

# DISPERSION OF PHONON WAVES IN MOLECULAR RARE-GAS SOLIDS

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Phonon dispersion relations for molecular rare-gas solids have been computed by a central-force rigid atom model. The model derives the intermolecular interaction from the Buckingham-Corner potential together with the Axilrod-Teller three-body term. It includes zero-point vibrations through potential parameters by a self-consistent method, and accounts for the contribution of cubic and quartic anharmonic potential terms as perturbation to the harmonic Hamiltonian. The effects of the three-body forces and the anharmonicity on the dispersion of phonon waves in the molecular rare-gas solids have been studied. It is seen that both the three-body forces and the anharmonicity increase the slopes of the dispersion curves in all the directions. The results are in reasonably good agreement with the latest observed data.

## INTRODUCTION

LOOKING at the nature and the behaviour of the mutual interaction of the spherical atoms constituting the molecular rare-gas solids ((Boato, 1964) mostly two-body central potentials (Horton, 1968; and Klein & Venables, 1976) have been proposed. However, the studies of the lattice stability (Jansen, 1974; and Huller, 1971), Cauchy discrepancy (Zucker & Chell, 1968; Huller, 1971) and vibrational properties (Barker *et al.*, 1971; Lurie & Skalyo Jr., 1974; and Zubov, 1974), have indicated that the lattice summation of a central 'two-body' potential is not an accurate representation of the many-body problem in the present case; and there may, in fact, be some contribution due to the non-central 'many-body' interactions. But such many-body effects have usually been omitted on the ground that due to the high stability of the closed shell electronic configuration, these contributions can at most be of high perturbation order (Margenau, 1939) or that they can play a significant role only at very small distances.

In view of the situation, it is expected that a more suitable model for the study of molecular rare-gas solids will be the one which uses a 'correct' two-body potential function and proper contribution of the many-body forces along with the usual considerations of zero-point quantum and anharmonic effects.

## INTERACTION POTENTIAL

The choice of the form of interaction potential has always been a serious hurdle in rightly predicting the observed vibrational properties of MRGS. Some workers (Jansen, 1964; and Huller, 1971) have used one piece power/exponential pair-potentials with two/three parameters. Investigations of the absorption spectra of diatomic argon by Tanaka and Yoshino (1970) and measurements of differential scattering cross-

sections of molecular argon by Parson *et al.* (1972) and Cavallini *et al.* (1970) have confirmed that heuristic LJ-potentials do not correctly describe the pair-interaction in solid argon. The use of only a two/three parameter potential function to describe the complicated potential curve over the total intermolecular separation seems unjust. The multiparameter series potentials used by Barker *et al.* (1971) have provided moderately better results after including the Axilrod-Teller (1949, 1951) type three-body forces. Recently, Zubov (1974) and Gewurtz and Stoicheff (1974) have concluded that these series pair-potentials are no better than even the heuristic LJ-potentials. It may be due to the reason that though these analytical potentials contain more than two/three parameters, yet all are single-piece potential functions. Obviously, it is too much to expect from a single piece potential function to describe the two halves of a potential curve on either side of the potential minimum. Guggenheim and McGlashan (1960) are also of the view that any inter-atomic potential cannot be represented adequately over the whole range of interparticle separation by a two/three parameter and one-piece potential function.

Buckingham and Corner (1947) have proposed a two-piece potential function;

$$\phi(r) = \epsilon [g_1(\alpha, \beta) \exp \alpha (1 - (r/r_m)) - g_2(\alpha, \beta) (r_m/r)^6 \{1 + \beta (r_m/r)^2\}], \text{ for } r \geq r_m,$$

and

$$\phi(r) = \epsilon [g_1(\alpha, \beta) \exp \alpha (1 - (r/r_m)) - g_2(\alpha, \beta) (r_m/r)^6 \{1 + \beta (r_m/r)^2\} \cdot \exp 4 (1 - (r/r_m))^3], \text{ for } r \leq r_m, \dots (1)$$

