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Anharmonic properties of Li

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The energies and lifetimes of phonons in metallic Li between 110 and 424 K are calculated using the self-consistent phonon theory and the effective ion-ion interaction developed by Dagens, Rasolt, and Taylor (DRT). The results are compared with the recent neutron scattering measurements of Beg and Nielson. Li turns out to be surprisingly harmonic, less anharmonic than Na or K, due to the strong Li ion-ion interaction which has a relatively soft repulsive core. The anharmonic corrections do improve agreement with the observed dispersion curves at 110 K, and they provide a good description of the phonon frequency changes with temperature, but the calculated phonon lifetimes are often two or three times the observed values. The remaining discrepancies with experiment suggest (i) the presence of three- or four-body interactions in Li which are not included in the DRT pseudopotential method, and (ii) that the phonons decay significantly via processes higher than those accounted for by cubic anharmonicity.

I. INTRODUCTION

Starting with the early work of Toya,[1] theoretical calculations of the lattice dynamics of alkali metals have progressed, during the past two decades, to the point where first-principles[2] calculations can be expected to yield reliable results. This is especially true in Na and K where it is possible to obtain good agreement with experiment at all temperatures, even those where anharmonic effects are comparatively large.[3,4] With their spherical Fermi surfaces, free-electron behavior, and fairly tightly bound ionic cores these two metals are, from the theoretical point of view, the easiest of the alkali metals to deal with. Rb and Cs are rather more difficult for two reasons. Firstly, the density of electrons is so low that the compressibility of the electron gas is negative for Cs and virtually so for Rb, rendering a calculation based on the electron gas as a zeroth-order approximation, highly questionable. Secondly, the rather large ionic cores of these materials are more loosely bound than in the lighter alkalis giving rise to appreciable core polarizabilities. This latter effect has yet to be included in a lattice-dynamic calculation for Rb and Cs, although Kukkonen[5] has incorporated it into the electron-electron scattering contribution to the thermal resistivity. Kukkonen suggested that the core-polarization effect could be included by renormalizing the density of the electron gas to an effective higher density. This has the additional benefit of removing the compressibility problem. Hence this type of approach applied to the lattice-dynamic problem might very well be the answer to the Rb and Cs problem, although this remains to be investigated.

This brings us to Li, the lightest of the alkali metals with the highest density of electrons and no significant core polarization. However Li has its own special problem which arises from the fact that the ionic core consists of only two 1s electrons. This means that the ionic potential seen by the p component of the conduction band is not shielded by the core, resulting in a strong scattering phase shift. The pronounced deviations from sphericity of the Fermi surface[6,7] are probably manifestations of this fact. This means that a properly constructed Li pseudopotential is highly nonlocal and relatively strong, which in turn means that the application of perturbation theory poses a serious problem. Hence although, superficially, the lattice dynamics of the alkali metals appears to be reasonably well understood, only Na and K seem to have no significant remaining difficulties in interpretation.

In this paper we address ourselves to the problem of anharmonic lattice dynamics in Li. Although there exists a number of calculations in the harmonic approximation (e.g., Refs. 8–13), there have been no attempts to evaluate the anharmonic contributions. In view of the fact that Li^+ is a very light ion it is conceivable that significant anharmonic effects could be present even at the lowest temperatures (liquid nitrogen) for which neutron scattering measurements have been made.[14] This point alone is worthy of investigation since many of the aforementioned calculations were adjusted to fit the low-temperature experimental data. In addition, the recent neutron measurements of Beg and Nielsen[15] of the phonon dispersion curves up to $T = 424$ K provide an interesting test of theory to see how well these can be reproduced from a first-

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principles point of view. In Secs. II–V we discuss the interionic potential used, the techniques to handle it, the lattice dynamics, and the comparison of our results with experiment over the entire temperature range. In our treatment there are no adjustable parameters determined from experiment and it can be regarded as a first-principles calculation.

II. THE INTERIONIC POTENTIAL

In the theory of simple metals, it is normal to replace the ionic potential seen by a conduction electron by a pseudopotential. This is then assumed to be a sufficiently weak perturbation on the system, that second-order perturbation theory can be used to generate the interionic potential. In view of our remarks in Sec. I concerning the strong scattering properties of Li, this assumption is highly questionable. But to go beyond second-order perturbation theory when calculating ion-ion interactions is a very difficult and unrewarding computation.[16] One way out of this dilemma is to follow the prescription provided by Dagens, Rasolt, and Taylor[13] (DRT). These authors first calculated the charge density induced by an isolated ion placed in an infinite electron gas of the same density as the metal. For this they used the self-consistent Hartree-Fock-Slater scheme with Kohn and Sham[17] exchange. They then generated the linear response (first-order) result using a pseudopotential screened by a dielectric function, formally equivalent to the Kohn and Sham exchange approximation, and they adjusted the parameters of the pseudopotential to make this second calculation agree with the first. By this procedure all the higher-order terms representing multiple-scattering events at a *single* ion site were folded into the pseudopotential, which could then be used in low-order perturbation theory. Using the DRT pseudopotential to second order in the interionic potential problem provides an effective sum of all higher contributions to the two-body pair potential. Hence it is entirely appropriate to use the DRT pseudopotential to second order for a calculation of a Li pair potential and this is what we have done. We should point out that no effects of N-body forces ($N \geq 3$) are folded into the pair potential and we do not include these forces in our calculation. It is quite probable that at least three-body forces play a significant role in Li and we shall comment on the possible influence of these forces in the discussion.

For our calculations we used the Geldart and Taylor[18] dielectric function to screen the pseudopotential. This dielectric function includes both exchange and correlation in the electron gas and is probably the most appropriate one to use for these problems.[19] Using the same combination of pseudopotential and screening, DRT obatined phonon dispersion curves approximately 5% higher than the experimental results of Smith *et al.*[14] at 90 K. The formulas used to calculate the interionic potential are given by Rasolt and Taylor.[20]

A particularly important feature of the DRT pseudopotential which is common to all realistic descriptions of Li, is the strong degree of nonlocality. This comes from the fact that the absence of p-electrons in the Li^+ core means that the p component of the conduction band is scattered much more strongly than the s component. As a result of this feature the corresponding interionic potential exhibits asymptotic Friedel oscillatory behavior of the form

$$V_{as}(r) = 2k_F(Ze)^2[A_3 \cos 2k_F r/(2k_F r)^3 + A_4 \sin 2k_F r/(2k_F r)^4 + \cdots] , \quad (1)$$

where the amplitude of oscillation is very large. This severely complicates the problem of anharmonicity since sums of this function in real space barely converge at infinite distance. This is because the number of neighbors summed over is r^2. Hence truncation of sums at any finite distance can lead to serious errors. To display this point we have plotted $r^2V(r)$ in Fig. 1, where it can be seen that the long-range oscillations are indeed very large, particularly compared to the DRT K interionic potential. Because of this, special techniques had to be developed to treat the dynamics of Li which were not necessary for Na (Ref. 3) and K (Ref. 4). These are described in the following paragraphs and Sec. III.

Although Eq. (1) contains only the first two terms of an infinite series, it gives a good description of the long-range oscillations of Li in the range of interest, and we shall truncate the series at that point. Strictly speaking the coefficient A_4 displays a weak logarithmic dependence on r, but for our purposes it is sufficient to regard it as a constant. Thus the problem of summing $V_{as}(r)$ over all neighbors can be solved by evaluating sums of functions of the form e^{ikr}/r^m. These can be computed easily to any desired accuracy by using a modified Ewald technique. We follow Duesbery and Taylor[21] and write, for the interionic potential at all values of r,

$$V_{II}(r) = V_{sr}(r) + V_{as}(r) . \quad (2)$$

The short-range part $V_{sr}(r)$ is of course left over when $V_{as}(r)$ is subtracted from $V_{II}(r)$.

