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PHYSICAL REVIEW B VOLUME 3, NUMBER 12 15 JUNE 1971

Simple Shell-Model Calculation of Lattice Dynamics and Thermal Expansion of Alkali Halides[*]

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A six-parameter shell model which takes into account anion polarizability, noncentral nearest-neighbor interactions, central second-neighbor interactions, and the effective charge of the core and shell of the anion has been utilized for the determination of the lattice dynamics of LiF, NaCl, KCl, and RbI. The model parameters are determined from experimental data on the long-wavelength optical-mode phonon frequencies, the three elastic constants, and the high- and low-frequency dielectric constants. By the incorporation of the pressure derivatives of these quantities into the lattice-dynamical model, the individual-mode Grüneisen parameters and the temperature dependence of the thermal-expansion coefficient are calculated. Reasonable agreement is found between the calculated values and the available experimental data on these quantities.

I. INTRODUCTION

The first complete lattice-dynamical treatment of alkali halides was done by Kellermann[1] in 1940 for NaCl using a rigid-ion model with full formal ionic charge. Since then a large number of treatments have appeared on diatomic cubic crystals using more complicated models, viz., the shell model,[2-4] deformation-dipole model,[5] breathing-shell model,[6] and others.[7] Many of these models employ a large number of parameters obtained from a fit of extensive phonon-dispersion data measured by neutron-scattering techniques. The use of a large number of fitting parameters sometimes yields physically unrealistic values for some of the model parameters, thus reducing the lattice-dynamical treatment to a mere curve-fitting procedure. Such models are thus unsuitable for crystals for which extensive data on phonon dispersion do not exist. Furthermore, these models are not easily adaptable to the calculation of other thermodynamical properties, such as the thermal expansion, without invoking additional model parameters. For example, in some calculations of the coefficient of thermal expansion, additional anharmonic parameters had to be invoked,[8] which in turn were evaluated by fitting the thermal-expansion data, thus rendering the so-called agreement between calculated and experimental values relatively insignificant.

In the present work, a simple shell model is used in which all the model parameters are obtained without recourse to phonon-dispersion data. The model takes into account short-range first- and second-neighbor interactions and assumes the anion to

TABLE I. Elastic constants, infrared eigenfrequency, high- and low-frequency dielectric constants, and their pressure derivatives for a number of alkali halides.

	C_{11} (10^{11} dyn/cm^2)	C_{12} (10^{11} dyn/cm^2)	C_{44} (10^{11} dyn/cm^2)	ϵ_0	ϵ_∞	ω_{TO} (10^{13}/sec)
LiF	11.37	4.76	6.37	8.42	1.90	5.73
NaCl	4.90	1.26	1.27	5.91	2.31	3.09
KCl	4.05	0.70	0.63	4.68	2.13	2.71
RbI	2.58	0.37	0.28	4.69	2.63	1.42

	$\frac{dC_{11}}{dP}$	$\frac{dC_{12}}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{1}{\epsilon_0}\frac{d\epsilon_0}{dP}$ $\left(\frac{10^{-12}\text{ cm}^2}{\text{dyn}}\right)$	$\frac{B}{n}\frac{dn}{dP}$	γ_{TO}
LiF	9.92	2.72	1.38	−4.87	0.13	2.15
NaCl	11.71	2.06	0.37	−10.10	0.28	2.26
KCl	12.77	1.61	−0.39	−10.57	0.33	2.46
RbI	13.51	1.32	−0.50	−13.20	0.45	2.37

$n^2 = \epsilon_\infty$

be polarizable with effective core and the shell charges, and is used for studying the lattice dynamics of LiF, NaCl, KCl, and RbI. This model is essentially of the same form as the shell model used by Peckham[9] for MgO, with the exception that an effective ionic charge is employed rather than a full formal charge. Since the polarizability of the anion is much larger than that of the cation in the alkali halides studied here,[10] the latter is neglected in the calculation. This approximation is used here for the explicit purpose of keeping the number of model parameters relatively low. These were determined from the long-wavelength optic-mode frequencies, elastic constants, and high- and low-frequency dielectric constants. This model is also shown to be easily adaptable to the calculation of lattice dynamics of the crystal at higher hydrostatic pressures. Mode Grüneisen parameters, the macroscopic Grüneisen constant, and the coefficient of linear expansion can be calculated with the knowledge of only the pressure derivatives of the above-mentioned quantities at room temperature.

