DISPERSION OF PHONONS IN IDEAL CRYSTALS

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Summary

A quasiharmonic central force rigid-atom model has been used to study the lattice vibrations of frozen rare gases. The model takes care of interactions up to fourth neighbour and estimates zero-point energy and its volume derivatives by the Debye theory of specific heats. The theoretical frequency distribution and phonon dispersion curves are found to compare reasonably well with the available experimental data. Various causes of the discrepancies and possibilities of improvement of the results are discussed.

I. Introduction

A full knowledge of vibration spectra and dispersion relations of ideal crystals, such as frozen rare gases (Dobbs 1960), is necessary for the satisfactory development of rigorous lattice dynamics. Owing to the lack of direct experimental data for lattice vibrations of these solids, all previous workers in the field had to satisfy themselves with comparison of their theoretical results and observed thermal properties such as specific heat, thermal expansion, etc. However, these properties depend on averages over the entire distribution of phonon frequencies and give less detailed information than when individual frequencies are considered. No satisfactory information about the nature of interatomic forces could therefore be obtained from earlier studies.

Recently, Jones and Woodfine (1965) have determined frequency distribution curves of solid argon by a spectroscopic method, and Daniels *et al.* (1967) have obtained phonon dispersion curves for solid krypton in the three principal symmetry directions by inelastic neutron scattering. Now it can be hoped that comparison of theoretical and experimental results may lead to a better understanding of interatomic forces in these simple solids.

The dispersion relations for rare gas solids have been discussed by some authors: Grindley and Howard (1965) calculated dispersion curves (for argon and krypton) in harmonic approximation, Horton and Leech (1963) in quasiharmonic approximation (neon, argon, krypton, and xenon), and Brown and Horton (1967) and Wallace (1967) after including cubic and quartic terms in the potential energy. However, all these authors use empirical $(n, 6)$ inverse power potentials, the validity of which is doubtful and has been questioned by Kihara and Koba (1952), Barron (1960), Guggenheim and McGlashan (1960), Munn (1965), and Walkley (1965). On the other hand (exp, 6) potentials are considered more realistic and theoretically justifiable. Gupta and Dayal (1966a, 1966b, 1967a, 1967b) have studied the specific heat, thermal expansion, and isothermal compressibility of these solids with a quasiharmonic central force model using an exponential potential. The results have been

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found to be in fair agreement with experimental data. It is therefore thought desirable to make a fresh study of the lattice vibration and dispersion relations of all these solids with the same model and to see, by comparison of the results with the above observed data, whether the exponential potential is really suitable.

In the present paper, frequency distribution and dispersion curves of neon, argon, krypton, and xenon are computed in quasiharmonic approximation using the model and technique of calculation given earlier by Gupta and Dayal (1966a, 1966b). The theoretical results show reasonably good agreement with the available observed data.

II. Quasiharmonic Central Force Model

The model chosen for this study assumes short range central two-body forces derivable from a potential of the form

$$\phi(r) = -Ar^{-6} + AB \exp(-r/\rho),\tag{1}$$

where A, B, and ρ are its parameters. These are found by solving the equations

$$-L_0 = F_{qh}(0),\tag{2}$$

$$P_0 = -(\partial F_{qh}(0)/\partial V)_0,\tag{3}$$

$$\beta_0 = V_0^{-1}(\partial^2 F_{qh}(0)/\partial V^2)_0^{-1},\tag{4}$$

where the zero suffix indicates the value of the variable at 0°K.

The first equation (2) relates the lattice sublimation energy $-L_0$ to the quasi-harmonic Helmholtz free energy at absolute zero

$$F_{qh}(0) = E_{st} + \left(\sum_{i,K} 2kT \ln \sinh\{h(i, K)/2kT\}\right)_0,\tag{5}$$

where E_{st} is the static lattice energy and the summation is carried out over all the states of vibration K and all polarization i $(1, 2, 3)$. The static lattice energy is calculated in the usual way by summing the interaction of all pairs of atoms in the lattice as

$$E_{st} = \tfrac{1}{2}N \sum_{jj'} \phi(r_{jj'}),\tag{6}$$

with

$$\phi(r_{jj'}) = -Ar_{jj'}^{-6} + AB \exp(-r_{jj'}/\rho)$$

for the potential function (1). The second equation (3) equates the external pressure $(P_0 = 0)$ to the zero-point pressure P_z of the solid, which is the sum of its static pressure and pressure due to vibrations at 0°K,

$$P_z = \frac{hV_0}{\sqrt{2}\,Nr_0^3}\left(\sum_{i,K} \frac{\partial v(i, K)}{\partial V}\right)_0,\tag{7}$$

where $V_0 \; (= Nr_0^3/\sqrt{2})$ is the molar volume and the other symbols have their usual

meanings. The third equation (4) is the well-known thermodynamic relation between isothermal compressibility β, volume V, and pressure P of a solid, expressed in terms of quasiharmonic Helmholtz free energy $F_{qh}(0)$ at absolute zero.