To evaluate the asymptotic part $V_{as}(r)$, in (1) we

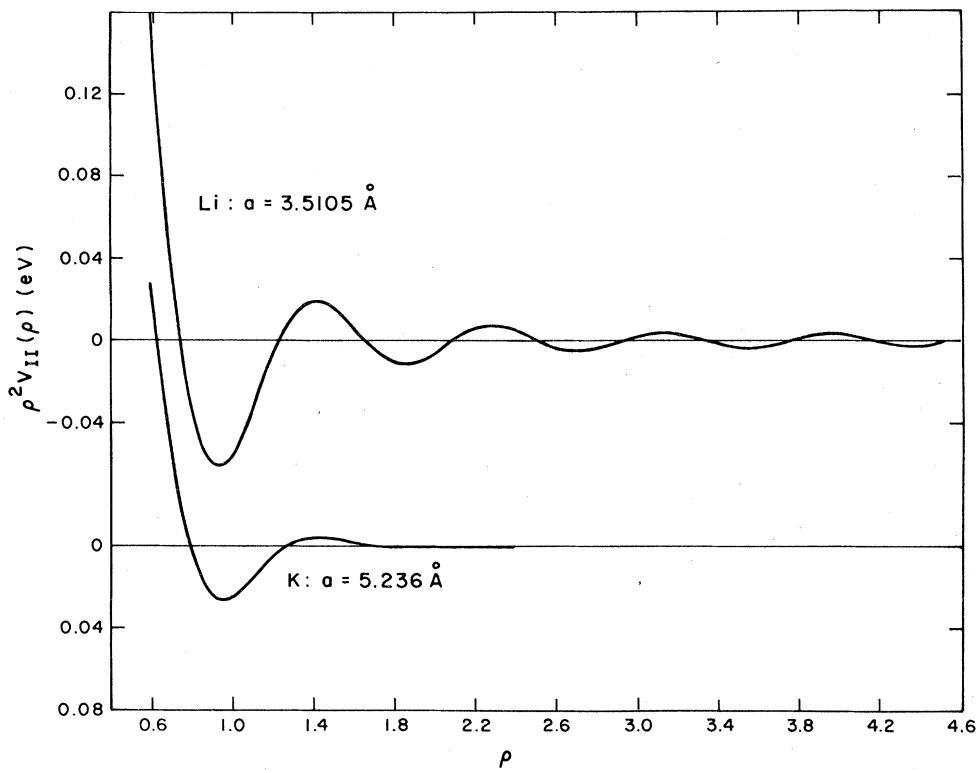

FIG. 1. Effective ion-ion interactions $\rho^2 V_{II}(\rho)$ in Li and K, where $\rho = r/a$ and a is the lattice constant.

use the Ewald-Fuchs[22] method to evaluate x^{-3} and x^{-4}, where $x = 2k_F r$. This employs the identity

$$\frac{1}{x^m} = \frac{2}{\Gamma(m/2)} \int_0^\infty \eta^{m-1} e^{-(\eta x)^2} d\eta$$

$$= \frac{2}{\Gamma(m/2)} \left(\int_0^\alpha \eta^{m-1} e^{-(\eta x)^2} d\eta + \int_\alpha^\infty \eta^{m-1} e^{-(\eta x)^2} d\eta \right)$$

$$\equiv \frac{2}{\Gamma(\frac{1}{2}m)} [J_m^Q(x) + J_m^R(x)] , \tag{3}$$

where $\Gamma(\frac{1}{2}m)$ is the gamma function. The second term $J_m^R(x)$ of this representation of $1/x^m$ converges rapidly as x increases (much more rapidly than $1/x^m$) while the first term $J_m^Q(x)$ can be evaluated rapidly in Fourier space. Using (3) we may write (1) as

$$V_{as}(r) = V_{as}^R(r) + V_{as}^Q(r) , \tag{4}$$

where

$$V_{as}^Q(r) = A_3[2/\Gamma(\tfrac{3}{2})] J_3^Q(x) \cos x + A_4[2/\Gamma(2)] J_4^Q(x) \sin x \tag{5}$$

and $V_{as}^R(r)$ is the corresponding expression with J_m^R replacing J_m^Q. The total potential is then

$$V_{II}(r) = [V_{sr}(r) + V_{as}^R(r)] + V_{as}^Q(r)$$
$$= V_{eff}(r) + V_{as}^Q(r) . \tag{6}$$

This representation raises the possibility of replacing $V_{II}(r)$ by $V_{eff}(r) = V_{sr}(r) + V_{as}^R(r)$, which ignores $V_{as}^Q(r)$ completely. This can sometimes be done by suitable choice of α. This is regularly done in the reciprocal space formulation of dynamics,[23] where the Ewald transformation is used to separate the entire potential into two parts, one evaluated in reciprocal space and the second evaluated in configuration space. With suitable choice of α the part in configuration space may be neglected. However, we found no value of α which made $V_{eff}(r)$ suitably convergent and at the same time made $V_{as}^Q(r)$ negligible. The long-range part of the potential, which is now collected in $V_{as}^Q(r)$, particularly affects the low-frequency T_1 branch along the [110] direction. For example, for a choice of $\alpha = 0$ ($V_{as}^Q = 0$), this branch is still unstable when the force constants are summed to 19 shells. For $\alpha = 0.17$ the $V_{eff}(r)$ converges after about 20 shells and the harmonic T_1 frequency at the zone boundary ignoring V_{as}^Q, is 0.54 MeV (the complete value including V_{as}^Q is 0.43 MeV). We chose $\alpha = 0.23$

which made $V_{\rm eff}$ negligible beyond 15 shells and evaluated $V^{Q}_{\rm as}(r)$ in reciprocal space.

III. DYNAMICS

In the pseudopotential description of Li, we write the metallic energy as the sum of terms depending only upon the volume plus the term

$$\phi = \sum_{l<l'} V_{\rm II}(\vec{r}_l - \vec{r}_{l'}), \tag{7}$$

which depends upon the positions $\vec{r}_l$ of the ions. The dynamics of ionic motion at a given volume then depends solely on $V_{\rm II}(\vec{r}_l - \vec{r}_{l'})$.

A. Quasiharmonic approximation

In the quasiharmonic approximation the frequency of a phonon having wave vector $\vec{q}$ and branch λ is

$$\omega(\vec{q}\lambda)^2 = \sum_{\alpha\beta} \vec{\epsilon}_\alpha(\vec{q}\lambda)\overleftrightarrow{D}_{\alpha\beta}(\vec{q})\vec{\epsilon}_\beta(\vec{q}\lambda), \tag{8}$$

where $\vec{\epsilon}(\vec{q}\lambda)$ is the phonon polarization vector and

$$\overleftrightarrow{D}_{\alpha\beta}(\vec{q}) = \frac{1}{m}\sum_{l'}(e^{-i\vec{q}\cdot\vec{R}_{l'}} - 1)\nabla_\alpha(l)\nabla_\beta(l')V_{\rm II}(r_{ll'}) \tag{9}$$

is the dynamical matrix.[24] The derivative of $V_{\rm II}(r_{ll'})$ is evaluated at $\vec{r}_{ll'} = \vec{R}_{ll'}$, the separation between the lattice points. Since $\vec{R}_l - \vec{R}_{l'}$ varies with T as the lattice expands, the quasiharmonic harmonic frequencies are temperature dependent.