It may be emphasized here that the aim of the present work is not to present yet another lattice-dynamical model that claims a better agreement with experimental data on phonon dispersion, but to suitably adapt one of the existing models for the calculation of mode Grüneisen parameters and the other derived quantities, the parameters of which are obtained from such experimental data for which pressure derivatives are available.

II. SIMPLE SHELL MODEL

The calculations for the lattice dynamics are based on a shell model first proposed by Dick and Overhauser[2] and later elaborated by Woods *et al.*[3] and Cowley.[4] Under the adiabatic assumption, the equations of motion can be written as

TABLE II. Model parameters at normal pressure and high pressure.

	A $\left(10^3\frac{\text{dyn}}{\text{cm}}\right)$	B $\left(10^3\frac{\text{dyn}}{\text{cm}}\right)$	A'' $\left(10^3\frac{\text{dyn}}{\text{cm}}\right)$	K $\left(10^3\frac{\text{dyn}}{\text{cm}}\right)$	Y/Z	Z (in units of e)
			Normal pressure			
LiF	118.505	−14.096	3.521	427.427	1.384	1.030
NaCl	64.263	− 7.487	−3.708	238.981	1.801	1.117
KCl	48.607	− 4.734	−1.956	550.617	3.155	1.124
RbI	35.650	− 3.504	−2.819	189.579	2.594	1.078
			High pressure[a]			
LiF	118.740	−14.124	3.665	428.969	1.387	1.029
NaCl	64.767	− 7.535	−3.590	242.583	1.815	1.115
KCl	49.339	− 4.800	−1.891	559.409	3.180	1.122
RbI	37.419	− 3.635	−2.726	212.615	2.751	1.073

[a] High pressure is 1 kbar for all crystals except for RbI where it is 2 kbar.

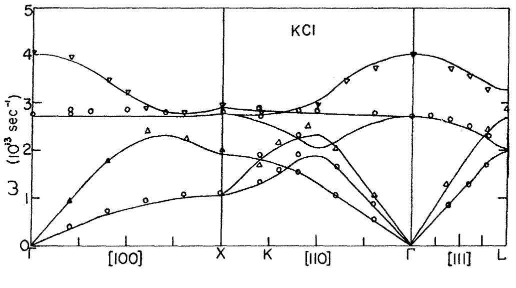

FIG. 1. Phonon dispersion in KCl. Experimental points are from Ref. 11.

$$-\underline{M}\cdot\omega^2\cdot\underline{u}=\underline{A}\cdot\underline{u}+\underline{B}\cdot\underline{w}\quad\text{and}\quad 0=\underline{B}^{\dagger}\cdot\underline{u}+\underline{D}\cdot\underline{w}; \tag{1}$$

$\underline{u}$ and $\underline{w}$ are the column matrices giving positions of the cores and displacements of the shells relative to the cores, respectively, and

$$\begin{aligned}\underline{A}&=\underline{R}+\underline{Z}\cdot\underline{C}\cdot\underline{Z}\ ,\\ \underline{B}&=\underline{T}+\underline{Z}\cdot\underline{C}\cdot\underline{Y}\ ,\\ \underline{D}&=\underline{S}+\underline{Y}\cdot\underline{C}\cdot\underline{Y}+\underline{K}\ ,\end{aligned} \tag{2}$$

where the matrices $\underline{R}$, $\underline{T}$, and $\underline{S}$ describe short-range core-core, core-shell, and shell-shell interactions and $\underline{C}$ describes the Coulomb coefficients. $\underline{Z}$, $\underline{Y}$, $\underline{K}$, and $\underline{M}$ are the diagonal matrices representing the effective ionic charge, the shell charge, the interaction of the core with its own shell, and the mass of the cores, respectively. Under the assumption that the short-range forces act through the shell,

$$\underline{R}=\underline{T}=\underline{S}$$

and the following secular equation results:

$$|\underline{M}\cdot\omega^2-\underline{A}-\underline{B}\cdot\underline{D}^{-1}\cdot\underline{B}^{\dagger}|=0\ . \tag{3}$$

Since $\underline{A}$, $\underline{B}$, and $\underline{D}$ are functions of the wave vector, the solution of this secular equation for different values of the wave vector in the first Brillouin zone gives the phonon dispersion.