where

$$g_1(\alpha, \beta) = (6 + 8\beta) [\alpha (1 + \beta) - (6 + 8\beta)]^{-1},$$

$$g_2(\alpha, \beta) = \alpha [\alpha (1 + \beta) - (6 + 8\beta)]^{-1},$$

which is theoretically sound and physically consistent in the sense that it contains both attractive as well as repulsive terms throughout in conformity with quantum mechanical calculations (Born & Mayer, 1932). The parameters  $\epsilon$  and  $r_m$  are respectively the depth of the potential well and separation of atoms at the minimum of  $\phi(r)$ . The parameter  $\alpha$  is a measure of the steepness of the exponential repulsion, and  $\beta$  is dimensionless ratio of the coefficients of dipole-quadrupole ( $r^{-8}$ ) and dipole-dipole ( $r^{-6}$ ) van der Waals attraction terms. The change in the function  $\phi$  in passing through  $r = r_m$  is only a discontinuity in the third and higher derivatives and is introduced for convenience to prevent  $\phi$  from becoming infinite as  $r$  tends to zero. The potential also resembles the potentials proposed by Barker and coworkers (1971) in the sense that it is also a multiparameter potential and contains the multipole interaction term in the van der Waals attraction. However, unlike their potentials, it includes the dipole-quadrupole term only, which is equivalent to the rapidly converging multipole series existing there. Thus it contains all the peculiarities of these analytical potentials, in addition to it being a two-piece potential and as such can describe the whole potential curve in a more satisfactory manner. The potential has not been used so far for the

study of lattice vibrations in the solids under consideration. It is, therefore, thought desirable to make a fresh study of MRGS on the basis of this potential function and using the well-known perturbation theory.

### THEORY

The MRGS are assumed to consist of hard-spherical rare-gas atoms executing vibratory motion at 'fcc' lattice sites. The potential energy, being dependent on the positions of the atoms in the lattice, is assumed as

$$\Phi = \Phi(r) + \Phi(r, \theta), \quad \dots (2)$$

where  $\Phi(r)$  is the sum over a central two-body potential and  $\Phi(r, \theta)$  is the lattice summation of angle-dependent non-central many-body potential. Arguments have been given both for (Copeland & Kestner, 1968) and against (Klein *et al.*, 1969) neglecting the terms beyond the triplet. However, Copeland and Kestner's suggestion in favour of neglecting the quadruplet and higher contributions is sound enough, as they explicitly show that these terms are insignificant in comparison to the triplet one. As such the non-central potential may almost be represented by the three-body potential, and the total potential energy may now be written as

$$\Phi = \sum_{ij} \phi(r)_{ij} + \sum_{ijk} \phi(r, \theta)_{ijk}, \quad \dots (3)$$

where  $\phi(r, \theta)_{ijk}$  vanishes when one of the atoms  $i, j, k$  is remote from the other two.

Following the Born-von Karman formalism, and proceeding as usual, the following secular equation is obtained

$$\det [D_{\alpha\beta}(kk'; K) - \omega^2 \delta_{\alpha\beta} \delta_{kk'}] = 0, \quad \dots (4)$$

with dynamical matrix

$$D_{\alpha\beta}(kk'; K) = (m_k m_{k'})^{1/2} \sum_{l'} \phi_{\alpha\beta}(lk; l'k') \exp i \cdot [2\pi K \cdot R(lk; l'k')],$$

where  $R(lk; l'k')$  is the equilibrium vector separation of atoms lying in the  $l$ th and  $l'$ th unit cells. The force constants  $\phi_{\alpha\beta}(lk; l'k')$  may be determined by using any suitable potential (eqn. 3).