The evaluation of zero-point energy E_z and its volume derivatives, occurring in equations (2)–(4), requires knowledge of the vibration spectrum, which itself is a function of the potential parameters to be determined. Therefore, they are estimated

TABLE 1

EXPERIMENTAL DATA AND COMPUTED QUASIHARMONIC PARAMETERS A, B, AND ρ FOR RARE GAS SOLIDS

Except where indicated, the values at 0°K of lattice constant α, compressibility β, sublimation energy L_0, zero-point energy E_z, Debye temperature θ, and Gruneisen parameter γ have been taken from Pollack's (1964) review

Solid	$\alpha \times 10^8$ (cm)	$\beta \times 10^{11}$ (cm² dyn⁻¹)	L_0 (cal mol⁻¹)	E_z (cal mol⁻¹)	θ (°K)	γ†	$A \times 10^{-58}$ (cm⁻⁶)	$B \times 10^{48}$ (cm⁻⁶)	$\rho \times 10^{-8}$ (cm)
Ne	4·462	10·00	448	154	66·60	3·22	0·13388	18·24467	0·31019
A	5·312	9·98	1846	187	83·66*	2·77	1·13529	32·64233	0·31553
Kr	5·644	3·99	2666	145	64·87*	2·51	2·42587	10·12222	0·36167
Xe	6·131	2·80	3828	123	55·00	2·87	4·71992	39·19334	0·33218

* Calculated using the data of Flubacher, Leadbetter, and Morrison (1961) and Beaumont, Chihara, and Morrison (1961).

† All γ values were read from the theoretical (γ, T) curves of Horton and Leech (1963).

by the Debye theory of specific heats (Gupta and Dayal 1966a, 1966b). Solution of these equations gives the following expressions for the parameters:

$$A = a - \frac{r_0^9 \, | \, 3\rho Y + (2\rho + r_0)X \, |}{\sqrt{2} \, S_1(r_0 - 7\rho)}, \tag{8}$$

$$B = b + \frac{3\sqrt{2} \, X \rho r_0^2}{S_2 A} \exp(r_0/\rho), \tag{9}$$

$$\rho = r_0 \left\{ \ln S_2 B - \ln\left(\frac{S_1}{r_0^6} - \frac{2(L_0 + E_z)}{NA}\right) \right\}^{-1}, \tag{10}$$

where

$$a = \frac{3 r_0^9 \, \rho}{\sqrt{2} \, S_1(r_0 - 7\rho)\beta_0} \qquad \text{and} \qquad b = \frac{6 S_1 \rho}{S_2 r_0^7} \exp(r_0/\rho), \tag{11}$$

with $r_0 = a_0/\sqrt{2}$, a_0 being the lattice constant of a face-centred cubic crystal. The quantities X and Y are defined as

$$X = -(9k\gamma_0/4\sqrt{2} \, r_0^3)\theta_0 \qquad \text{and} \qquad Y = -X(1 + \gamma_0), \tag{12}$$

while S_1 and S_2 are crystal potential constants occurring in the static lattice energy expression

$$E_{st} = \tfrac{1}{2} N (-S_1 A r_{jj'}^{-6} + S_2 AB \exp(-r_{jj'}/\rho))_{r=r_0}, \tag{13}$$

and are defined as

$$S_1 = \sum_m M_m(\sqrt{m})^{-6} \qquad \text{and} \qquad S_2 = \sum_m \exp\{-r_0(\sqrt{m}-1)/\rho\}, \qquad (14)$$

where M_m is the number of the mth neighbours and the summation is carried out over the entire crystal. The expressions for A and B contain ρ and that of ρ contains A and B explicitly, and therefore these cannot be evaluated independently. An iteration method (Gupta and Dayal 1966a, 1966b) has been used for the evaluation of the parameters. The experimental data used and the parameters computed are given in Table 1.

