Unified study of lattice dynamics of alkali metals with the use of a general tensor force model

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The phonon dispersion relations for lithium, sodium, potassium, rubidium, and cesium along the principal symmetry directions are deduced on the basis of a general tensor force model. This model incorporates the electron-ion interactions separately, satisfies the symmetry requirements of the lattice, and reproduces the observed crossover of Δ_1 and Δ_5 branches in lithium without producing similar crossovers in any other alkali metal. Besides, the theoretical dispersion curves of all alkali metals are in very good agreement with the corresponding experimental (or homologous) dispersion curves. It is shown that crossover of dispersion curves along the $[\zeta 00]$ direction in an alkali metal is highly sensitive to the strength of the electron-ion interactions, but the failure of the previous models to produce a crossover in lithium is entirely due to their intrinsic deficiencies. The role played by the umklapp processes in producing a crossover and the apparent variation in the nature and range of atomic interactions in alkali metals as well as the relevance of the unified approach to their lattice-dynamical study are discussed.

I. INTRODUCTION

In spite of the availability of the experimental phonon frequencies of lithium,[1] sodium,[2] potassium,[3] and rubidium,[4] theoretical studies of lattice dynamics of alkali metals based on a variety of phenomenological models[5–9] and pseudopotential models[10,11] have not, so far, succeeded in ascertaining whether the nature and range of interatomic forces vary from one alkali metal to another. Most of the phenomenological models[5–7] fail to produce a crossover in lithium along the $[\zeta 00]$ direction, while others[8] produce it not only in lithium but also in other alkali metals. Besides, some pseudopotential models[10] produce, at different wave vectors, a crossover in lithium, whereas the rest[11] do not, even though all of them incorporate more or less the same short-range ion-ion interactions. The nonavailability of the experimental phonon frequencies of cesium is an additional constraint in this context. On the contrary, the degree of homology exhibited by the experimental phonon frequencies of lithium, sodium, potassium, and rubidium seems to suggest that the observed crossover in lithium is not an anomalous property but manifests itself at small values of atomic mass and nearest-neighbor distance in alkali metals,[12] and hence the phonon frequencies of cesium determined by exploiting this homology[13] should be equivalent to their experimental values. Further, the success of the axially symmetric force (AS) models,[9] which conform to the translational symmetry of the lattice, in reproducing the crossover in lithium at $\zeta \sim 0.5$ without producing similar crossovers in other alkali metals, supports this view.

A detailed analysis of various force-constant models reveals that many of them do not satisfy the symmetry requirements of the lattice and the crossover produced by them is a spurious result.[14] It is therefore essential to investigate the lattice dynamics of all alkali metals using a model which is free from any basic deficiencies in order to ascertain the differences in the nature and range of their atomic interactions. Since the mathematical complexities forbid the use of pseudopotential models to isolate the factors responsible for the observed crossover in lithium, the authors

have, for the first time, made use of a general tensor force (GTF) model[15] which incorporates the volume forces separately, for this purpose. The unified study, described in this paper, reveals the circumstances under which the dispersion curves of an alkali metal cross over along $[\zeta 00]$ direction.

II. THEORY

In order to deduce the phonon frequencies of alkali metals, the short-range ion-ion interactions and the long-range electron-ion interactions are expressed, respectively, in terms of general tensor forces[15] and an electron gas model which satisfies the translational symmetry of the lattice.[9] When the range of the former is extended up to third nearest neighbors, the diagonal and off-diagonal elements of the matrix D^i could be written as[16]

$$MD_{xx}^i = 4\{2\sigma_1(1 - C_x C_y C_z) + \sigma_2 S_x^2 + \lambda_2(S_y^2 + S_z^2)$$
$$+ \sigma_3[2 - C_{2x}(C_{2y} + C_{2z})] + \lambda_3(1 - C_{2y}C_{2z})\} , \quad (1)$$

and

$$MD_{xy}^i = 4\{2\tau_1 S_x S_y C_z + \tau_3 S_{2x} S_{2y}\} , \quad (2)$$

where $S_x = \sin(q_x a/2)$, $S_{2x} = \sin(q_x a)$, $C_x = \cos(q_x a/2)$, and $C_{2x} = \cos(q_x a)$, etc., M is the mass of the ion, a is the lattice parameter and σ_n, λ_n, and τ_n are the nth-neighbor tensor force constants. On the other hand, the elements of the matrix D^e, which include the contributions from umklapp processes, are given by[9]

$$MD_{xy}^e = \frac{C'}{2}\left\{ \sum_g \frac{(g-q)_x(g-q)_y S(g-q)F(g-q)}{(g-q)^2 + F(g-q)/a^2} \right\} , \quad (3)$$

where C' is an adjustable constant related to the bulk modulus K_e of the electron gas, g is a reciprocal-lattice vector, $S(\eta)$ is the interference factor which has been evaluated exactly over the atomic polyhedron for bcc structure,[17] and the simple random-phase approximation, the Vashishta-Singwi approximation,[18] as well as the Taylor ap-

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TABLE I. Relevant experimental data for alkali metals and the calculated values of their force constants.

