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Anharmonic Lattice Dynamics in K

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The lattice dynamics of K at $T = 9$, 99, 215, and 299 °K is studied employing an effective pair ion-ion potential and the self-consistent (SC) theory for anharmonic crystals. The effective potential was derived from first principles following the method that Geldart *et al.* developed successfully for Na. The purpose of the present paper is (i) to test whether the potential derivation can be extended successfully to K and (ii) to compare the SC anharmonic theory with experiment and the standard anharmonic perturbation theory used by Buyers and Cowley. For all the symmetry directions except the Δ_1 branch, the phonon frequencies computed here at 9 °K lie within 2% of the observed frequencies verifying the validity of the K ion-ion potential. The total anharmonic shifts in frequency (quasiharmonic + anharmonic) with temperature are comparable but $\backsim$ 20% greater than those computed by Buyers and Cowley. Given the scatter in the observed shifts, both calculations agree equally well with experiment.

I. INTRODUCTION

In a recent paper Glyde and Taylor[1] presented calculations of phonon frequencies and lifetimes in Na over the temperature range $T = 5-361$ °K using the self-consistent theory of anharmonic lattice dynamics. To describe Na an effective ion-ion potential, derived from the calculations of Geldart *et al.*,[2] which employs the Geldart-Taylor[3] screening function, was used. The encouraging agreement between theory and experiment both at liquid-nitrogen and room temperatures in Na has prompted us to do a similar calculation for K, where there are data available,[4,5] to test extensions of this method.

As in the case of Na there can be found in the literature (e.g., see the review article by Joshi and Rajagopal[6]) large numbers of lattice dynamic calculations for K using a wide variety of models in the harmonic approximation. However, to our knowledge only Buyers and Cowley[5] have calculated anharmonic contributions to the phonon frequencies and lifetimes of K. In their calculations, Buyers and Cowley employed a semiempirical pseudopotential with parameters chosen by fitting the computer harmonic phonon dispersion curves to those observed at 9 °K. This potential was then used to compute the quasiharmonic and the cubic and quartic anharmonic contributions to the phonon frequencies and lifetimes at higher temperatures via standard perturbation theory. Their calculated frequency shifts and lifetimes gave reasonable agreement with their experimental results at 99, 215, and 299 °K.

As in the case of Na the present interatomic potential is derived following the procedure of Geldart *et al.*[2] and Basinski *et al.*[7] This is more fundamental in the sense that no fitting to solid data is employed. The derivation is discussed briefly in Sec. II. The resulting phonon frequencies calculated using the self-consistent theory are then presented and discussed in Sec. III.

II. THEORETICAL MODEL

A. Effective Ion-Ion Potential

To compute the effective ion-ion potential, a knowledge of both the bare electron-ion interaction and the conduction-electron dielectric function is necessary. In K, where nonlocal effects are not important, the interionic potential may be written in the form

$$U_{\mathrm{II}}(r)=\frac{(Ze)^2}{r}-\frac{2(Ze)^2}{\pi}\int_0^\infty \frac{F(q)\sin qr}{qr}\,dq\ ,$$

$$F(q)=\frac{1}{Z^2}\,M(q)^2\,\frac{q^2Q(q)}{q^2+Q(q)}\ ,$$

where Z is the valence. $M(q)$ is the bare electron-ion matrix element and $Q(q)$ is the static electron-gas screening function related to the dielectric function by the equation

$$\epsilon(q)=1+Q(q)/q^2\ .$$

To calculate $M(q)$ we have used a single orthogonalized plane wave (OPW) to represent the conduction-electron wave function. This interacted with the K^+ ion via a potential which was constructed to fit the spectroscopic terms of the free ion using a procedure similar to that of Prokofjew.[8] The parameters defining this potential are given in the Appendix. Following Geldart *et al.*[2] the nonlocal terms in the one-OPW matrix element were averaged over the volume of the Fermi sphere and added to the local term after verifying that no significant error was introduced by this procedure.