The contribution of the cubic and quartic anharmonic terms is included in the potential through the potential parameters, using the perturbation theory (Klein *et al.*, 1969; and Maradudin *et al.*, 1961). For this purpose, the expression of the potential energy

$$\Phi = \Phi_0 + \Phi_2 + \Phi_3 + \Phi_4, \quad \dots (5)$$

truncated at the fourth order is used, instead of that terminated at the second order corresponding to the quasiharmonic approximation. As such the expression for the free-energy may be expressed in the form

$$F = F_0 + F_2 + F_3 + \dots (6)$$

Here,  $F_3$  and  $F_4$  are the cubic and quartic contributions to the quasiharmonic free energy  $F_{qh}$  ( $= F_0 + F_2$ ), which is expressed as

$$F_{qh} = E_{st} + k_B T \sum_{Kj} \ln (2 \operatorname{Sinh} (\hbar w(Kj)/2kT_B)) \quad \dots (7)$$

where  $E_{st}$  is the static lattice energy and other symbols have their usual meanings. According to Flinn and Maradudin (1968) for a 'fcc' lattice with nearest neighbour central force interaction, the cubic and quartic contributions to the free energy at  $0^\circ K$  are given by

$$F_3(0) = - \frac{E_z^2}{48N} \cdot \frac{1.481}{(16(1.0227)^2)} \cdot \frac{[\phi''''(r_0)]^2}{[\phi''(r_0)]^3} \quad \dots (8)$$

and

$$F_4(0) = \frac{E_z^2}{48N} \cdot \frac{\phi''^V(r_0)}{\phi''(r_0)^2}$$

In these expressions  $\phi''(r_0)$ ,  $\phi''''(r_0)$  and  $\phi''^V(r_0)$ , represent respectively the second, third, and fourth derivatives of the total potential energy (eqn. 3), and evaluated for nearest neighbour distance  $r_0$  at  $0^\circ K$ .  $E_z$  is the zero-point energy per mole of the solid, and other symbols have their usual meanings.

#### NUMERICAL COMPUTATION

For the computation of the eigen frequency spectra, we make use of the BC-potential function (1), the three parameters ( $\alpha$ ,  $r_m$ , and  $\epsilon$ ) of which are evaluated by solving the following equilibrium equations :

$$\begin{aligned} L_0 &= -F_{qh}(0), \\ P_0 &= -(F_{qh}(0)/V)_0, \\ \text{and } X_0 &= V_0 (\sigma^2 F_{qh}(0)/V^2)_0. \end{aligned} \quad \dots (9)$$

Here the subscript '0' refers to the value of the corresponding variable at  $0^\circ K$ , and  $V$  is the molar volume. The symbols  $L$ ,  $P$ , and  $X$  denote respectively the sublimation energy, pressure, and bulk modulus of the solid. The expressions of the quasiharmonic parameters  $\alpha$ ,  $r_m$ , and  $\epsilon$  so obtained contain the dimensionless parameter  $\beta$ , given (Margenau, 1939) as

$$\beta = e^2/Ah \nu_c$$

with  $\nu_c = \frac{e}{2\pi} (f/AM)^{1/2}$ ,  $\dots (10)$

where  $A$  and  $\nu_c$  are respectively the polarizability and classical frequency of the atoms constituting the lattice. Symbols  $e$ ,  $M$ , and  $f$  indicate respectively charge, mass, and number of electrons in the atom, and  $h$  is the well-known Planck's constant.

A. *Three-body forces* — In order to include the effect of three-body forces (TBF) in these quasiharmonic parameters, precisely the same method is followed, except that in place of using only the two-body interaction energy  $\Phi(r)$ , the total potential energy (eqn. 2) has been used for the computation, where the three-body interaction energy  $\Phi(r, \theta)$  is replaced by the Axilrod-Teller (1949, 1951) (AT) expression

$$\Phi_{AT}(r, \theta)_{ijk} = \Omega \sum_{ijk} [(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k) / (R_{ij}^3 R_{jk}^3 R_{ki}^3)] \quad \dots \quad (11)$$

Here the summation is over the entire crystal;  $\theta_i$ ,  $\theta_j$  and  $\theta_k$  are the interior angles of the dipolar triangle with sides  $R_{ij}$ ,  $R_{jk}$  and  $R_{ki}$ , and  $\Omega = (9/16) IA^2$  is the triplet interaction coefficient depending upon the ionization energy ( $I$ ) and polarizability ( $A$ ) of the interacting atoms. The AT-term (eqn. 11) represents merely the long-range part of the three-body-potential. The short-range part (Jansen, 1964) of this potential, which is almost identical in nature (repulsive) and form to that of the long-range one, has rather doubtful validity (Swenberg, 1967) and as such is not taken into account.