Metal	Li	Na	K	Rb	Cs
M (10^{-27} kg)	11.65	38.18	64.91	142.00	220.70
a (Å)	3.484	4.240	5.226	5.628	6.050
$\nu_{L,T}(100)$ (THz)	8.800	3.580	2.210	1.320	0.943[a]
$\nu_L(\frac{1}{2}\frac{1}{2}0)$ (THz)	9.150	3.890	2.380	1.445	1.054[a]
$\nu_{T_1}(\frac{1}{2}\frac{1}{2}0)$ (THz)	1.900	0.930	0.530	0.345	0.260[a]
$\nu_{L,T}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ (THz)	7.000	2.880	1.780	1.110	0.789[a]
Reference	1	2	3	4	13
C_{11} (GPa)	14.35	8.16	4.15	3.12	2.47
C_{12} (GPa)	12.08	6.79	3.40	2.62	2.06
C_{44} (GPa)	10.75	5.70	2.84	1.86	1.48
Reference	20	21	22	23	24
$\sigma_1(10^{-3}\,\mathrm{N\,m^{-1}})$	836	1125	587	359	338
$\tau_1(10^{-3}\,\mathrm{N\,m^{-1}})$	730	1257	673	453	435
$\sigma_2(10^{-3}\,\mathrm{N\,m^{-1}})$	−1635	458	81	41	144
$\lambda_2(10^{-3}\,\mathrm{N\,m^{-1}})$	855	98	137	166	86
$\sigma_3(10^{-3}\,\mathrm{N\,m^{-1}})$	195	3	33	31	16
$\lambda_3(10^{-3}\,\mathrm{N\,m^{-1}})$	−105	−10	−24	−32	−4
$C'(10^{-3}\,\mathrm{N\,m^{-1}})$	5035	269	571	711	401

[a]Homologous frequencies.

proximation[19] expressions were used for the screening function, $F(\eta)$.

The evaluation of seven GTF constants and C' that appear in the dynamical matrix elements is precluded by the homogeneity of some of their relations with the zone-boundary frequencies along the principal symmetry directions and the elastic constants.[16] This difficulty was overcome by neglecting one of the third nearest-neighbor GTF constants, τ_3, and the remaining seven force constants were evaluated uniquely, by making use of the experimental values of four zone-boundary frequencies and three elastic constants, which are given in Table I. Numerical values of the force constants so obtained in the case of lithium, sodium, potassium, rubidium, and cesium are also listed in this table.

III. RESULTS

The phonon frequencies of lithium, sodium, potassium, rubidium, and cesium have been calculated along the principal symmetry directions of the crystal using three different expressions for $F(\eta)$ in the evaluation of the force constants. The increase in the number of force constants and their homogeneous relations preclude the use of different sets of zone-boundary frequencies or elastic constants in their evalutation. Notwithstanding the influence of the screening functions on the numerical values of the force constants, no significant differences were found among the phonon frequencies deduced from these three sets of force constants. Besides, the neglect of either σ_3 or λ_3 (instead of τ_3) to circumvent the homogeneity of the force-constant relations had hardly any effect on the calculated phonon frequencies of alkali metals, provided no other relations are made use of in the evaluation of the rest. Hence, only the results obtained from the set shown in Table I are con-

sidered here. The dispersion curves obtained by plotting these phonon frequencies of lithium, sodium, potassium, rubidium, and cesium as a function of the reduced wave vector ζ along the principal symmetry directions are shown in Figs. 1, 2, and 3, respectively. The experimental frequencies of lithium,[1] sodium,[2] potassium,[3] and rubidium,[4] as well as the homologous frequencies of cesium,[13] are also plotted as a function of ζ in the respective figures to facilitate their comparison with the theoretical frequencies.