Although the one-OPW approximation has been shown to be a good one for Na,[9] it does not necessarily follow that the same is true for K. To check this point we have repeated the calculations of Taylor *et al.*[9] using our K^+ potential instead of the Prokofjew Na^+ potential. That is, for energy-conserving transitions at the Fermi level we have evaluated the so-called "Schrödinger" part of the bare electron-ion matrix element defined by Eq. (4.4) of Vosko *et al.*[10] as follows:

$$\vec{\mathrm{M}}_s(\vec{\mathrm{k}}',\vec{\mathrm{k}})=\int_r d\vec{\mathrm{r}}\,B^*_{\vec{\mathrm{k}}'}(\vec{\mathrm{r}})[\nabla U_s(\vec{\mathrm{r}})]\,B_{\vec{\mathrm{k}}}(\vec{\mathrm{r}})\ . \qquad (1)$$

$B_{\vec{\mathrm{k}}'}(\vec{\mathrm{r}})$ is a Bloch state of momentum $\vec{\mathrm{k}}'=\vec{\mathrm{k}}+\vec{\mathrm{q}}$ and $U_s(\vec{\mathrm{r}})$ is defined as the sum of the free-ion potential and the Hartree term due to the conduction electrons. For energy-conserving transitions, Eq. (1) can be rewritten [Eqs. (3.12) and (3.19) of Ref. 9]

$$\vec{\mathrm{M}}_s(\vec{\mathrm{k}}',\vec{\mathrm{k}})=i\vec{\mathrm{q}}\,\gamma(q)\ .$$

We have evaluated $\gamma(q)$ using both the one-OPW approximation and the Kohn variational method[11] (KVM) which has been summed to convergence and is the exact solution for the one-electron problem in a spherical cell. As is shown in Fig. 1, the one-OPW version of $\gamma(q)$ agrees quite well with the KVM version. A check of the form factors resulting from the two procedures reveals that they differ significantly only for $1.9k_F \lesssim q \lesssim 2k_F$, where the difference is still only 3% of the Fermi energy. Hence the one-OPW approximation seems to be very reasonable for K as well as Na.

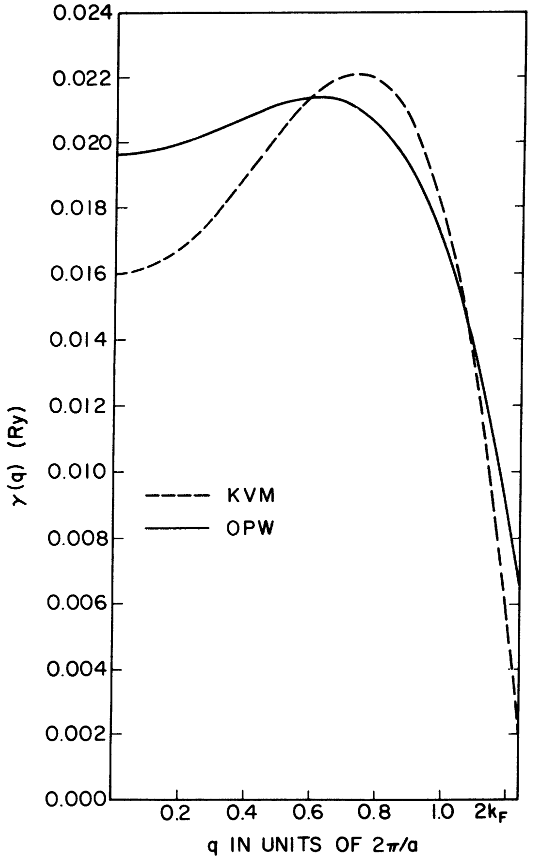

FIG. 1. Function $\gamma(q)$ of Eq. (2) as computed using the one-OPW approximation and the Kohn variational method (KVM).