III. Phonon Spectra and Dispersion Curves

Proceeding in the usual way the secular equation for the determination of the phonon frequencies ν may be written in the form

$$\left| \mathbf{M}\binom{K}{kk} - 4m\pi^2\nu^2\mathbf{I} \right| = 0, \qquad (15)$$

where $\mathbf{M}$ is the dynamical matrix, $\mathbf{I}$ the unit matrix of order three, and m is the mass of atoms constituting the monatomic lattice. The elements $M_{jj'}\binom{K}{kk}$ of the dynamical matrix may be expressed as the sum of l coupling coefficients $A_{jj'}^l$, which are defined

$$A_{jj'}^l = \phi''_{jj'}^l(1 - \exp 2\pi i \mathbf{K} . \mathbf{r}^l), \qquad (16)$$

where $\phi''_{jj'}^l$, is the second partial derivative with respect to (x, y, z) of the potential ϕ^l between an atom and its lth neighbour, and $\mathbf{K}$ and $\mathbf{r}^l$ are respectively the phonon wave vector and the position vector of the point. The force constants of second and higher neighbours bear signs opposite to that of the first. Their magnitudes also decrease very rapidly as one goes over to the higher neighbours. At distances of the neighbours higher than the fourth, the magnitudes become much less to 1% of those of the nearest neighbours. The present work, therefore, takes $l = 1, 2, 3,$ and 4 and ignores the contributions of higher neighbours.

To keep the labour of computation within reasonable limits and to avoid too much approximation, the phase space of the first Brillouin zone is divided into $10 \times 10 \times 10$ equal parts. In accordance with Born's cyclic boundary condition and symmetry considerations of the zone it is only necessary to solve the secular equation (15) for 48 non-equivalent points lying within 1/48 part of the whole zone. These with associated proper statistical weights are equivalent to 1000 phase points and yield 3000 frequencies.

The frequency spectra are found to range up to 2×10^{12} sec^{-1} only. Histograms are therefore prepared with interval length $\Delta\nu = 0 \cdot 1 \times 10^{12}$ sec^{-1}. The function $g(\nu)$ giving the total number of frequencies in the interval $\nu - \frac{1}{2}\Delta\nu$ to $\nu + \frac{1}{2}\Delta\nu$ is determined from these histograms. In each case curves of the frequency distribution function $g(\nu)$ versus ν have been drawn and are shown in Figure 1. This is done in such a manner that the areas under the curves are equal to the areas under the histograms. The small fluctuations in the curves have also been smoothed out, as

they give no indication of any real effect in the simple solids. The curves have not been normalized and the units of $g(\nu)$ are arbitrary. The phonon dispersion $(\nu(q), q)$ curves (Fig. 2) in the directions [100], [110], and [111] are drawn by selecting frequencies corresponding to the points $(Q, 0, 0)$, $(Q, Q, 0)$ and (Q, Q, Q). q is a reduced wave vector and is expressed as $q = aK$, where K is a phonon wave vector. The dispersion curves for krypton (Fig. 2(c)) are compared with experimental values of Daniels et al. (1967). Such data for the other rare gases are not available at present.
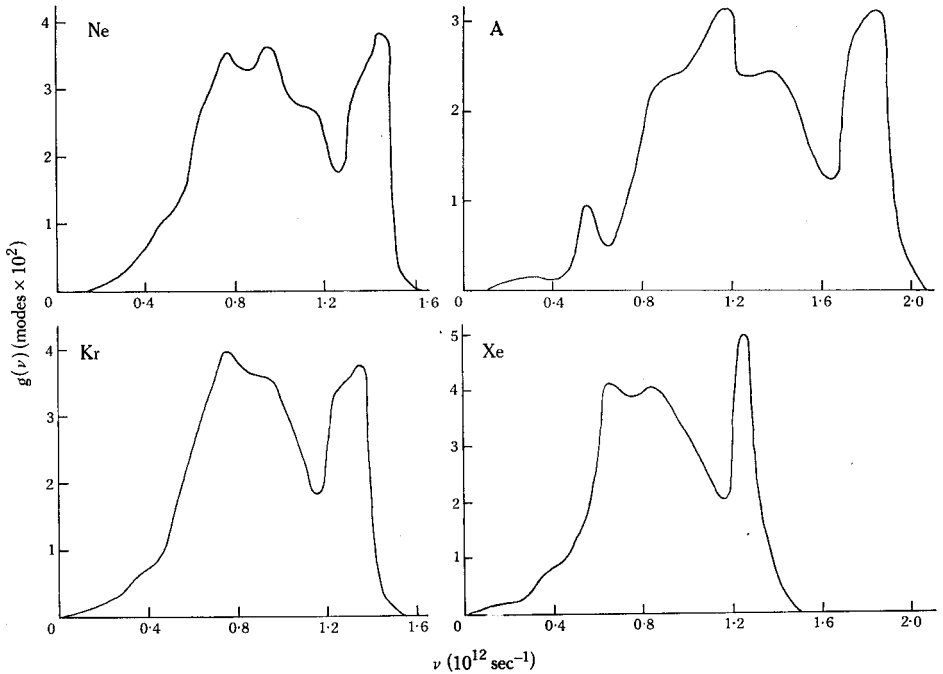

Fig. 1.—Frequency distribution curves for solid neon, argon, krypton, and xenon at 0°K.