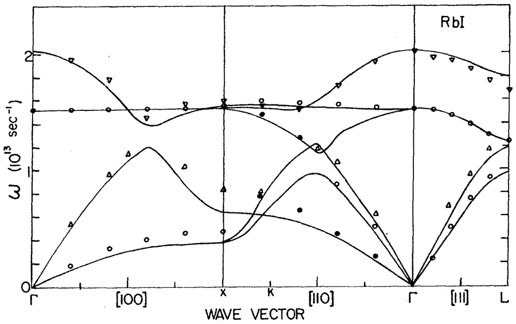

FIG. 2. Phonon dispersion in RbI. Experimental points are from G. Raunio and S. Rolandson [Phys. Status Solidi 40, 749 (1970)].

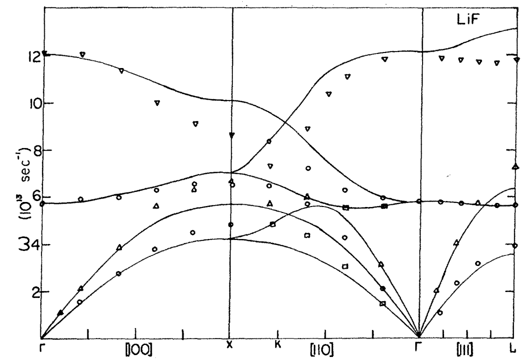

FIG. 3. Phonon dispersion in LiF. Experimental points are from G. Dolling, H. G. Smith, R. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson [Phys. Rev. 168, 974 (1968)].

In the alkali halides studied here, the polarizability of the positive ion is much smaller than that of the negative ion,^{10} hence the former is neglected. The first-neighbor forces are assumed to be noncentral which gives rise to two force constants A and B. The second-neighbor anion-anion interaction is assumed to be central, giving rise to one force constant A''. (Our central second-neighbor force-constant matrix differs from that of Peckham^9 which has two independent parameters.) Second-neighbor cation-cation interaction is neglected. In

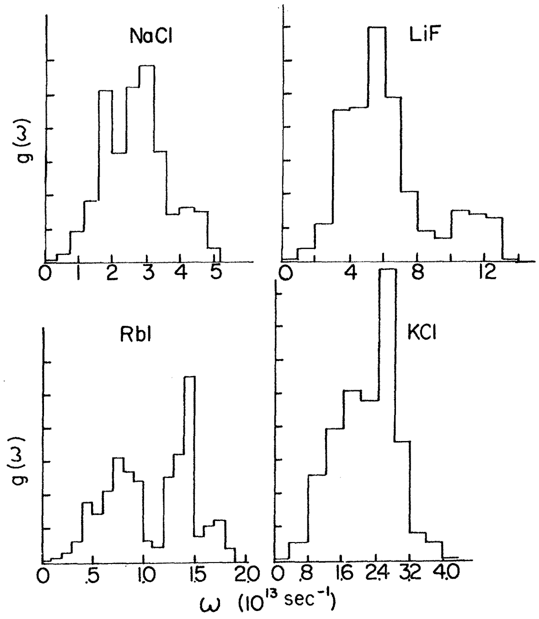

FIG. 4. Phonon density of states.

addition to these model parameters, one uses the core-shell interaction for the anion K, the shell charge for anion Y, and the effective ionic charge Z.