With $V_{\rm II}(r)$ written as the sum in (6), the $\overleftrightarrow{D}_{\alpha\beta}(\vec{q})$ has two parts

$$\overleftrightarrow{D}_{\alpha\beta}(\vec{q}) = \overleftrightarrow{D}^{R}_{\alpha\beta}(\vec{q}) + \overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{r}). \tag{10}$$

The first part $\overleftrightarrow{D}^{R}_{\alpha\beta}(\vec{q})$ is obtained by substituting $V_{\rm eff}(r)$ directly into (9). The second part is obtained by substituting $V^{Q}_{\rm as}(r)$ in (9) in the form

$$V^{Q}(r) = \int \frac{d^3Q}{(2\pi)^3} e^{i\vec{Q}\cdot\vec{r}} F(\vec{Q}),$$

which reduces $\overleftrightarrow{D}^{(Q)}_{\alpha\beta}(\vec{q})$ to

$$\overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{q}) = \frac{1}{m\Omega_0}\sum_{\vec{\tau}}{}' [(\vec{q}+\vec{\tau})_\alpha(\vec{q}+\vec{\tau})_\beta F(|\vec{q}+\vec{\tau}|) - \tau_\alpha\tau_\beta F(|\vec{\tau}|)]. \tag{11}$$

The Fourier transform $F(\vec{Q})$ needed in this expression was evaluated directly from (5) and the integrals involved reduce to exponential integrals and Dawson's integral. A sum over $\vec{\tau}$ of three reciprocal-lattice points was sufficient to obtain $\overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{q})$ with $\alpha = 0.23$ in (3). By writing $\overleftrightarrow{D}_{\alpha\beta}(\vec{q})$ as a sum of two parts following the Ewald-Fuchs method, we can evaluate $\overleftrightarrow{D}_{\alpha\beta}(\vec{q})$ exactly in spite of the long-range character of $V_{\rm II}(r)$.

B. Self-consistent harmonic approximation

The lowest-order self-consistent phonon theory[25–27] is the self-consistent-harmonic (SCH) approximation in which the phonon frequencies are again given by expressions (8) and (9). Now, however, the derivative of $V_{\rm II}(r_{ll'})$ in (9) is averaged over the relative vibrational amplitudes, $\vec{u}(ll') = \vec{u}(l) - \vec{u}(l')$, of the ions about their lattice points

$$\langle \nabla_\alpha(l)\nabla_\beta(l')V_{\rm II}\rangle = [(2\pi)^3|\overleftrightarrow{\Lambda}|]^{-1/2} \times \int d^3u \exp(-\tfrac{1}{2}\vec{u}\cdot\overleftrightarrow{\Lambda}^{-1}\cdot\vec{u}) \times \nabla_\alpha(l)\nabla_\beta(l')V_{\rm II}. \tag{12}$$

The width of this Gaussian distribution is

$$\Lambda_{\alpha\beta}(ll') = \langle u_\alpha(ll')u_\beta(ll')\rangle = \frac{\hbar}{mN}\sum_{\vec{q}\lambda}(1 - e^{i\vec{q}\cdot\vec{R}(ll')})\vec{\epsilon}_\alpha(\vec{q}\lambda)\vec{\epsilon}_\beta(\vec{q}\lambda) \times \frac{\coth[\frac{1}{2}\beta\hbar\omega(\vec{q}\lambda)]}{\omega(\vec{q}\lambda)}, \tag{13}$$

where $\hbar$ is Planck's constant, m is the mass, $\beta = (kT)^{-1}$, and N is the number of atoms in the crystal. Since the $\omega(\vec{q}\lambda)$ in (13) are the SCH frequencies, Eqs. (9), (12), and (13) must be evaluated interatively until self-consistent.

The $\overleftrightarrow{D}^{R}_{\alpha\beta}(\vec{q})$ part of $\overleftrightarrow{D}_{\alpha\beta}(\vec{q})$ can be evaluated straightforwardly in the SCH approximation since for this part $V_{\rm eff}(r)$ replaces $V_{\rm II}(r_{ll'})$ in (9). However, $\overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{q})$ cannot be evaluated in the same way since the average (12) introduces correlations between the atomic motions and the reduction of $D^{Q}_{\alpha\beta}(\vec{q})$ to the reciprocal space expression (11) requires no correlation between the atoms. Since $V_{\rm eff}(r)$ continues out to 15 shells and $V^{Q}_{\rm as}(r)$ accounts for the remainder, we thought it would be a good approximation to ignore the averaging for atoms separated more than 15 shells and use the quasiharmonic value of $\overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{q})$ for these atoms $[\Lambda_{\alpha\beta}(ll') \ll R^2(ll')]$. This turned out to be the case for all branches except the T_1 [110] branch, which depends heavily on the long-range part of the potential. To improve this branch, we approximated the outer shell averaging by an uncorrelated Einstein model like Gaussian averaging of the same width in $\overleftrightarrow{D}^{Q}_{\alpha\beta}(\vec{q})$. This improved the T_1 [110] branch but the frequencies of this branch still showed unrealistic variation with wave vector. This point is discussed further in Sec. V.

C. SCH + cubic approximation

The SCH approximation includes all the even anharmonic terms that would appear in a first-order perturbation evaluation of the anharmonic shift to the phonon frequencies.[28] This includes notably the quartic anharmonic term. The leading correction to the SCH approximation in perturbation theory is the cubic anharmonic term. This term is also the leading term in a second-order self-consistent theory. Here we simply add the cubic term as a perturbation to the SCH frequencies.

The phonon frequencies with the cubic term included are identified with the peak in the one-phonon response function,[29] $A(\vec{q}\lambda, \omega)$, of form

$$\frac{8\omega^2(\vec{q}\lambda)\Gamma(\vec{q}\lambda, \omega)}{[-\omega^2+\omega^2(\vec{q}\lambda)+2\omega(\vec{q}\lambda)\Delta(\vec{q}\lambda, \omega)]^2+[2\omega(\vec{q}\lambda)\Gamma(\vec{q}\lambda, \omega)]^2} \tag{14}$$

which appears in the one-phonon part of the dynamic form factor (see Sec. III D). The expressions for $\Delta(\vec{q}\lambda, \omega)$ and $\Gamma(\vec{q}\lambda, \omega)$ are given in Eqs. (5) and (6), Ref. 3 and two approximations were made in their evaluation. Firstly, the cubic anharmonic coefficient

$$\left\langle \frac{\partial^3 V_{\rm II}(r_{ll'})}{\partial r_\alpha(l)\partial r_\beta(l')\partial r_\gamma(l'')} \right\rangle \tag{15}$$

was summed out to five shells only. Tests by comparing phonon frequencies obtained with three- and five-shell summations showed this gave all frequencies within 2% for $q \gtrsim 0.1(2\pi/a)$. Secondly, the self-consistent harmonic frequencies $\omega(\vec{q}\lambda)$ used in Δ and Γ were those given by the first part of $\overleftrightarrow{D}_{\alpha\beta}(\vec{q})$ in Eq. (10) only. Tests of the dependence of Δ and Γ on $\omega(\vec{q}\lambda)$ showed this could lead to 10% error in Δ and Γ or ~2% in the final SCH + cubic frequencies.

