpha}{v} C_{11}^{\#} \) and \( \frac{\alpha}{v} C_{11}^{\#} \). \( \frac{\alpha}{v} C_{11} \) can easily be obtained by expanding the Kellarmann's expression. Toya has obtained an expression for it as

\[ \frac{\alpha}{v} C_{11} = \frac{1}{\nu} \left[ \frac{8\pi}{3} \frac{e^2}{\nu} - .368 \frac{e^2}{r_s} \right]. \]

\( \frac{\alpha}{v} C_{11}^{\#} \): Toya has neglected the contribution due to the exchange repulsion between ion cores. However, this can be evaluated easily. If \( r_1 \) and \( r_2 \) be the
distances of the nearest and next nearest neighbours, \( v(r_1) \) and \( v(r_2) \) be the repulsive potentials for the nearest and next nearest ions respectively, the contribution to \( C_{11} \) may be evaluated as in Dayal and Tripati's paper. We get

\[
\kappa(C_{11} - C_{11}) = \frac{1}{v} \left[ \frac{4}{9} r_1^2 \frac{d^2 v(r_1)}{dr_1^2} - r_2 \frac{dv(r_2)}{dr_2} \right],
\]

\[
\kappa C_{11} = \frac{1}{v} \left[ \frac{8}{9} r_1 \frac{d^2 v(r_1)}{dr_1^2} + \frac{8}{9} r_1 \frac{dv(r_1)}{dr_1} + r_2 \frac{dv(r_2)}{dr_2} \right],
\]

and

\[
\kappa(C_{11} + C_{11}) = \frac{1}{v} \left[ \frac{8}{9} r_1 \frac{d^2 v(r_1)}{dr_1^2} - \frac{8}{9} r_1 \frac{dv(r_1)}{dr_1} \right].
\]

\( \kappa C_{11} \): Expanding the modified expression for the electronic coupling coefficient we obtain, neglecting the term with \( K_\alpha \neq 0 \) as done by Toya,

\[
\kappa C_{11} = \frac{1}{v} \left[ - \frac{4\pi e^2}{3} \frac{d^2 v(r_1)}{dr_1^2} - \frac{2}{3} \frac{D_0}{D} \frac{\xi_0}{v} \right] + \frac{.60a^2}{r_s} \left[ - \frac{3}{4} \frac{Be^2}{r_s} \left( \frac{4}{9\pi} \right)^{1/3} \right].
\]

We have

\[
\kappa C_{11} = \frac{1}{v} \left[ -2(V(r_s) - E_0) + 2 \frac{D_0}{D} \frac{\xi_0}{v} \right] + \frac{(.60a^2 - .368 - .2036B)}{r_s} \frac{e^2}{r_s}.
\]

\( C_{12} \): The value of \( C_{12} \) can be calculated by Fuchs' relation

\[
(C_{11} - C_{11}) = \frac{.048}{v} \frac{e^2}{r_s}.
\]

Using the following values for potassium from Toya's paper,

\[
\begin{align*}
r_s &= 2.56 \times 10^{-8} \text{cm}, \\
V(r_s) - E_0 &= -.02 \text{ ev}, \\
\xi_0 &= 2.06 \text{ ev}, \\
B &= 1.21, \\
\gamma &= 1,
\end{align*}
\]

the elastic constants \( C_{11} \) and \( C_{12} \) and compressibility have been computed by modified and unmodified expressions and compared with the experimental values in Table I. As shown by Fuchs as well as Toya the electronic term does not contribute to \( C_{11} \). For this reason its value has not been given here.
Table I. Comparison of the experimental and calculated values of $C_{11}$, $C_{12}$ and $\frac{1}{\varepsilon}$ (in units of $10^{11}$ dynes/cm²).

<table>
<thead>
<tr>
<th>Elastic constants</th>
<th>Calculated from Toya's expression $\alpha=1$</th>
<th>Calculated from modified expression $\alpha=1.07$</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c C_{11} + \beta C_{12}$</td>
<td>0.326</td>
<td>0.431</td>
<td>-</td>
</tr>
<tr>
<td>$\beta C_{11}$</td>
<td>0.034</td>
<td>0.034</td>
<td>-</td>
</tr>
<tr>
<td>$C_{11}$ (total)</td>
<td>0.360</td>
<td>0.465</td>
<td>0.441</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>0.321</td>
<td>0.404</td>
<td>0.379</td>
</tr>
<tr>
<td>$1/\varepsilon$</td>
<td>0.300</td>
<td>0.430</td>
<td>0.400</td>
</tr>
</tbody>
</table>

§ 4. Vibration spectrum and specific heat of potassium

In an earlier preliminary report from this laboratory (P.L. Srivastava and R.S. Srivastava) on the specific heats of sodium and potassium it was shown that the theoretical and experimental values of specific heat do not agree with the observed values. The calculations were made by Blackman's sampling technique, with a very coarse mesh of 125 points in the Brillouin zone. No attempt was made to use a finer mesh as this was not likely to reduce the discrepancy substantially.

In the case of the modified expression used in the present paper we decided to use a finer mesh of points and divided the reciprocal space into miniature cells whose axes are one-tenth of the axes of the ordinary reciprocal lattice cell. From the considerations of symmetry one is required to solve the secular determinant for only forty-seven non-equivalent points including the origin lying within the first Brillouin zone. This gives 3000 frequencies corresponding to 1000 points in the first Brillouin zone when proper account is taken of all the symmetrically equivalent points. These forty-seven representative points have been derived by Dayal and Sharan. The electrostatic coupling coefficients $[xy]_E$ for all the 47 points have been taken from the work of P.L. Srivastava and R.S. Srivastava. The $[xy]_R$ and $[xy]_E$ have been calculated by us from the formula indicated above. The coupling coefficients $[xy]_E$ were computed with a modified interference factor with $\alpha=1.07$.