The model parameters are determined from the three elastic constants C_{11}, C_{12}, and C_{44}, the high- and low-frequency dielectric constants ϵ_∞ and ϵ_0, respectively, and the long-wavelength TO mode frequency ω_{TO} with the help of the following relations:

$$\begin{aligned} C_{11} &= (A + A'')/2a - 2.55604(eZ)^2/aV_a \,, \\ C_{12} &= (A'' - 2B)/4a + 0.11298(eZ)^2/aV_a \,, \\ C_{44} &= (A'' + 2B)/4a + 1.27802(eZ)^2/aV_a \,, \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} &= \frac{4\pi e^2}{3V_a} \frac{Y^2}{K + A + 2B} \,, \\ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} &= \frac{4\pi e^2}{3V_a}\left(\frac{Z^2}{A + 2B} + \frac{(Y + Z^2)}{K}\right) \,, \end{aligned} \tag{5}$$

and

$$\mu\omega_{\mathrm{TO}}^2 = \frac{(A + 2B)K}{K + A + 2B} - \frac{4\pi e^2[Z + (A + 2B)Y/(K + A + 2B)]^2}{3V_a} \frac{\epsilon_\infty + 2}{3} \,, \tag{6}$$

where a is the nearest-neighbor distance, μ is the reduced mass, and $V_a\,(= 2a^3)$ is the unit cell volume.

The experimental values of the input data and the calculated model parameters at atmospheric pressure are given in Tables I and II. The calculated phonon dispersion along the symmetry directions is presented in Figs. 1–3 for KCl, RbI, and LiF. The agreement for KCl is remarkably good in spite of the fact that experimental neutron data[11] were obtained at 115 °K, while the input data for the calculations were at 300 °K. For RbI and NaCl (not presented), results are moderately successful. Except for a slight discrepancy for the longitudinal and transverse acoustic branches near the X critical point, the over-all agreement may be regarded as good. By far the worst agreement was obtained for LiF. The longitudinal branches, in particular, show poor agreement. However, even for this case, considering the fact that all the model parameters were obtained from macroscopic data, the predicted phonon dispersion may be regarded as a reasonably approximate description. It is believed that the agreement between the calculated and the experimental phonon dispersion in a general direction, if such is available, would not be any worse than that shown in Fig. 3. For an elaborate shell model in which the model parameters are obtained by fitting neutron data in symmetry directions, the agreement is not necessarily guaranteed in the other directions. However, it is likely that a simple shell model, such as the one presented here, may predict the over-all phonon spectrum of a solid, albeit approximate, and may yield reasonable values for various derived thermodynamic properties.

Figure 4 shows the calculated phonon density of states for some representative alkali halides. The temperature dependence of the Debye characteristic temperature is shown in Fig. 5. The over-all agreement may be considered satisfactory. The results of an elaborate shell model for RbI are also shown in Fig. 5.

III. MODE GRÜNEISEN PARAMETERS AND THERMAL-EXPANSION COEFFICIENT

Since all the model parameters of the present simple shell model can be obtained from Eqs. (4)–(6) it is possible to calculate the lattice dynamics of a crystal as a function of pressure, provided the pressure dependence of the required input data is also available. The mode Grüneisen parameters

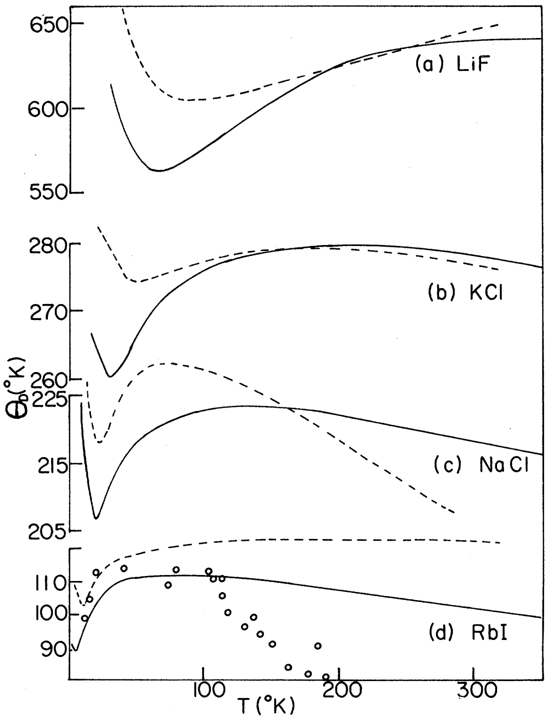

FIG. 5. Temperature dependence of Debye-characteristic temperature. Solid lines represent present calculations. Dashed lines in (a), (b), and (c) represent experimental data from W. T. Berg and J. A. Morrison [Proc. Roy. Soc. (London) A242, 467 (1957)] and K. Clusius, J. Goldman, and A. Perlick [Z. Naturforsch. 4a, 424 (1949)]. Dashed line in (d) represents calculations of Raunio and Rolandson [Phys. Status Solidi 40, 749 (1970)]. Circles represent experimental data from K. Clusius, J. Goldman, and A. Perlick [Z. Naturforsch. 4a, 424 (1949)].