D. Dynamic form factor

To complete this section, we note that the coherent inelastic cross-section for neutrons scattering from crystals is proportional to the dynamic form factor, $S(\vec{Q}, \omega)$. This $S(\vec{Q}, \omega)$ is usually expanded in powers of scattering from single phonons, pairs of phonons,

$$\begin{aligned} S(\vec{Q}, \omega) &= S_1(\vec{Q}, \omega) + S_2(\vec{Q}, \omega) + S_{12}(\vec{Q}, \omega) \\ &= S_p(\vec{Q}, \omega) + S_2(\vec{Q}, \omega) + \cdots , \end{aligned} \tag{16}$$

and so on. The term $S_{12}(\vec{Q}, \omega)$ represents the interference contribution between the one- and two-phonon cases. For all phonons considered here the $S_p(\vec{Q}, \omega) + S_2(\vec{Q}, \omega)$ in Eq. (16) was calculated and this was usually dominated by the one phonon part

$$S_1(\vec{Q}, \omega) = [n(\omega)+1]|F(\vec{Q}, \vec{q}\lambda)|^2 A(\vec{q}\lambda, \omega)\Delta(\vec{Q}-\vec{q}) , \tag{17}$$

where $F(\vec{Q}, \vec{q}\lambda)$ is the structure factor[30] and $n(\omega)$ is the Bose function.

IV. RESULTS

A. Low-temperature phonons

The representation of the Li ion-ion interaction used in the present calculations is shown in Fig. 1. The phonon energy dispersion curves for Li at 110 K calculated in the self-consistent harmonic approximation with the cubic term added (SCH + cubic) using this ion-ion interaction are shown in Fig. 2. A comparison of the calculation and observed phonon energies shows good overall agreement with some clear discrepancies.

In assessing the meaning of these discrepancies, it is interesting to compare first the quasiharmonic (QH) and SCH + cubic phonon energies. In a previous QH calculation using the same ion-ion interaction as in Fig. 1, DRT[13] noted significant discrepancies with experiment around the $\vec{Q}^* = \vec{Q}(a/2\pi) = (1, 0, 0)$ point and along the $L[qq0]$ branch. Here in Fig. 2 we see that the discrepancy around $\vec{Q}^* = (1, 0, 0)$ has effectively been removed. This is partly because the SCH + cubic energy is lower than the QH value (see Table I) and partly because the additional single point due to Beg and Nielson[15] (see Table I) lies higher than the original values of Smith *et al.*[14] However, the discrepancy along $[qq0]$ L at higher q remains. We shall see that the SCH + cubic theory does not predict a large enough downward shift due to anharmonicity with temperature for this branch (for example, the discrepancy along $L[qq0]$ is greater at 293 K). Thus some of the discrepancy here might be due to additional anharmonic contributions. However, these are unlikely to reduce the phonon energy by more than 1%–2% on the basis of the temperature shifts discussed below. Most of the discrepancy thus results from the representation of the ion-ion interaction. Since this ion-ion interaction simulates the nonlinear electron screening between a pair of ions to all orders in perturbation theory, the discrepancy probably reflects the role of three- and four-ion interactions in Li which are not represented in the present pair ion interaction.

B. Temperature shifts

The SCH + cubic phonon energies for Li at 293 K are compared with the observed values of Beg and

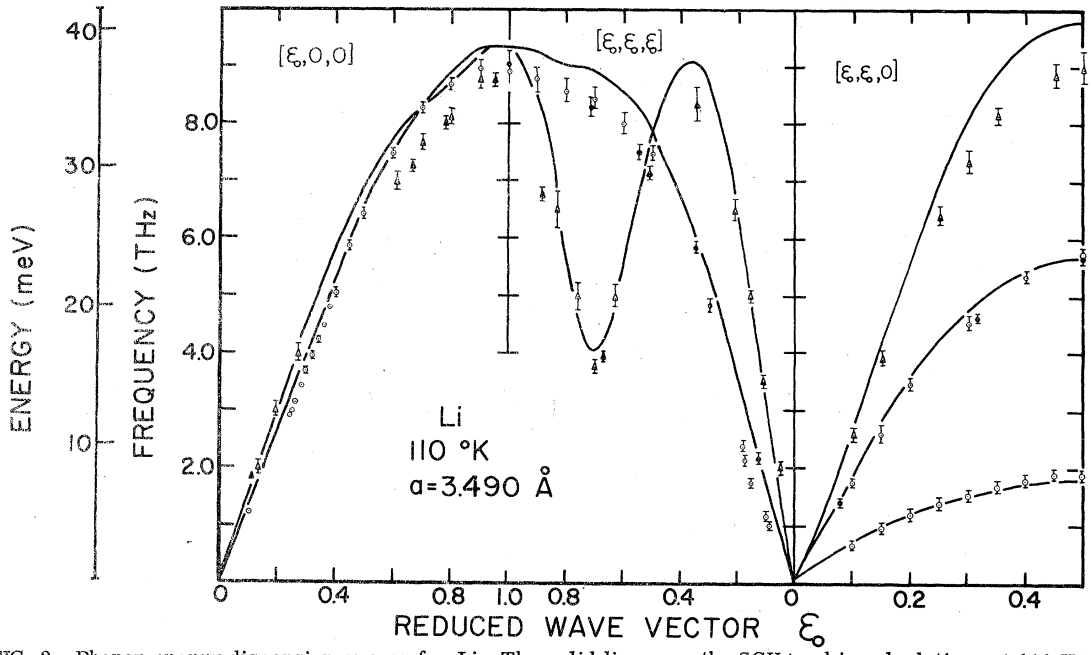

FIG. 2. Phonon energy dispersion curves for Li. The solid lines are the SCH+cubic calculations at 110 K, the open triangles (circles) are the longitudinal-(transverse) phonon energies observed by Smith *et al.* (Ref. 14 and unpublished data) at 98 K, and the solid triangles and circles are the corresponding values observed by Beg and Nielsen (Ref. 15) at 110 K.

Nielsen in Fig. 3. There we see that the discrepancy along $[qq0]L$ noted at 110 K has increased and, in addition, the calculated phonon energies along $[qq0]T_2$ and along $[qqq]L$ clearly lie above the observed values. These discrepancies show that the theory does not predict a large enough downward shift in phonon energy with temperature.

The $[qq0]T_2$ branch in Fig. 3 is interesting since the intrinsic anharmonic shifts in the phonon energy from the QH to SCH, and on adding the cubic term, are both negative in Na and K. Here the QH-SCH shift is negative but very small (see Table I). Also the cubic shift is very small (see Table I and Fig. 4). Generally the cubic shifts and the total shifts are smaller in Li as a percentage of the phonon energy than in K and Na. For example, for the longitudinal phonon at $\vec{Q}^* = (0.5, 0.5, 0)$ the percentage shift in energy between 110 and 424 K (0.94 of the melting point) is 5.5% (calculated 3.9%) in Li. In K, this phonon has an energy shift of 8% (calculated 9%) between 90 and 311 K (0.93 of the melting point).[4] The corresponding shifts for the T_2 phonon at $\vec{Q}^* = (0.5, 0.5, 0)$ between the above temperatures are 10.2% (calculated 3.4%) in Li and 9% (calculated 8.8%) in K. The percentage shift in the calculated QH frequency with temperature is also smaller in Li than in K. The magnitudes of the temperature shifts in Li are shown in Fig. 5.

As a summary statement, the calculated shifts with temperature are too small. This probably means ultimately that the representation of the ion-ion interaction in the replusive region is too soft given the better agreement of the SCH+cubic theory with experiment in K and Na.