IV. DISCUSSION

It is obvious from Figs. 1, 2, and 3 that the Δ_5 branch of lithium crosses over Δ_1 at $\zeta \sim 0.48$ and then becomes degenerate with the latter at the zone-boundary point H, while the corresponding branches of sodium, potassium, rubidium, and cesium do not cross over at any wave vector before they degenerate at H. In addition, Λ_1 and Λ_3 branches of all alkali metals degenerate at the point P. Thus the present GTF model has succeeded in reproducing the crossover in lithium at a wave vector which is very nearly equal to its experimental value, without producing a similar crossover in any other alkali metal as well as the degeneracies at H and P, which are consistent with the translational symmetry of the lattice. Besides, the overall agreement between the experimental (or homologous) and theoretical phonon frequencies of alkali metals is extremely good, along all branches except Σ_3, the maximum discrepancy between the corresponding frequencies being $< 5\%$, which is of the same order as the uncertainties associated with these calculations. However, the neglect of the force constant τ_3, and the use of the smallest zone-boundary frequency $\nu_{T_1}(\frac{1}{2}\frac{1}{2}0)$, which is invariably associated with large experimental errors, in the evaluation of the force constants, are
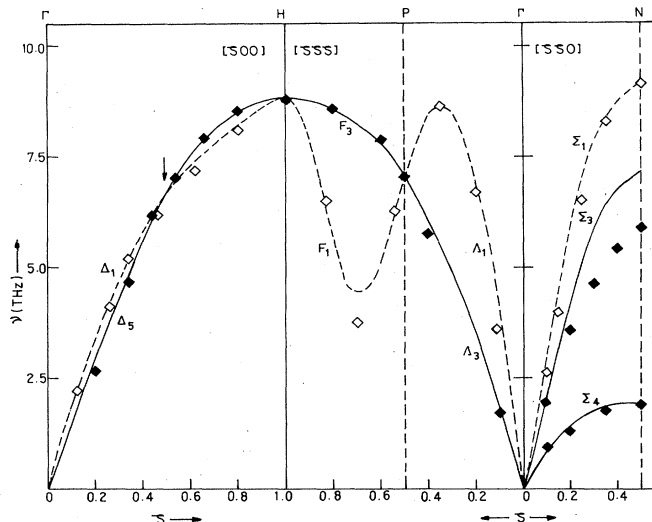
FIG 1. Dispersion curves of lithium along the principal symmetry directions. Theoretical frequencies: longitudinal (– – –), transverse (——); experimental frequencies (Ref. 1): longitudinal (◇), transverse (◆). The arrow indicates the wave vector $\zeta_c = 0.48$ at which Δ_1 and Δ_5 cross over.

FIG. 3. Dispersion curves of rubidium and cesium along the principal symmetry directions. Theoretical frequencies: rubidium (——), cesium (– – –); experimental frequencies: rubidium (Ref. 4) longitudinal (△), transverse (▲); homologous frequencies: cesium (Ref. 13) longitudinal (▽), transverse (▼).

solely responsible for the failure and success of the present model in reproducing the experimental phonon frequencies along Σ_3 and Σ_4 branches, respectively, in all alkali metals. It may be recalled, in this context, that no lattice-dynamical model has succeeded so far in deducing the exact phonon frequencies of alkali metals along these two branches, and hence very few models have, in fact, made use of these zone-boundary frequencies in their force-constant evaluation. Consequently, the lattice-dynamical results of the
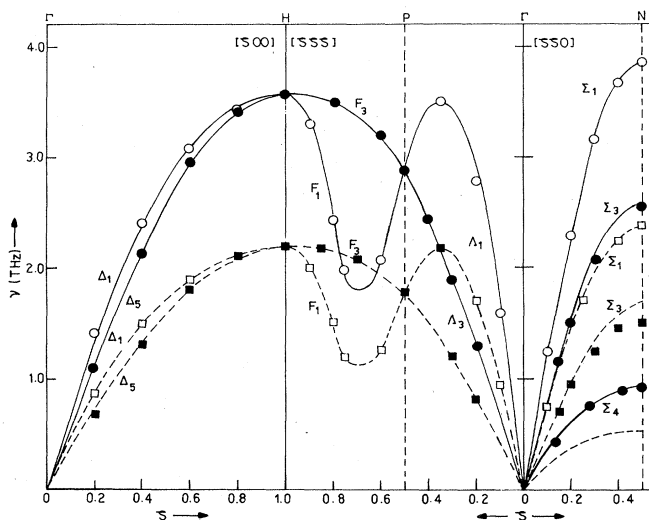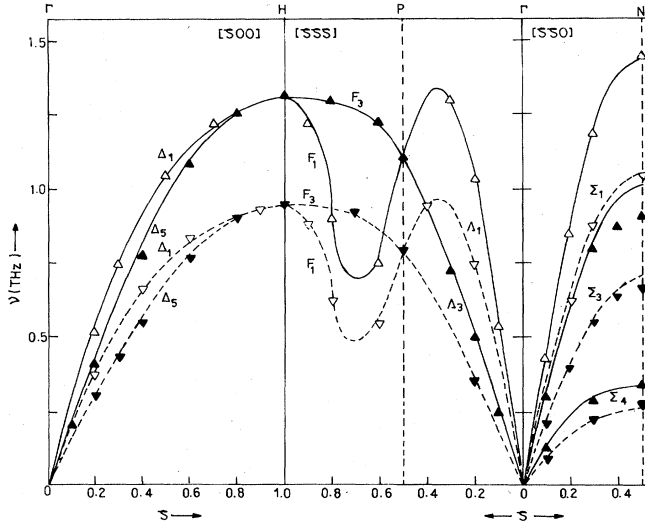

FIG. 2. Dispersion curves of sodium and potassium along the principal symmetry directions. Theoretical frequencies: sodium (——), potassium (– – –); experimental frequencies: sodium (Ref. 2) longitudinal (○), transverse (●), potassium (Ref. 3) longitudinal (□), transverse (■).

present unified study acquire considerable significance when compared with those of previous studies based on inadequate models and confined to two or three alkali metals.