Triple-dipole interaction energy has been computed, following Axilrod (1951), by taking one atom as origin and choosing various pairs from the rest of the atoms in the lattice to form all possible atomic triplets. The triangles are counted within a distance of  $r_0\sqrt{15}$  only from the origin, because while summing over a larger portion of the lattice the magnitude of three-body interaction energy decreases with the ninth power of the radius of the region of the summation and as such becomes negligible. The magnitude of the three-body interaction energy thus computed is given in Table I, together with the values of the constant  $\Omega$  used in the calculation. The values of the constant  $\Omega$  for neon and xenon have been taken from the paper of Chell and Zucker (1968) for argon from Fischer and Watts (1972), and for krypton from Bobetic *et al.* (1972). Axilrod (1951), Chell and Zucker (1968) and Doran and Zucker (1971) have calculated  $\Phi(r, \theta)$  for fcc lattice using four, ten, and six neighbour interactions respectively. These values have also been cited in Table I for comparison.

B. *Anharmonic Correction* — The quasiharmonic parameters as determined above are used to find out the cubic and quartic contributions  $F_3(0)$  and  $F_4(0)$ , to the free energy at 0 °K. After introducing these anharmonic corrections in the equilibrium

TABLE I  
*Interaction energies of triplet of atoms in 'fcc' lattice*

Solid	$\Omega$ (erg(A) <sup>9</sup> 10 <sup>12</sup> )	$\phi$ (3-body)			
		The present Authors'	Axilrod	Chell and Zucker(1968)	Doran and Zucker (1971)
Neon	1.677	14.669	8.90	14.68	14.85
Argon	73.20	133.50	92.85	136.60	138.00
Krypton	220.40	232.65	227.76	236.90	239.04
Xenon	749.00	377.32	333.57	376.00	380.45

conditions (eqns. 9) of the lattice, approximate anharmonic parameters  $\epsilon$  and  $r_m$  to the first order are obtained. In this way, by successive approximation, self-consistent values of the parameters have been determined. To reduce the computer time, the dimensionless steepness parameter  $\alpha$  is not recalculated after making the anharmonic corrections. The zero-point energy and its derivatives occurring in equations describing the equilibrium of the lattice have been evaluated using the Debye's theory of specific heats. The computation takes care of all neighbour interactions and uses the crystal data as shown in Table II.

The lattice constant for neon has been taken from the paper of Batchelder *et al.* (1967), for argon from Peterson *et al.* (1966), for krypton from Losee and Simmons (1968) and for xenon from Sears and Klug (1962). Bulk modulus for all the MRGS have been derived from the values of isothermal compressibilities observed by Urvas *et al.* (1967). Sublimation energy and zero-point energy have been taken from the review article of Pollack (1968). The Debye characteristic temperatures have been taken from the work of Fenichel and Sarin (1966). Gruneisen parameters for all the solids have been taken from the theoretical curves of Horton and Leech (1963). The

TABLE II

*Lattice constant (a), bulk modulus ( $X_0$ ), sublimation energy ( $L_0$ ), zero-point energy ( $E_z$ ), Debye temperature ( $\theta_D$ ), Gruneisen parameter ( $\gamma_0$ ), atomic polarizability (A) and classical frequency ( $\nu_c$ ) for molecular rare-gas solids at 0 K.*

Solid	$a \times 10^8$ (cm)	$X_0 \times 10^{-10}$ (dyne/ cm <sup>2</sup> )	$L_0$ (Cal/ mol)	$E_z$ (Cal/ mol)	$\theta_D$ (K)	$\gamma_0$	$A \times 10^{24}$ (cm <sup>3</sup> )	$h\nu_c$ (eV)
Neon	4.4637	1.12	448	154	74.6	3.22	0.39	25.7
Argon	5.3111	2.67	1846	187	93.1	3.10	1.63	17.5
Krypton	5.6459	3.44	2666	145	72.1	2.80	2.46	14.7
Xenon	6.1317	3.60	3828	123	64.0	2.87	4.00	12.2