C. Phonon groups

The dynamic form factor, $S(\vec{Q}, \omega)$, calculated with SCH+cubic theory for the longitudinal polarization at $\vec{Q}^* = (2-\xi, 2-\xi, 2-\xi)$ with $\xi = 0.677$ is compared with the corresponding observed phonon groups in Figs. 6 and 7. The calculated $S(\vec{Q}, \omega)$ includes the one-phonon scattering, the two-phonon scattering, and the interference between these two [see Eq. (16)]. The $S(\vec{Q}, \omega)$ is also convoluted with a Gaussian function of full width at half-maximum equal to the instrument resolution width (~1.3 meV) shown by the horizontal bar with the observed groups to make the comparison with experiment more direct. This comparison shows that although the calculated phonon group has approximately the correct shape, its overall width is too small (i.e., ≈2.5 meV at 424 K compared with ≈4.0 meV, both including the resolution width). Also, the calculated $S(\vec{Q}, \omega)$ does not reproduce the large intensity on the low-energy side of the observed phonon group. This would have to come from the two phonon or interference contribution to $S(\vec{Q}, \omega)$ in the theory. Large intensities on the low-frequency sides of some phonons groups have been observed in K,[31] and these could be re-

TABLE I. Selected phonon energies (meV) and intrinsic phonon group widths 2Γ (meV) (phonon lifetime $\tau = \Gamma^{-1}$). [a]

Phonon		Model	Temperature 110 K	293 K	424 K
(1, 0, 0)L		QH	40.0	39.3	38.5
		SCH	39.8	38.9	38.0
	$\hbar\omega$	SCH + cubic	38.6	36.9	36.0
		Obs.	37.5 ± 1.0	35.8 ± 1.0	33.1 ± 1.0
	2Γ	Calc.	0.3	0.3	0.7
		Obs.	···	1.94 ± 0.6	3.85 ± 0.6
(0.5, 0.5, 0)L		QH	41.2	40.2	39.0
		SCH	42.3	41.7	40.8
	$\hbar\omega$	SCH + cubic	41.0	40.6	39.4
		Obs.		36.5 ± 1.0	
	2Γ	Calc.	0.6	0.8	1.0
		Obs. [b]	···	0.0 ± 0.3	3.12 ± 0.45
(0.5, 0.5, 0)T_2		QH	24.1	23.9	23.8
		SCH	24.0	23.9	23.6
	$\hbar\omega$	SCH + cubic	23.5	23.1	22.7
		Obs.			
	2Γ	Calc.	0.3	0.8	1.8
		Obs.	···	2.20 ± 0.5	2.77 ± 0.64
(0.5, 0.5, 0)T_2		QH	7.3	7.3	7.3
		SCH	(5.6)	(7.6)	(8.6)
	$\hbar\omega$	SCH + cubic	(5.1)	(6.6)	(7.5)
		Obs.		8.6 ± 0.6	
	2Γ	Calc.	0.3	1.6	2.8
		Obs.	···		
(0.677, 0.677, 0.677)L		QH	17.2	16.9	16.7
		SCH	17.5	17.8	18.1
	$\hbar\omega$	SCH + cubic	16.8	16.3	16.0
		Obs.	16.4 ± 0.2	15.1 ± 0.5	13.0 ± 0.5
	2Γ	Calc.	0.3	1.2	1.7
		Obs.	···	3.23 ± 0.22	3.69 ± 0.5
(0.5, 0.5, 0.5)L		QH	32.8	32.2	31.2
		SCH	33.2	32.8	32.2
	$\hbar\omega$	SCH + cubic	32.4	31.8	30.8
		Obs.			
	2Γ	Calc.	0.3	0.6	0.8
		Obs.	···		

[a] Observed values are those of Beg and Nielsen. [b] 2Γ for (0.435, 0.435, 0)L phonon.

produced by including the interference terms.

To investigate this intensity further, we show the interference contribution for this phonon at three different wave vectors $\vec{Q}$ which have the equivalent reduced wave vector ξ in Fig. 8. There we see the interference contribution is large but does not contribute much scattering intensity at low energy. Apparently the observed intensity at low energy arises from scattering from three or more phonons.

In Figs. 9 and 10 we compare the calculated $S(\vec{Q}, \omega)$ with the observed phonon groups of Beg and Nielsen for some second transverse phonons along the [110] direction. Again the calculated $S(\vec{Q}, \omega)$ is convoluted with a Gaussian of width given by the experimental resolution width shown by the horizontal bars under the observed groups. As in Fig. 6 the calculated $S(\vec{Q}, \omega)$ reproduces the observed group shapes well but the calculated linewidth is too small at high temperature. We find that the calculated width of the $[\xi\xi 0]T_2$ phonon with $\xi = 0.079$ is given entirely by the resolution width as in the observed case shown and we have not shown the calculation of this phonon group.

From Fig. 5 and the phonon groups shown in Figs. 6–10 we see that the calculated phonon life-

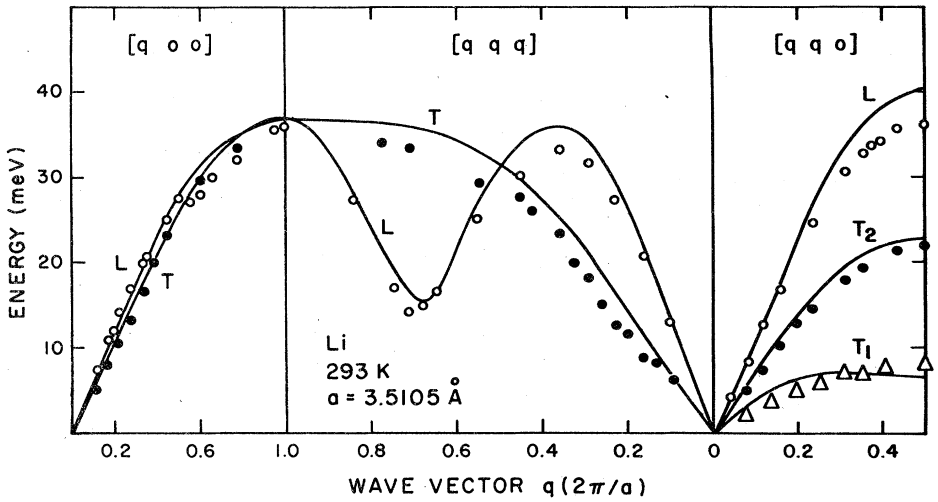

FIG. 3. Phonon energy dispersion curves for Li at 293 K. The solid lines are the SCH+cubic calculations and the open (solid) circles are the longitudinal (transverse) energies observed by Beg and Nielsen.