For simple metals with small ion cores such as K, electron-gas theory may be used for the conduction-electron dielectric function. However, the choice of electron-gas screening is quite critical,[2,12] and we have used the Geldart-Taylor[3] calculation of the dielectric function, since on comparison[13] with other functions it appears to be the best one available. These authors evaluated a consistent set of low-order corrections to the Lindhard or random-phase approximation (RPA) screening function and also constructed an approximate sum of the higher-order terms. The resulting $Q(q)$ satisfies all the known analytic properties of the exact function and takes the form

$$Q(q)=Q_0(q)\left(1+\frac{g_1(q)}{1-Cf_0(q)}\right)\ ,$$

where

$$Q_0(q)=\frac{4k_F}{\pi a_0}\,f_0(q),$$

$$f_0(q)=\frac{1}{2}+\frac{4k_F^2-q^2}{8k_Fq}\ln\left|\frac{q+2k_F}{q-2k_F}\right|\ .$$

k_F is the Fermi wave number, a_0 is the Bohr radius, and C is determined by the condition that

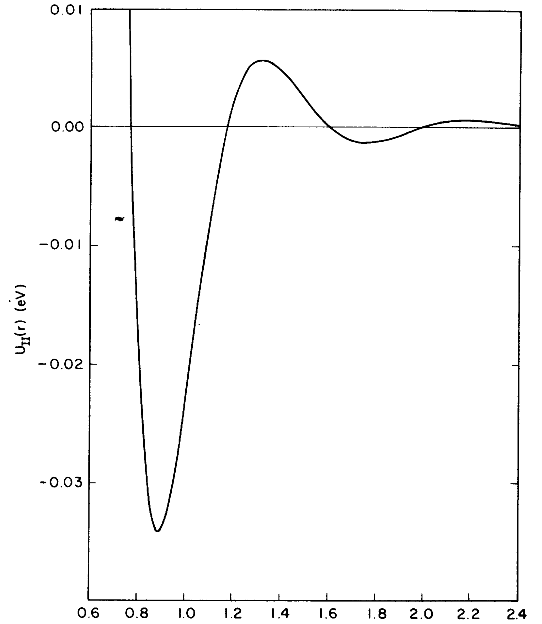

FIG. 2. Effective ion-ion potential $U_{II}(r)$ in eV for K at $T = 9\,°\mathrm{K}$. a is the $9\,°\mathrm{K}$ lattice constant.

$Q(q)$ must satisfy the compressibility theorem. The function $g_I(q)$ does not have a simple analytic form and is interpolated from Table II of Geldart and Taylor.[3]

The resultant effective ion-ion potential at $9\,°\mathrm{K}$ is displayed in Fig. 2. Although this potential is relatively insensitive to small changes in density, it was recalculated at the density corresponding to each temperature considered.

B. Anharmonic Theory

Perturbative treatments of anharmonicity[14] begin by expanding the crystal potential in a power series of the atomic displacements $u_\alpha(l)$:

$$V = V_0 + V_2 + V_3 + V_4 + \cdots \quad . \tag{2}$$

Here, all the derivatives are evaluated at the equilibrium spacing $R(0)$ of the static lattice of $T = 0\,°\mathrm{K}$. The second term is

$$V_2 = \frac{1}{2} \sum_{lx,l'y} \left(\frac{\partial^2 V}{\partial x(l)\, \partial y(l')} \right)_{R(0)} u_x(l) u_y(l') \tag{3}$$

and the harmonic frequency $\omega(qj)$, for a phonon with wave vector q and branch j, is obtained as a diagonal element of this force-constant matrix. Thermal expansion is then allowed for as a perturbation by finding the change in these harmonic force constants with volume. This provides the "quasiharmonic" frequencies. The quartic V_4 and cubic V_3 terms are then included as first- and second-order perturbations, respectively. We denote here the total perturbative correction to $\omega(qj)$ by

$$2\omega(qj)\Delta(qj,\omega) = 2\omega(qj)[\Delta_T(qj) + \Delta_4(qj) + \Delta_{33}(qj,\omega)] \quad , \tag{4}$$

and the reader is referred to Buyers and Cowley[5] for the explicit expressions for the thermal-expansion (Δ_T), quartic (Δ_4), and cubic (Δ_{33}) contributions.