The phenomenal success of the present GTF model in reproducing the experimental dispersion curves of alkali metals including the crossover in lithium at the correct wave vector, clearly establishes that there is hardly any variation in the nature or range of their atomic interactions, and thus supports the earlier conclusion that a high degree of homology exists among their phonon frequencies.[12] The numerical values of the force constants listed in Table I are consistent with this view. Nevertheless, the umklapp contributions to the volume forces which restore the translational symmetry to the GTF model play an important role in the success of the unified approach to the lattice dynamics of alkali metals. For example, it was shown in Ref. 9 that the umklapp contributions to the transverse modes (Δ_5) along [$\zeta 00$] direction increases faster with the wave vector, than the normal and umklapp contributions to the longitudinal modes (Δ_1). Further, it is obvious from Table I that the numerical values of C', which represent the strength of electron-ion interactions associated with sodium, potassium, rubidium, and cesium, are an order of magnitude smaller than that associated with lithium. This implies that the binding between the lattice and the electrons is weak in all alkali metals except lithium, especially because the p electrons are far more effective than the s electrons in screening out the nuclear charge. Smaller values of C' in turn give rise to smaller excess umklapp contributions to the transverse modes, which can never match the excess ion-ion contributions to the longitudinal modes at any wave vector in the range 0.0–1.0. As a consequence, Δ_5 and Δ_1 branches of these metals do not cross over at any wave vector. Besides, the weak electron-ion interactions have hardly any influence on the lattice dynamics of these alkali metals, and hence their dispersion curves are insensitive to the manner in

which the volume forces are incorporated in a model. It is precisely because of this reason that all force-constant models, including those which did not conform to the symmetry requirements of the lattice, could reproduce the experimental phonon frequencies of sodium and potassium.

On the contrary, the strong electron-ion interactions in lithium manifest themselves with a large positive value of C'. The excess umklapp contributions to the transverse modes become, respectively, equal to and greater than the excess ion-ion contributions to the longitudinal modes at and above some wave vector, ζ_c, and the Δ_5 branch crosses over the Δ_1 branch at that wave vector. It should therefore be obvious from the numerical values of C' that the phonon dispersion curves of lithium, and especially their crossover along [$\zeta 00$] direction, are highly sensitive to the manner in which the umklapp contributions are taken into account in the volume forces. Consequently, the neglect of umklapp contributions, which invariably destroys the translational symmetry,[5,8] their incorrect inclusion due to the evaluation of the interference factor over a sphere of equivalent volume,[6] or ignoring the volume forces altogether,[7] resulted in the failure of earlier models to reproduce the phonon dispersion curves of lithium. It follows from this discussion that the failure of a variety of lattice-dynamical models and the corresponding differences in the dispersion curves of alkali metals should be attributed to their intrinsic inadequacies rather than to any variation in the nature or range of atomic interactions. The present investigations have thus resolved the controversy regarding the latter by reproducing very accurately the experimental dispersion curves of all alkali metals. In addition, the unified approach has established that the observed crossover is not an anomalous property but a manifestation of strong electron-ion interactions in lithium, and hence the degree of homolo-

gy exhibited by the phonon frequencies of alkali metals is consistent with this view. Although the assumptions regarding the nature and range of the ion-ion interactions influence the numerical values of C' associated with any alkali metal, the passive role played by the former cannot be ascertained from these investigations.

In conclusion, the GTF model has reproduced very accurately the experimental phonon dispersion curves of lithium, including the crossover of the Δ_1 and Δ_5 branches, sodium, potassium, and rubidium, as well as the homologous phonon dispersion curves of cesium, by incorporating the volume forces which conform to the translational symmetry of the lattice. The dispersion curves of an alkali metal cross over when the excess ion-ion contributions to the longitudinal modes are compensated by the excess umklapp contributions to the transverse modes at some wave vector along [$\zeta 00$] direction. Since the latter increases with the strength of the electron-ion interactions, larger values of C' reproduce the observed crossover in lithium while the smaller values of C' suppress it in other alkali metals. Nevertheless, any variation in the nature and range of atomic interactions in alkali metals is not consistent with either the unequivocal success of this unified approach to their lattice dynamics or the degree of homology exhibited by their phonon frequencies.

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