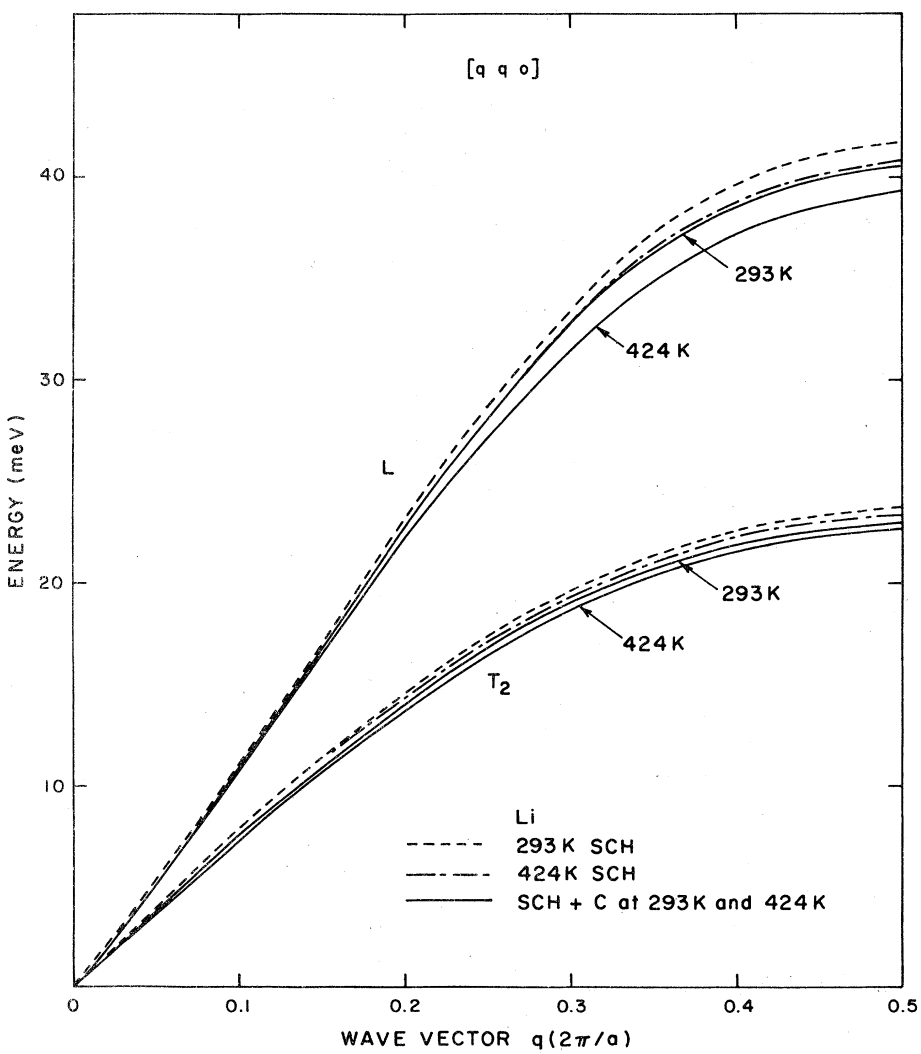

FIG. 4. Self-consistent harmonic (SCH) and the self-consistent harmonic with the cubic term included (SCH+cubic) dispersion curves along the [110] direction.

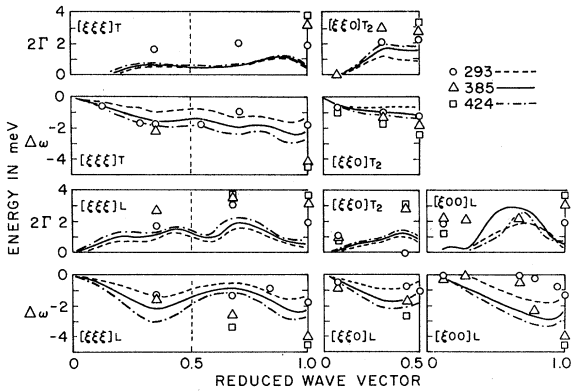

FIG. 5. Phonon energy shifts $\hbar\Delta\omega$ between 110 K and the temperatures indicated, and the intrinsic full width at half-maximum 2Γ of the phonon groups at the temperatures indicated. The lines are the SCH+cubic calculations and the points are the observed values of Beg and Nielsen.

times are often three or four times the observed lifetimes. A discrepancy of a factor of two is characteristic of calculations made using the SCH+cubic theory, for example in K. There a comparison of the SCH+cubic lifetimes with a molecular dynamics determination[32] using the same effective ion-ion interaction showed that a factor of two discrepancy could be attributed to the SCH+cubic theory rather than the potential. In the SCH+cubic theory, a single phonon can decay to two phonons via the coupling through the cubic anharmonic term. Clearly, higher order processes are important. The shortest-lived phonon compared to the frequency is the longitudinal $\vec{Q}^* = (\xi, \xi, \xi)$ with $\xi \approx 0.68$ phonon which vibrates approximately seven times before it decays.

V. DISCUSSION

The aim of this study has been to examine the anharmonic properties of lithium, both for its intrinsic interest and as a means of testing the effective ion-ion interaction. Perhaps the most surprising single result of Sec. IV is that lithium is not very anharmonic. To put the results in perspective we compare in Table II the percentage anharmonic frequency shift of three phonons with

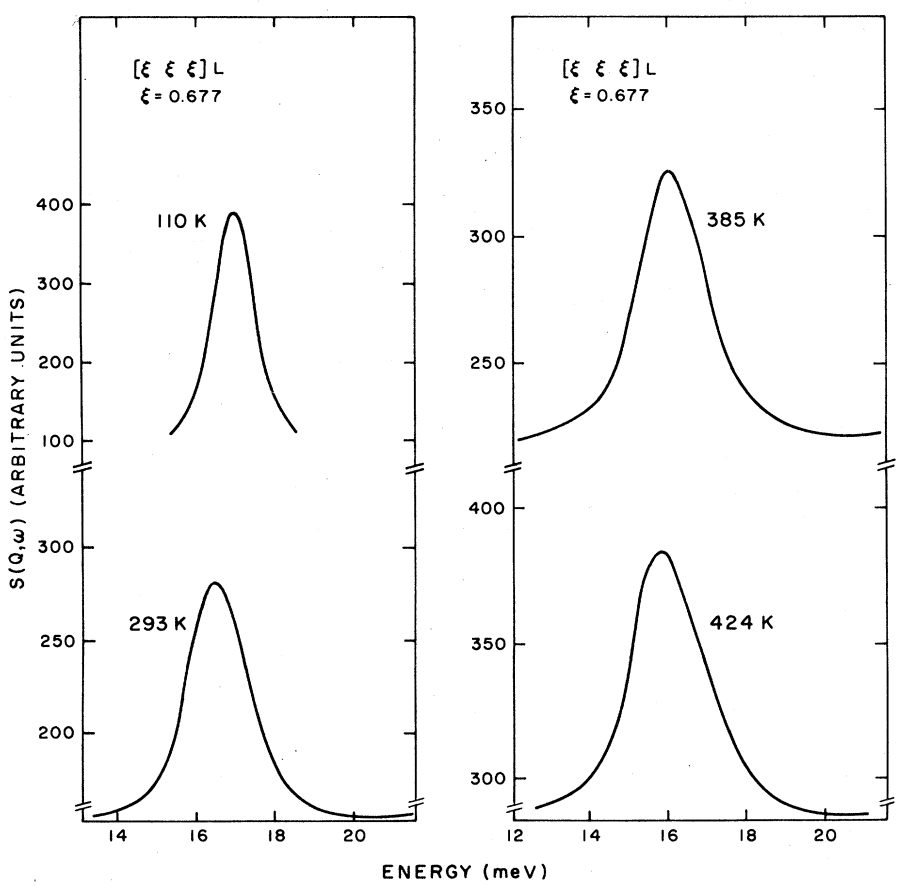

FIG. 6. Calculated $S(\vec{Q}, \omega) = S_1(\vec{Q}, \omega) + S_2(\vec{Q}, \omega) + S_{12}(\vec{Q}, \omega)$ for the longitudinal phonon at $\vec{Q}^* = \vec{Q}\, a/2\pi = (1.323, 1.323, 1.323)$.