then can be calculated for the normal modes using the relation

$$\gamma_i(\vec{k}) = -\frac{d\ln\omega_i(\vec{k})}{d\ln V} = \frac{B}{\omega_i(\vec{k})}\left(\frac{\partial\omega_i(\vec{k})}{\partial P}\right)_T , \tag{7}$$

where $\omega_i(\vec{k})$ is the frequency of the ith branch at a wave vector $\vec{k}$, and B is the isothermal bulk modulus of the crystal. Mode Grüneisen parameter can be obtained by calculating the mode frequencies at two different pressures, and assuming linear dependence.

The pressure dependence of the elastic constants[12] and the high- and low-frequency dielectric constants[13] are available for all the four alkali-halide crystals studied here. The pressure dependences of $\vec{k}=0$, ω_{TO}, LiF, KCl, and RbI are available from the infrared measurements.[14] No reliable experimental value of γ_{TO} is available for NaCl. It is calculated by assuming $(eZ)^2/V_a$ to be independent of pressure for this crystal. This corresponds to $\gamma_Z = -d\ln Z/d\ln V = -0.5$ Calculation of γ_{TO} under this assumption shows a good agreement with experiment for other alkali halides also. For NaCl under this assumption we obtained a value of 2.26 for γ_{TO}, which is in very good agreement with that calculated from a Born-Mayer–type potential.[15] The experimental values of the input data and the calculated values of the model parameters are also given in Tables I and II.

TABLE III. Transition pressures for NaCl to CsCl phase transition and $\gamma_{\mathrm{TA}}(X)$.

Material	$\gamma_{\mathrm{TA}}(X)$	Transition pressure (kbar)
LiF	1.62	∞ [a]
NaCl	0.19	300 [b]
KCl	−1.46	20 [c]
RbI	−2.52	4 [c]

[a] To date no transition pressure has been reported for LiF.

[b] W. B. Bassett, Taro Takahasi, Ho-kwang Mao, and J. S. Weaver, J. Appl. Phys. 39, 319 (1968).

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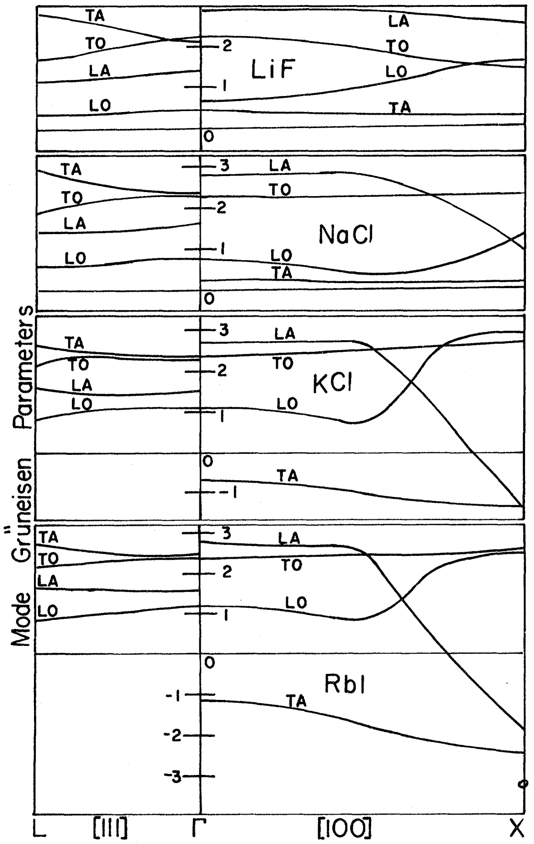

FIG. 6. Mode Grüneisen parameters. Circle on lower right-hand corner is experimental value of $\gamma_{\mathrm{TA}}(X)$ of RbI from Ref. 16.