Even this mesh of points was found to be too coarse to give accurate values of specific heats at very low temperatures. Within this range only the central part of the Brillouin zone contributes to the thermal energy. We, therefore, have separated out the central part consisting of 8 miniature cells of the zone and subdivided it into a still finer mesh having 64 miniature cells. The frequencies for the additional points were calculated and proper statistical weights were assigned. The computation of the frequencies has been made from the secular determinant given earlier. The numerical values of the frequencies along the three principal symmetry directions have been given in Table II.
Table II. Comparison of $\omega_T$ (calculated from Toya's expression) and $\omega_m$ (from modified expression) in the three principal symmetry directions [100], [110] and [111]. in units of $(e^2/\pi M)^{1/2} = 7.03 \times 10^{13}$ sec.

<table>
<thead>
<tr>
<th>$q = (\pi/r_0) (\vec{q},0,0)$</th>
<th>Longitudinal L</th>
<th>Transverse $T_1$ or $T_2$</th>
<th>Transverse $T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{q}$</td>
<td>$\omega_T$</td>
<td>$\omega_m$</td>
<td>$\omega_T$</td>
</tr>
<tr>
<td>0.2</td>
<td>0.622</td>
<td>0.742</td>
<td>0.530</td>
</tr>
<tr>
<td>0.4</td>
<td>1.091</td>
<td>1.303</td>
<td>0.985</td>
</tr>
<tr>
<td>0.6</td>
<td>1.225</td>
<td>1.623</td>
<td>1.336</td>
</tr>
<tr>
<td>0.8</td>
<td>1.582</td>
<td>1.794</td>
<td>1.564</td>
</tr>
<tr>
<td>1.0</td>
<td>1.642</td>
<td>1.825</td>
<td>1.642</td>
</tr>
</tbody>
</table>

Table III. Specific heats of potassium (cal mole$^{-1}$ deg$^{-1}$).

<table>
<thead>
<tr>
<th>Temperature $^\circ$K</th>
<th>$C_v$(calculated)</th>
<th>$C_v$(observed)</th>
<th>$C_v-\gamma T$(observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.070</td>
<td>0.050</td>
<td>0.0494</td>
</tr>
<tr>
<td>6.0</td>
<td>0.219</td>
<td>0.179</td>
<td>0.176</td>
</tr>
<tr>
<td>8.0</td>
<td>0.467</td>
<td>0.389</td>
<td>0.385</td>
</tr>
<tr>
<td>10.0</td>
<td>0.752</td>
<td>0.660</td>
<td>0.655</td>
</tr>
<tr>
<td>12.0</td>
<td>1.089</td>
<td>0.990</td>
<td>0.984</td>
</tr>
<tr>
<td>16.0</td>
<td>1.817</td>
<td>1.650</td>
<td>1.640</td>
</tr>
<tr>
<td>20.0</td>
<td>2.490</td>
<td>2.360</td>
<td>2.350</td>
</tr>
<tr>
<td>24.21</td>
<td>3.088</td>
<td>2.890</td>
<td>2.880</td>
</tr>
<tr>
<td>36.0</td>
<td>4.287</td>
<td>4.150</td>
<td>4.130</td>
</tr>
</tbody>
</table>
For comparison, we have also given the frequencies as given by Toya's unmodified expressions. In some cases, the latter differs slightly from the values given in Toya's paper. It seems to us that Toya has probably neglected the effect of the next nearest neighbours in \([xy]^2\) in these cases. The difference between the two sets of frequencies shows immediately the nature of change brought about by the introduction of the multiplier \(\alpha\) in the \(g\) function.

The \(C_v\) have been calculated by numerical computation from histograms, as in the earlier work from this laboratory (Dayal and Sharan\(^{20}\)). For this purpose the frequency spectrum was divided into intervals of \(\Delta\nu = 2 \times 10^{12}\) sec\(^{-1}\).

The calculated and observed values of \(C_v\) at different temperatures are given in Table III. The experimental data of \(C_v\) have been taken from the work of Roberts\(^{21}\) and Simon and Zeidler.\(^{22}\) The coefficient \(\gamma\) of the electronic specific heat has been taken from the work of Roberts as 0.00047 cal mole\(^{-1}\) deg\(^{-2}\). The experimental and theoretical \(\theta-T\) curves are given in Fig. 1. The \(\theta-T\) curve from the original expression of Toya has also been given there for comparison. In this case a coarser mesh of 125 points per Brillouin zone has been used. It is obvious that the agreement with the modified formula is much better than with the unmodified one. Possibly the agreement could be made still better by increasing the value of \(\alpha\) but in this case the elastic constants will show greater discrepancy. It may be possible to obtain better agreement both in the elastic constants and \(C_v\) by changing the other parameters of the Toya's expression such as \(B, D_0/D,\) etc., but this has not been tried by us.

As it is, the introduction of a constant multiplier in the argument of the \(g\) function is too primitive a modification to reproduce experimental data in all finer details. The present results, however, leave no doubt about the essential correctness of Toya's approach to the lattice dynamics of metals.

References

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