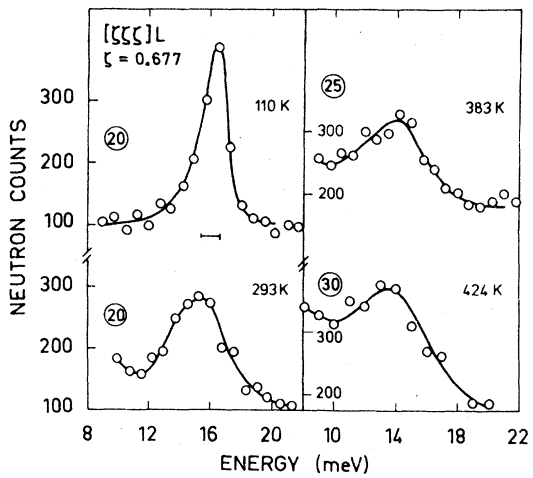

FIG. 7. Phonon groups observed by Beg and Nielsen (Ref. 15) for the same phonon shown in Fig. 6, $\vec{Q}^* = (2-\xi,\ 2-\xi,\ 2-\xi)$.

temperature in Li with those in Na and K which show that Li is the least anharmonic of the three. We might expect lithium to be the most anharmonic of the alkali metals, and possibly of all metals, since its mass is small. However, if the interionic forces are strong these forces can counteract the effects of a light mass by providing a strong restoring force as an ion vibrates away from its lattice point. This will keep the vibrational amplitudes small. The large phonon frequencies in Li do indeed suggest strong restoring forces. For example, the maximum phonon frequency in Li is 2.5 times that in Na and 4.0 times that in K, while on the basis of the mass difference alone ($\omega \propto m^{-1/2}$) we expect ratios of only 1.8 and 2.4, respectively.

To make these points more precise, we consider

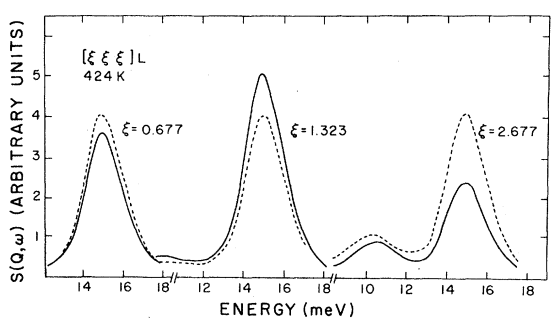

FIG. 8. Calculated $S_1(\vec{Q},\omega)+S_2(\vec{Q},\omega)$ (dashed line) and the $S_p(\vec{Q},\omega)+S_2(\vec{Q},\omega)$ (solid line) for three phonons having identical reduced wave vector $\xi = 0.677$ and $\vec{Q}^* = (0.677,\ 0.677,\ 0.677)$, $Q^* = (1.323,\ 1.323,\ 1.323)$ and $\vec{Q}^* = (1.677,\ 1.677,\ 1.677)$. The difference between the dashed and solid lines, is the interference contribution.

the usual expansion of the interionic potential ϕ in powers of the atomic displacements u. Schematically, this is

$$\phi = \phi_0 + \tfrac{1}{2}\phi_2 u^2 + \tfrac{1}{3}\phi_3 u^3 + \tfrac{1}{4}\phi_4 u^4 + \cdots . \tag{18}$$

A traditional[34,35] measure of the importance of the anharmonic terms is the ratio of the RMS vibrational amplitude to the interionic spacing $\delta = \langle u^2\rangle^{1/2}/R$. Table III shows estimates of δ at the melting point of Li, Na, and K. The $\langle u^2\rangle$ is estimated from

$$\langle u^2\rangle = (\hbar/k)^2\,(9kT/M\Theta_D^2)\,, \tag{19}$$

which is the harmonic result in the high-temperature limit using a Debye approximation to the frequency spectrum. (An accurate value of δ obtained using the exact frequency spectrum calculated

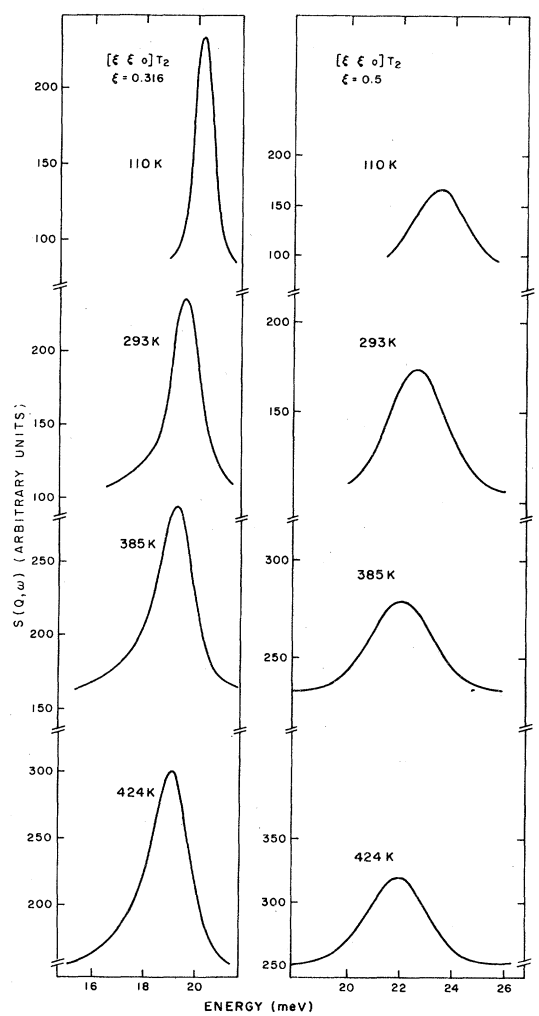

FIG. 9. As Fig. 6 for the phonons indicated.

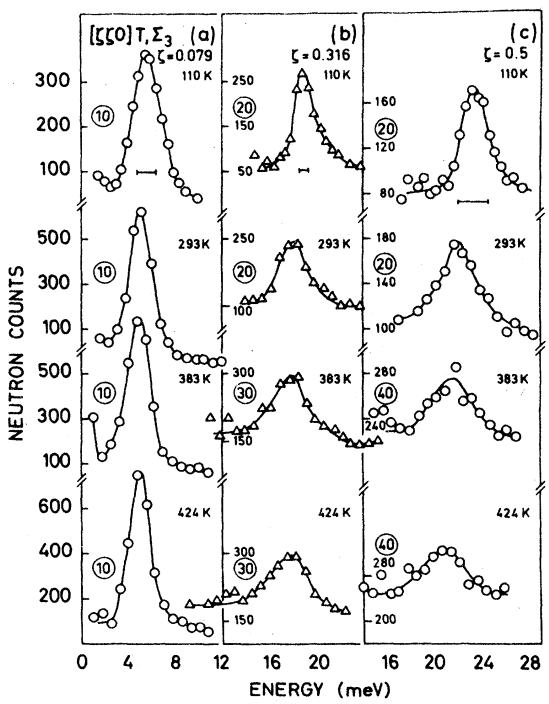

FIG. 10. As Fig. 7 for the phonons indicated.

from the SCH + cubic frequencies gives[30] $\delta = 17\%$ for Na at $T = 361$ K). Clearly the larger value of Θ_D for Li has counteracted the smaller mass to give comparable values of δ in Li, Na, and K. On this basis we expect Li to have comparable or marginally smaller anharmonic shifts as noted in Table II. The larger Θ_D for Li reflects the substantially stronger ion-ion interaction (see Fig. 1).

As noted in Sec. I, the stronger ion-ion interaction in Li can be readily understood in terms of the ion cores. The ions interact via the conduction electrons through an ion-electron-ion indirect interaction. The lithium ion has only two core electrons, both in an s state. This means that a conduction electron in a state having p-wave character sees directly the strong Coulomb potential of the nucleus unshielded by the core electrons. As a result the indirect ion-electron-ion interaction will be strong in Li, much stronger than in Na or K where the larger ions shield the Coulomb potential more effectively. It is interesting that a smaller mass (fewer nucleons) is balanced by a stronger interaction (fewer core electrons) in such a way that the Lindemann[36] ratio, δ, is roughly held constant.