TABLE III

*Parameters with TBF of the Buckingham-Corner potential function for MRGS*

Solid	$\beta$	$\alpha$	$r_m \times 10^8$ (cm)		$\epsilon \times 10^{16}$ (erg)	
			Quasi-harmonic	Anharmonic	Quasi-harmonic	Anharmonic
Neon	0.14	14.275	3.225	3.25	46.074	44.111
Argon	0.15	13.203	3.780	3.80	206.084	200.165
Krypton	0.16	11.655	4.050	4.10	281.292	263.459
Xenon	0.16	13.598	4.300	4.30	504.375	501.719

TABLE IV

*Parameters without TBF of the Buckingham-Corner potential function for MRGS*

	$\beta$	$\alpha$	$r_m \times 10^8$ (cm)		$\epsilon \times 10^{16}$ (erg)	
			Quasi-harmonic	Anharmonic	Quasi-harmonic	Anharmonic
Neon	0.14	14.086	3.230	3.285	43.177	42.827
Argon	0.15	13.028	3.833	3.850	169.242	169.533
Krypton	0.16	11.658	4.085	4.085	237.950	238.250
Xenon	0.16	13.179	4.337	4.338	380.328	380.550

atomic polarisability and classical frequencies have been taken from the paper of Margenau (1939). The quasiharmonic and anharmonic parameters, with and without three-body forces, thus computed are shown in Tables III and IV.

The frequency spectra have been computed using the secular equation (eqn. 4). The potential parameters calculated at 0 °K and zero atmospheric pressure (Tables III and IV) have been used for determining the potential energy  $\Phi(r)$ , and the coupling coefficients  $D_{\alpha\beta}(kk'; K)$  for 8000 wave vectors  $K$ , which reduce to 268 non-equivalent ones including that corresponding to the origin.

#### PHONON DISPERSION

The phonon dispersion ( $\nu(\mathbf{q}, \mathbf{q})$ ) curves in the three principal symmetry directions [100], [110], and [111] have been plotted by picking up frequencies corresponding to the points (QOO), (QOQ), and (QQQ);  $\mathbf{q}$  being a reduced wave vector expressed as  $\mathbf{q} = \mathbf{a}K$ . For each of the solids four sets of dispersion curves viz. quasiharmonic without and with TBF, and anharmonic without and with TBF have been drawn. These curves along with the available inelastic neutron scattering, data of various workers are displayed in Figs. 1-4.

The phonon dispersion curves (Figs. 1-4), for MRGS at 0°K and zero atmospheric pressure, show a very close resemblance with each other except for a scale factor. The characteristic similarity in the shape of the curves may be due to the occurrence of identical crystal structure (fcc) and similar chemical nature (being elements of zero group). From the point of view of lattice dynamics, this similarity in the dispersion curves arises (Brockhouse, 1966) on account of the presence of strong central interaction between the first neighbours. It is quite consistent as the set of curves have been obtained with a central force model, and the predominance of the first neighbour interaction has been marked in the rapid decrease of the magnitude of the force constants  $\phi_{n\beta}(1-1')$  as one goes over to higher neighbours in the present case.

Figs. 1-4 show that the variation of the scale factor is not regular from neon to xenon. The heights of different branches for argon are maximum decreasing through

krypton to xenon on one side and to neon on the other in all the directions. The regular decrease in the heights of different branches or the scale factor from argon to xenon may be due to regular increase in the atomic masses. Theoretically the scale factor for the frequencies is of the order of the inverse square root of their mass ratio. However, the scale factor appearing in case of neon and argon is just the reverse and is inconsistent with the theoretical considerations. Everything, including the electronic structure of the atoms constituting the two solids, being similar, the discrepancy may be attributed to certain inherent differences in the interatomic force-system present therein. This conclusion is in conformity with the earlier findings of Gupta and Dayal (1966) from their studies of thermal properties and equation of state of these solids. They suggested that the interatomic forces in neon are analogous to those in helium and that the usual pair-potentials, which are applicable to heavy rare-gas solids, are not suitable for neon.