The one-phonon neutron scattering cross section is proportional to the response function[14]

$$\frac{2\omega(\lambda)\Gamma(\lambda,\omega)}{[-\omega^2 + \omega(\lambda)^2 + 2\omega(\lambda)\Gamma(\lambda,\omega)]^2 + [2\omega(\lambda)\Gamma(\lambda,\omega)]^2} \quad , \tag{5}$$

where $\lambda \equiv qj$ and $\Gamma^{-1}(\lambda,\omega)$ is the inverse phonon lifetime due to the cubic term. The observed (and hence calculated) phonon frequency $2\pi\nu(T)$ at temperature T is associated with the center of the peak in this function.

The self-consistent theory of lattice dynamics has been derived by many authors,[15] and applied chiefly to the rare-gas crystals,[16-20] where the reader is referred for full discussion. Here we outline its content only for comparison with perturbation theory. In a metal such as K, it is convenient to introduce quasiharmonic (QH) (or reference) frequencies defined by

$$\omega^2_{\mathrm{QH}}(qj) = \frac{1}{M} \sum_{l \neq l'} (e^{i\vec{q}\cdot\vec{R}(ll')} - 1) \times \sum_{xy} \epsilon_x(qj)\epsilon_y(qj) \left(\frac{\partial^2 V}{\partial x(l)\, \partial y(l')} \right)_{R(T)} \quad , \tag{6}$$

in which the second derivative is evaluated directly at the observed spacing $R(T)$. These correspond to the frequencies $\omega^2(qj) + 2\omega(qj)\Delta_T(qj)$ of the perturbation case.

The self-consistent-harmonic (SCH) frequencies can then be derived[21] by including all the even anharmonic terms ($V_4 + V_6 + V_8 + \cdots$) in (2) as a first-order correction to ω_{QH}. The total may be written in closed form giving the SCH frequencies as

$$\Omega^2_{qj} = \frac{1}{M} \sum_{l \neq l'} (e^{i\vec{q}\cdot\vec{R}(ll')} - 1) \times \sum_{xy} \epsilon_x(qj)\epsilon_y(qj) \left\langle \frac{\partial^2 V}{\partial x(l)\, \partial y(l')} \right\rangle \quad , \tag{7}$$

in which the second derivative is now averaged over the vibrational (Gaussian) distribution of the atoms in their unit cells implied by the Ω^2_{qj}. The difference between ω_{QH} and Ω provides a measure of the even anharmonic terms. Since odd derivative terms are known to be important,[14] the cubic term is added as a perturbation giving a shift to Ω_{qj} of

$$\Delta(\lambda,\omega) = \frac{1}{2\hbar^2} \sum_{\lambda_1\lambda_2} |\langle V(\lambda,\lambda_1,\lambda_2)\rangle|^2$$

$$\times\left(\frac{n_1+n_2+1}{(\Omega_1+\Omega_2+\omega)_p}+\frac{n_1+n_2+1}{(\Omega_1+\Omega_2-\omega)_p}+\frac{n_2-n_1}{(\Omega_1-\Omega_2+\omega)_p}+\frac{n_2-n_1}{(\Omega_1-\Omega_2-\omega)_p}\right), \tag{8}$$

and an inverse phonon lifetime,

$$\Gamma(\lambda,\omega)=\frac{\pi}{2\hbar^2}\sum_{\lambda_1\lambda_2}\left|\langle V(\lambda,\lambda_1,\lambda_2)\rangle\right|^2\{(n_1+n_2+1)\times[\delta(\Omega_1+\Omega_2-\omega)-\delta(\Omega_1+\Omega_2+\omega)]+(n_2-n_1)[\delta(\Omega_1-\Omega_2-\omega)-\delta(\Omega_1-\Omega_2+\omega)]\}. \tag{9}$$

The SCH + C frequencies (with the cubic term added) are now identified with the center of a response function (5); but one in which Ω_{qj} replaces $\omega(qj)$, and $\Delta(\lambda,\omega)$ and $\Gamma(\lambda,\omega)$ are given by (8) and (9), respectively.