TABLE II. Percentage anharmonic shift $\Delta\omega/\omega$ in phonon frequency calculated using the SCH + cubic theory for Li between 90 and 424 K ($T_m = 451$ K), for Na between 5 and 361 K ($T_m = 371$ K), and for K between 5 and 311 K ($T_m = 335$ K). The observed values in the brackets are: Li [Beg and Nielsen (Ref. 15)] and K [Buyers and Cowley (Ref. 33)].

Phonon	Li	Na	K
(1.0, 0, 0)	−7.2%	−12.8%	−17.5%
	(−12 ± 6%)		(−14%)
(0.5, 0.5, 0)L	−4.0%	−10.0%	−11.5%
	(−6 ± 3%)		(−10%)
(0.5, 0.5, 0)T_2	03.5%	−10.8%	−14.5%
	(−11 ± 3%)		(−14%)

TABLE III. Estimates of the expansion parameter $\delta = \langle u^2\rangle^{1/2}/R$ [using Eq. (19)] at the melting temperature T_m.

	M (amu)	T_m (K)	$a_0(T_m)$ (Å)	$\Theta_D(T_m)$ (K)	$(\langle u^2\rangle^{1/2}/R)$ (%)
Li	7	453	3.54	430	12.7
Na	23	371	4.25	160	14.2
K	39	337	5.34	100	13.3

To compare the relative sizes of the cubic and quartic anharmonic terms, we turn to the more precise expansion parameter for (18) pointed out by Horner.[37] He noted that the expansion parameter should include a measure of the size of the derivatives of ϕ in (18) as well as noting that each derivative brings a factor of $1/R$. The size of these derivatives is fixed largely by the steepness of the repulsive part of ϕ which we could represent crudely by

$$\phi(r) = \epsilon(\sigma/r)^n ,$$

where the index n measures the steepness of $\phi(r)$. The derivatives of $\phi(r)$ are

$$\phi^m(r)|_{r=R} \sim \phi_0(n/R)^m .$$

A more appropriate expansion parameter is then $\lambda = n\delta = n\langle u^2\rangle^{1/2}/R$, which is approximately the ratio of the kinetic to the potential energy. If n and hence λ is small, the Taylor-series expansion converges rapidly.

In the rare-gas crystals, where n is large ($n \approx 12$) we find a large shift in frequency Δ_4 due to the quartic anharmonic term. This shift is approximately given by the difference in the SCH and QH frequencies. This Δ_4 is about twice the shift Δ_3 due to the cubic anharmonic term, the difference between the SCH and SCH + cubic frequencies. In the Alkali halides, the quartic (Δ_4) and cubic (Δ_3) anharmonic frequency shifts are comparable in size suggesting that λ is smaller there than in the rare-gas crystals. From Table I we see that the difference in the SCH and QH frequencies is very small in Li, while the cubic anharmonic shift Δ_3 is relatively much larger. This means that in Li the quartic term is small compared to the cubic

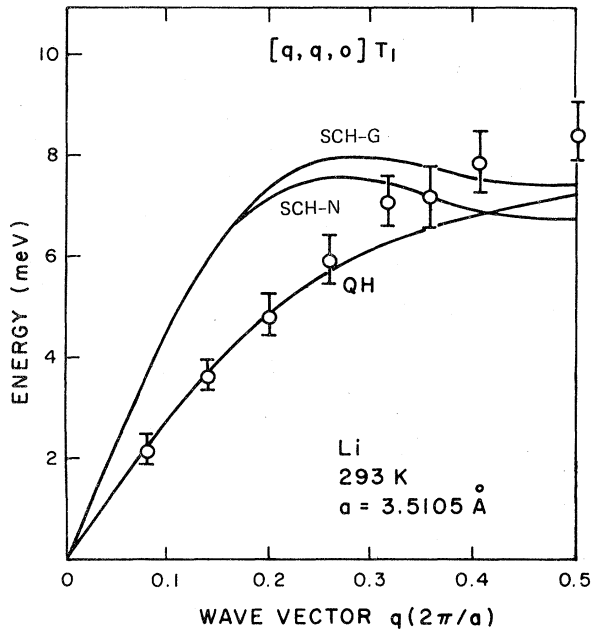

FIG. 11. Transverse T_1 [110] phonon energy dispersion curve in (a) the quasiharmonic approximation (QH), (b) the self-consistent harmonic approximation (SCH) with the force constants for the fifteenth shell and beyond approximated by the nonaveraged QH force constants (SCH-N), and (c) the SCH approximation with the fifteenth shell force constant and beyond obtained by averaging with an uncorrelated spherical Gaussian function (SCH-G).

term so that the core of the interionic potential is quite soft (n small). A small Δ_4 is also required to get agreement with experiment since Δ_4 is generally positive and in general, lower frequencies are required to improve agreement at high temperature (see Fig. 3). The Δ_4 is larger in Na and K, suggesting that the core of the ion-ion interaction is steeper in these larger ion metals. The softer core in Li is consistent with weak shielding of the Coulomb interaction which leaves the net ion-ion interaction closer to $1/r$.

Finally, we note that the agreement of the calculated frequencies and anharmonic shifts with experiment in Li is not as good as in Na or K. Lower frequencies at high T (see Fig. 3) or larger negative shifts (see Table II) are required to improve the agreement with experiment. Since Δ_3 is always negative, a generally larger cubic term is called for in Li. This is not the case in K and Na where agreement is much better. This error in Li probably arises from the breakdown of the pseudopotential method limited to second order in the ion-electron interaction when this interaction is as strong as in the Li case. As discussed in Sec. II, the DRT ion-ion interaction used here is constructed to simulate all the nonlinear higher-order contributions between pairs of ions. Thus the present discrepancy probably reflects the presence of three- or four-body forces. A three-body force leads to an additional class of cubic terms in Δ_3 which could substantially increase its size.

To conclude, we note that the long-range nature of the Li ion-ion interaction shown in Fig. 1 made the calculations difficult. This affected particularly the $[qq0]T_1$ branch, and the frequencies of this branch did not stabilize even for force constant summations out to 30 shells of neighbors. The QH frequencies could be obtained exactly by expressing $V_{II}(r)$ as the sum of a $V_{\text{eff}}(r)$, which became negligible after 15 shells of neighbors, and an asymptotic part which was evaluated in reciprocal space.

In the SCH approximation, averaging of the force constants involving the asymptotic part turned out to be important for the $[qq0]T_1$ branch and could not be done exactly in reciprocal space. Figure 11 shows the dispersion curves of this branch with no averaging of the asymptotic part and for an independent Einstein model averaging using a Gaussian distribution of appropriate width. This branch is clearly sensitive to the averaging of the distant neighbor force constants. It is also likely that the dip in the $[qq0]L$ branch in the region $q \approx 0.7$ is sensitive to the distant neighbor force constants. In Fig. 3 this $[q00]L$ branch does fall as far below the transverse branch as suggested by experiment and this may be due to our approximate treatment of the distant neighbor force constants.

Note added in proof: We thank Dr. H. G. Smith for permission to quote the previously unpublished data shown in Fig. 2.

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[2]By "first principles" we mean calculations based on potentials or pseudopotentials whose parameters have been determined from fundamental considerations such as atomic spectra or charge densities. We do not include in this category force-constant models obtained by fitting to metallic properties.

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