IV. DISCUSSION OF RESULTS

The curves of the frequency distribution function $g(\nu)$ versus ν for these solids (Fig. 1) show a number of peaks. By smoothing the closer ones these may easily be reduced to two, the broader maximum lying in the middle and the sharper peak lying towards the higher end of the spectrum. The peak corresponding to higher frequency would be a little higher than the hump. The shapes of the curves are not surprising if one considers the fact that anisotropy in these solids is not very large, with the result that the maxima of two transverse branches are not far apart and thus give rise to a hump in frequency distribution curves at lower frequencies. Moreover, it is a characteristic feature (Born and Huang 1956) of the frequency distributions for monatomic cubic lattices that these have two maxima, one near about $\frac{1}{2}\nu_L$ and the other close to the upper frequency limit ν_L. The frequency distribution curves therefore show a good agreement with theory. All these curves are also very similar
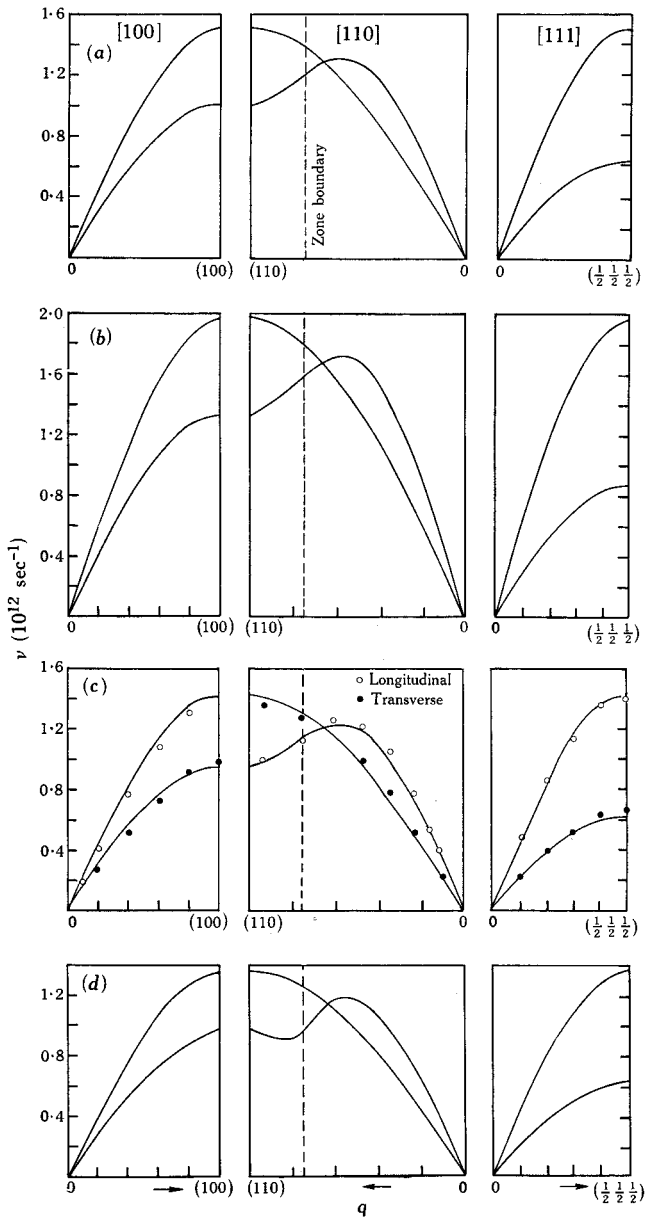
Fig. 2.—Phonon dispersion curves for (*a*) solid neon at 0°K, (*b*) solid argon at 0°K, (*c*) solid krypton at 0°K, and (*d*) solid xenon at 0°K in the [100], [110], and [111] directions. In (*c*) are also shown experimental points for longitudinal and transverse modes at 79°K and 300 atm from Daniels *et al.* (1967).

to the histogram calculated for argon by Grindley and Howard (1965) based on a sample of 108 000 points in the Brillouin zone and using a (12, 6) potential, and by Hartmann and Elliott (1967) from a nearest neighbour shell model for 12 000 points in the reciprocal space. Positions of humps, peaks, and cutoff frequencies ν_L for argon are shown in Table 2, along with those calculated with different models at 0°K for comparison. It is seen that agreement is satisfactory.