III. NUMERICAL RESULTS AND DISCUSSION

A. $T=9\,^\circ$K Harmonic Dispersion Curves

The phonon frequency dispersion curves computed in the SCH + C approximation at $T=9\,^\circ$K are shown in Fig. 3. Since the QH frequencies differ only very slightly from the SCH + C at this temperature, they are not plotted. The agreement with the experimental results of Cowley *et al.*[4] is good though not as good as that obtained for Na.[1] The computed Δ_1 branch is a little low as are some points on the Λ_1, F_3, and Σ_1 branches. These discrepancies are quite small. With one exception the calculated points for all but the Δ_1 branch miss the experimental error bars by less than 2%. One of the more obvious sources of error in the calculation is the neglect of electron-electron umklapp scattering, which has been shown to have a significant effect on phonon frequencies[22] and which could easily account for the discrepancies in the Δ_1 branch. Hence, we conclude that the agreement between theory and experiment is satisfactory, which demonstrates the validity of the effective ion-ion potential in K.

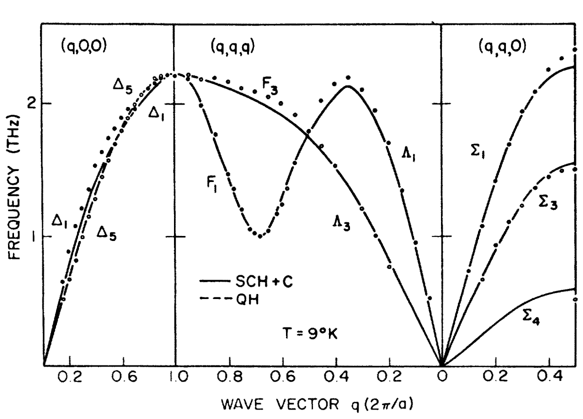

FIG. 3. Phonon-frequency dispersion curves (in 10^{12} Hz) for K at $T=9\,^\circ$K, as computed in the SCH + C approximation. The longitudinal experimental points are plotted as closed circles and the transverse as open circles.

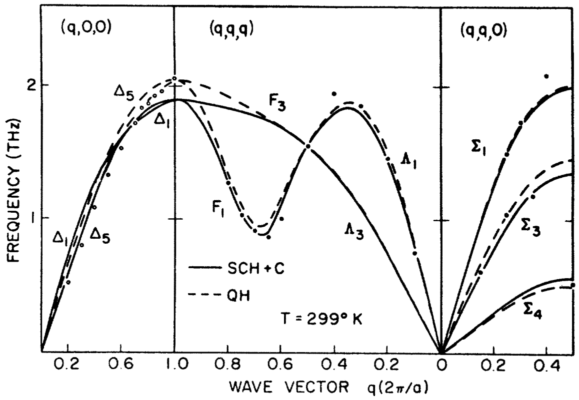

FIG. 4. Phonon-frequency dispersion curves (in 10^{12} Hz) for K at $T=299\,^\circ$K. The longitudinal experimental points are plotted as closed circles and the transverse as open circles.

B. Anharmonic Contributions

In Fig. 4 are displayed the room-temperature phonon dispersion curves calculated in both the QH and SCH + C approximations. The difference between these two curves gives the explicit anharmonic effects which are clearly significant at room temperature. There are not enough experimental data to decide whether or not the SCH + C curves give better agreement than do the QH curves. It is interesting to note that the [110] branches of the phonon spectrum exhibit the same anharmonic effects as were noted for Na.[1] That is, (i) for the Σ_1 branch the upward shift from the QH to the SCH case is canceled by the cubic shift so that the QH and SCH + C values are nearly the same; (ii) for the Σ_3 branch the QH to SCH shift and the cubic shift are both downward resulting in a large anharmonic shift; and (iii) for the Σ_4 branch the net shift is *upward* due to a very large QH to SCH shift which is only partially canceled by the downward cubic shift. Another feature of the Na calculation was the presence of a pronounced flattening of the Δ_1 branch at room temperature[1] for $q \sim 0.6(2\pi/a)$ which seemed to be confirmed by experiment. This flattening is not nearly so obvious in the SCH + C results in Fig. 4 and unfortunately no experimental data are available for the Δ_1 branch.