The variation of the mode Grüneisen parameters with the wave vector along the [100] and [111] directions are presented in Fig. 6. The circle in the case of RbI represents an experimental measurement[16] of $\gamma_{\mathrm{TA}}(X)$. It may also be noted that while our work was underway, Barsch and Achar[17] have calculated the zone boundary γ_{TA}'s of certain crys-

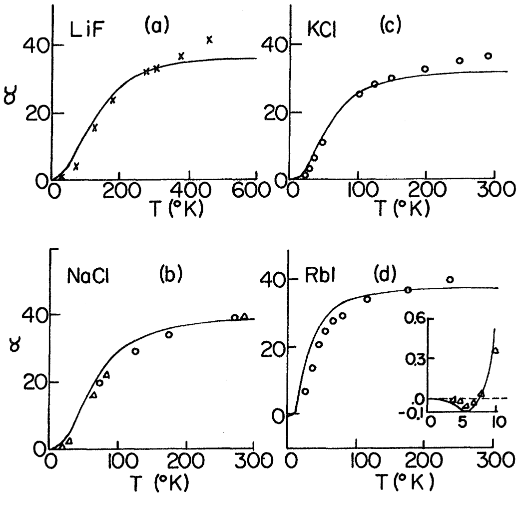

FIG. 7. Coefficient of linear thermal expansion as a function of temperature. Sources of experimental data are as follows: (a) *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1957), 4.73. (b) Circles, same as (a); triangles, G. K. White, Proc. Roy. Soc. (London) A286, 204 (1965). (c) P. P. Meinke and G. M. Graham, Can. J. Phys. 43, 1853 (1965). (d) Circles, D. E. Schuele and C. S. Smith, J. Phys. Chem. Solids 25, 801 (1964); triangles, G. K. White, Proc. Roy. Soc. (London) A286, 204 (1965).

tals in a similar manner. However, their treatment differs from ours in two significant ways: (i) They did not make use of the experimental pressure dependence of $\vec{k} \sim 0\gamma_{\mathrm{TO}}$; and (ii) they did not obtain ω_i or γ_i as a function of $\vec{k}$, nor did they derive the thermal expansion of the crystals from these results.

It is of interest to note that the present model predicts negative-mode Grüneisen parameters for some TA modes of KCl and RbI (Fig. 6). A negative γ_{TA} indicates a decrease in the stiffness of the lattice under compression, predicting a first-order transition.[18] It is well known that NaCl-type crystals undergo a pressure-induced phase transition to the CsCl structure. This fact is not obscured by the present model. In Table III, the mode Grüneisen parameter for the TA mode at the X critical point is compared with the transition pressure for the crystals under study. A perusal of the table indicates that a definite correlation between the softening of this particular mode and the transition pressure exists.

Under the framework of a quasiharmonic approximation, the thermal-expansion coefficient can be calculated as a function of temperature according to the relation

$$\alpha(T)=\sum_i C_i\gamma_i/3BV\,, \tag{8}$$

where C_i is the Einstein specific-heat function for ω_i, and V is the crystal volume. The sum extends to all normal modes. The calculations are compared with the experiment in the Fig. 7. The thermal-expansion coefficient is negative at low temperature for RbI. The present model predicts this behavior well. As may be seen from Eq. (8), it is chiefly the low-frequency mode $-\gamma_i$'s which contribute to the low-temperature Grüneisen constant, and hence to the thermal expansion, and tend to make the latter negative if the former are predominantly negative. The over-all agreement between the observed and calculated α is very good. Slight deviation at high temperatures is expected. At high temperatures, anharmonic effects neglected in the present calculations become significant. Some of this deviation may be compensated by using experimental values of C_v, the specific heat at constant volume in Eq. (8), instead of the calculated harmonic values. The agreement between the experimental and calculated values is particularly significant when one remembers that the thermal-expansion coefficient was calculated over a wide range of temperature only from the elastic constants, long-wavelength TO phonon frequency, high- and low-frequency dielectric constants, and their pressure dependence. It may be further emphasized that no fitting parameters were used.

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