Jones and Woodfine (1965) investigated the absorption spectrum of solid argon at 55°K and 80°K respectively with 0·5% xenon and 1·0% krypton as uncharged impurities. The experimental curves do show both hump and peak in the appropriate region of the phonon frequencies but there are long tails well above the cutoff frequency ν_L. The two distribution curves differ regarding structural details as well as the position of the high frequency peak (Table 2). At the lower temperature

TABLE 2

POSITIONS OF HUMP, PEAK, AND CUTOFF FREQUENCY ν_L IN THE FREQUENCY DISTRIBUTION CURVES OF SOLID ARGON

Feature	Present Work* $(10^{-8}$ cm$)$	Grindley and Howard (1965)† $(10^{-8}$ cm$)$	Hartmann and Elliott (1967)‡ $(10^{-8}$ cm$)$	Jones and Woodfine (1965)§ $(10^{-8}$ cm$)$	
				a	b
Hump	1·20	1·39	1·32	1·26	0·81
Peak	1·84	1·92	1·86	1·92	1·86
ν_L	2·07	2·07	2·04	Long tail	Long tail

* Quasiharmonic central force rigid-atom model.
† Harmonic central force model.
‡ Simple shell model of polarizable defects.
§ Experimental results with (a) 0·5% xenon at 55°K and (b) 1·0% krypton at 80°K.

the frequency distribution curve shows more detailed structure, while at high temperature the high peak shifts to the lower frequency side and the tail above ν_L increases. Recent theoretical studies by Hartmann and Elliott (1967) and Martin (1967) indicate that impurities will shift the peaks. The experimental tails must be due to anharmonic effects, which certainly should be important near the melting point where the measurement on argon with krypton as impurity is made. It is therefore unreasonable to make a comparison of the quasiharmonic frequency distribution curve of pure argon at 0°K with the experimental curve obtained with an impure specimen and at temperatures different from zero. However, a crude comparison of our theoretical curves and the experimental results for argon (with krypton as impurity) obtained at 55°K lends some support to our model.

The phonon dispersion curves (Fig. 2), which we have plotted in the principal symmetry directions for all these solids at 0°K and zero atmospheric pressure, are rather similar to each other and show the following features. The two transverse branches in [100] and [111] directions are degenerate. At the point $(1, 1, 0)$, which is equivalent to the $(0, 0, 1)$ point, the [110] L branch is degenerate with the [001] T_1 branch and the [110] T_2 is degenerate with [001] L. All these characteristics are

common to face-centred cubic solids (Dolling and Woods 1965). Horton and Leech (1963) have also calculated such dispersion curves with reduced $(n, 6)$ potentials in quasiharmonic approximation. These curves are very similar to ours. The effect of inclusion of higher neighbour interaction over the force constant of the first neighbour is to reduce its magnitude (Section III) and to decrease the frequency of lattice vibration. Therefore, if the range of interaction had been restricted to the nearest neighbour only instead of fourth neighbours, the dispersion curves would have moved a little upwards keeping their lower ends fixed at $q = 0$ in all three directions. Recently, Daniels et al. (1967) have measured phonon dispersion relations on a single crystal of f.c.c. krypton for the symmetric [100], [110], and [111] branches by triple axis neutron spectrometry at 79°K and 300 atm pressure. Some experimental points taken from these curves are shown in Figure 2(c). Obviously, the shapes of the experimental curves in all three directions are similar to ours. The agreement between the theoretical and observed curves (Fig. 2(c)) is also not unreasonable. However, no comments can be made at this stage about the suitability of the model owing to different conditions of temperature and pressure and the error margin accompanying the observed data (Daniels et al. 1967).

V. Conclusions

The present study together with earlier work (Gupta and Dayal 1966a, 1966b, 1967a, 1967b) shows that it is reasonable to derive the central, short range, pairwise additive forces between closed shell atoms constituting the ideal (rare gas) solids from an (exp, 6) potential. The lower values of Debye functions θ also suggest that the model needs modification in a way that would include some interaction to enhance their values at all temperatures. As well as this, the model would be further improved by taking into account the contributions of cubic and quartic terms of the potential energy expansion. Availability of inelastic neutron scattering results over a wide range of temperatures and volumes and improved data of zero-point properties would certainly be helpful for further understanding of the nature of interatomic forces in simple solids.

VI. Acknowledgment

VII. References

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