To display the anharmonic effects more clearly we plot the total shift in frequency Δ in going from $9\,^\circ$K to a given temperature T,

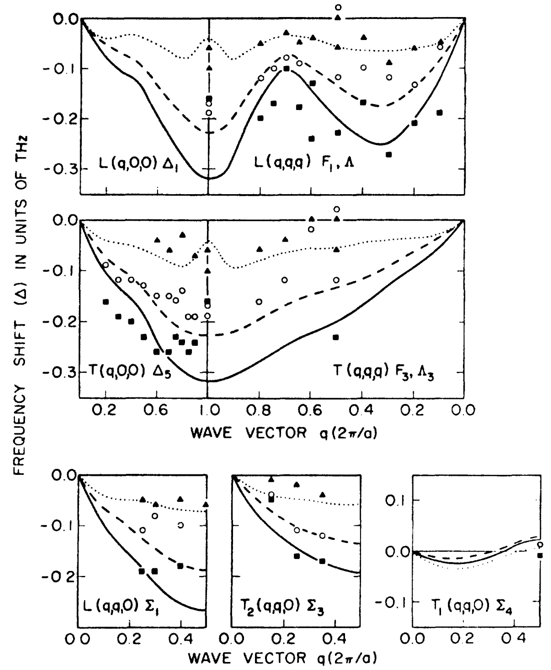

FIG. 5. Total phonon frequency shift, $\Delta(T)=\nu(T)-\nu(9\,^\circ\mathrm{K})$, compared with experimental points. Squares and solid lines are for 299 °K, circles and dashed lines for 215 °K, and triangles and dotted lines for 99 °K.

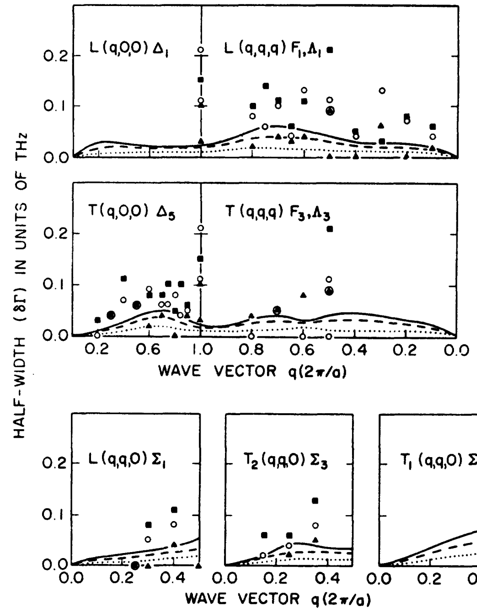

FIG. 6. Half-width Γ of the computed phonon group at half the peak height. The phonon lifetime $\tau=\Gamma^{-1}$. For notation see Fig. 5 caption.

$$\Delta(T)\equiv\nu(T)-\nu(9\,^\circ\mathrm{K})\,, \tag{10}$$

in Fig. 5. This will include both the quasiharmonic shift plus the explicit anharmonic shifts shown in Fig. 4. This presentation allows direct comparison with the experiments and calculations of Buyers and Cowley.

From Fig. 5 we see that the computed shifts agree broadly with experiment. More accurate data are really required for a more definite statement. At $T=299$ °K the shifts computed here are ~20% greater than those computed by Buyers and Cowley. Since the potentials used in both calculations fit the 9 °K data well, this difference is probably not due to the different potential forms used. Rather, since the QH shift is the greatest and since Buyers and Cowley used a perturbation QH treatment rather than a recalculation of the frequencies at each volume, the difference is probably due to a difference in QH shift. However, it is fair to say that there is little difference between the two computed results given the vast difference in method and both agree reasonably with experiment.

Although the calculated phonon frequencies and shifts appear to be quite satisfactory, the same can hardly be said for the widths as can be seen in Fig. 6. Despite the fairly large scatter in the experimental widths it is quite clear that the theoretical results are too low by at least a factor of 2. This same deficiency was noted in the Na calculations[1] and is clearly due to neglect of higher-order terms, particularly when we observe that Buyers and Cowley encountered similar difficulty.[5] These could be three-body potential contributions to the cubic term, electron-electron umklapp scattering, or simply higher-order anharmonic terms. On the

TABLE I. Computed K anharmonic elastic constants as functions of temperature. The units are 10^{10} dyn cm^{-2}. The experimental values are read from the graphs plotted by Marquardt and Trivisonno (Ref. 25).

	C_{11}		C_{12}		C_{44}		$C'=\frac{1}{2}(C_{11}-C_{12})$	
T(°K)	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.
9	4.17	4.3	3.49	3.5	2.97	2.9	0.34	0.37
99	3.90	4.1	3.28	3.4	2.71	2.6	0.31	0.34
215	3.59	3.9	2.95	3.3	2.30	2.1	0.32	0.31
299	3.28	3.7	2.66	3.1	2.10	1.9	0.31	0.28

TABLE II. Parameters defining the K^+ potential. The potential is in rydbergs with r in a.u.

	α	β	γ	δ
$0 \leq r \leq 0.1053$	−122.96	19.00	0	310.0
$0.1053 \leq r \leq 0.4412$	−37.85	15.19	0.2198	
$0.4412 \leq r \leq 0.5111$	40.98	−19.58	15.56	
$0.5111 \leq r \leq 1.106$	−2.031	2.399	4.329	
$1.106 \leq r \leq 1.90$	−0.7800	1.015	5.859	
$1.90 \leq r \leq 4.00$	0.6966	−1.791	11.19	
$4.00 \leq r \leq 6.31$	0.0019	0.9882	0.0746	
$6.31 \leq r \leq \infty$	0	1.000	0	

other hand, calculations of the phonon group width in Al due to the cubic anharmonic term by Sandström and Högberg[23] and Koehler *et al.*[24] do not seem quite so decidedly below the observed widths—although they often differ by a factor of 2 at some points in the Brillouin zone.

Finally, the elastic constants as functions of temperature are listed in Table I and compared with the experimental results of Marquardt and Trivisonno.[25] The over-all agreement with experiment is quite good. Because of its relatively small size, C' is very sensitive to small errors in the potential and usually proves rather difficult to calculate with any accuracy. Some of the error in C_{11} and C_{12} may well be due to the neglect of electron-electron umklapp scattering, but C' is independent of this approximation.[22]

IV. CONCLUSION

We conclude that an effective pair ion-ion potential derived following the method developed by Geldart *et al.*[2] for Na describes K well. This follows from the excellent agreement between the low-temperature computed and observed phonon-frequency dispersion curves and from the agreement within the accuracy of the data between the computed and observed anharmonic frequency shifts with temperature. The poor agreement between the computed and observed phonon lifetimes alludes to some many-body contribution either in the potential or in the ionic correlations.

The total frequency shifts computed here are greater than those computed by Buyers and Cowley[5] using perturbation theory by ~20%. Since in Na the explicit anharmonic shifts were essentially the same when calculated in the SC and perturbation methods, this difference is most probably due to the difference in the QH theory employed in the two cases.

APPENDIX

The K^+ potential used for the calculations in this paper was constructed to fit the spectroscopic terms of the free ion using a procedure similar to that of Prokofjew.[8] Prokofjew divided r space into a number of regions and assumed that in each region the ionic potential could be written in the form

$$V(r) = -Q(r)/r^2, \quad Q(r) = \alpha r^2 + 2\beta r + \gamma \; .$$

Across each boundary, $Q(r)$ and its derivative were constrained to be continuous. Prokofjew then adjusted the remaining parameters to fit the spectroscopic-term values of Na^+. Later attempts to use the method on K^+ were not successful.[26] However, it turns out that the difficulties can be overcome by adding a term δr^3 to $Q(r)$ in the innermost region. In Table II are listed the parameters defining the K^+ potential, which reproduces the spectroscopic term values listed by Moore[27] to better than 1% accuracy. The same method has also been used successfully to generate Mg^{++}, Al^{+++}, and Ca^{++} potentials.[28]

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Band Structure of NiS as Calculated Using a Simplified Linear-Combination-of-Muffin-Tin-Orbitals Method

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Hexagonal NiS undergoes a first-order metal-to-nonmetal transition as the temperature is lowered below 264 K. NiS appears to be a "normal Pauli-paramagnetic *d*-band metal" above the transition temperature T_t, while below T_t it is antiferromagnetic (moment $\sim 1.7\mu_B$) and either metallic or semimetallic. By use of a simplified (linear-combination-of-muffin-tin-orbitals) method that no longer requires a secular equation to be calculated as a function of energy, the band structure for NiS is calculated. These results indicate that the S *p* bands overlap the bottom of the *d* bands as hypothesized by White and Mott. It appears that this overlap increases with temperature, as a result of lattice vibrations which are included in the calculation through a Debye-Waller factor. We suggest a Mott-Hubbard transition occurs for a critical electron-phonon coupling which may be associated with a critical temperature.

I. INTRODUCTION

NiS is one of the many transition-metal compounds that undergoes a first-order metal-to-nonmetal (M-NM) phase transition as the temperature is lowered.[1] Mott[2] has ascribed this transition in NiS to a Hubbard gap since neutron-diffraction[3] results indicate the moment is $1.55\mu_B$ below the transition temperature T_t of 264 K but is less than $0.5\mu_B$ above T_t. Mott further supports the Hubbard-gap model by the fact that the high-temperature phase appears to be a normal *d*-band metal, $\rho \sim 10^{-4}$ Ω cm and the magnetic susceptibility is temperature independent ($\sim 2.25\times10^{-6}$ emu/gm). More recently, White and Mott[4] concluded that NiS undergoes a metal-metal transition (low-temperature resistivity $\rho_{LT} \sim 10^{-2}$ Ω cm). Koehler[5] arrives at the same conclusion on the bases of his low-temperature resistivity and susceptibility measurements.

White and Mott[4] hypothesize that the moments and the Hubbard gap form as a result of the discontinuous lattice expansion that occurs as T is lowered below T_t. (Hexagonal lattice parameters c and a increase by 1% and 0.3%, respectively, without a change in structure.[6,7]) Our present work implies an alternative explanation since the energy bands of NiS, calculated with the linear-combination-of-muffin-tin-orbitals (LCMTO) method,[8,9] are more sensitive to an average electron-phonon coupling or Debye-Waller correction[10] to the potential than to a discontinuous change in lattice parameters. Consequently, the discontinuous lattice expansion that occurs as the temperature is lowered below T_t appears to result from the spontaneous appearance of local moments as a critical electron-phonon coupling is reached.

There are few theoretical studies such as ours of the M-NM transition in transition-metal compounds based on complete energy-band calculations. Energy bands are difficult to calculate since these transition-metal compounds usually form in structures with more than one molecule per unit cell and the potentials contain large non-muffin-tin contributions. As a result, commonly used first-principles calculational techniques are difficult to apply.[11] The orthogonalized-plane-wave (OPW) method cannot easily treat the *d* bands, and the Korringa-Kohn-Rostoker (KKR) method cannot treat the non-muffin-tin part of the potential. Augmented-plane-wave (APW) and linear-combination-of-atomic-orbitals (LCAO) methods can treat the non-muffin-tin potential but require a large basis set when there are several atoms per unit cell. The LCMTO method,[8,9] however, has the advantage of being able to treat the non-muffin-tin potential with a small basis set, thus making it convenient for complex systems such as NiS.

In addition, the LCMTO has the added advantage, not found with KKR and APW, that the secular equation need not be calculated as a function of the energy E, which serves as a nonlinear varia-