The dispersion curves possess all the characteristic features (Dolling & Woods, 1965) of fcc monatomic solids. The two transverse branches in [100] and [111] directions are degenerate. At the point (110) which is equivalent to the (001) point the  $[110]_L$  branch is degenerate with  $[001]_{T_1}$  branch and the  $[110]_{T_2}$  is degenerate with  $[001]_L$  branch. The inclusion of three body forces and anharmonic terms have much improved the results in all the directions. Comparison of the theoretical curves with the available experimental data shows improvement over the quasiharmonic results in almost all the directions.

*Neon* — Neon has been investigated firstly by Leake *et al.* (1969) and later by Skalyo *et al.* (1972) using the inelastic neutron scattering technique. Recently, Endoh *et al.* (1975) have observed the low-frequency phonons of 'fcc-neon' along the high-symmetry directions at temperatures 6.5°K and 23.7°K using inelastic neutron scattering. The comparison of our theoretical curves and the experimental one shows (Fig. 1) that our quasiharmonic without TBF theoretical curves drawn at 0°K and zero

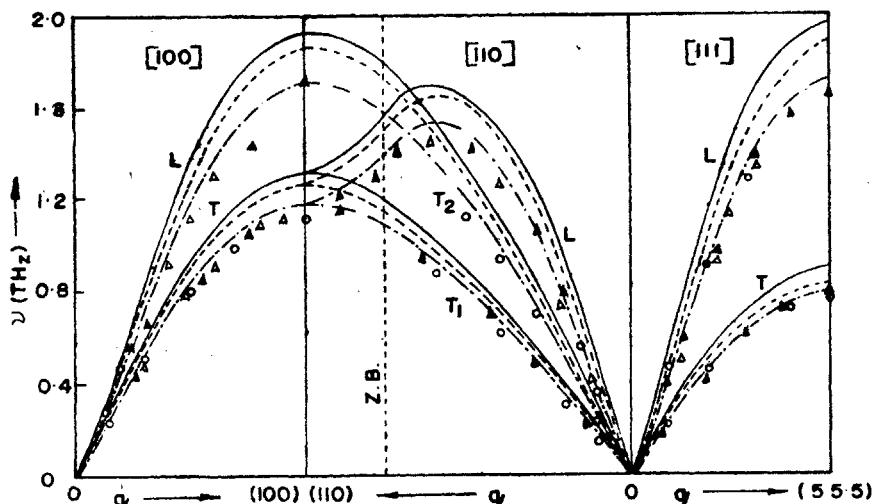


Fig. 1. Phonon dispersion curves for solid neon : (—) anharmonic with TBF, (---) anharmonic without TBF, (- · - ·) quasiharmonic with TBF, and (· · ·) quasiharmonic without TBF. Experimental points : (▲) [Leake *et al.* (1969)] (Δ) [Skalyo *et al.* (1972)] and (○) [Endoh *et al.* (1975)].



atmospheric pressure with lattice spacing 4.4637 Å are much better than the quasi-harmonic with TBF and the anharmonic ones. It is rather surprising that a quantum solid like neon gives better results with a quasiharmonic model than with an anharmonic one. Perhaps, there is difference in the nature of actual interactions present in neon and the one taken here for study. Rather, the Buckingham-Corner potential function relates the long and short range behaviour in a very rigid and inflexible way (Tricky & Green, 1973).

It is seen that both the three-body forces and the anharmonicity increase the slopes of the dispersion curve in all the directions. The anharmonic curves without and with TBF are approximately the same. It seems that in neon, the effect of anharmonicity is stronger than that of the TBF, and as such suppresses the effect of the latter.

*Argon* — Egger *et al.* (1968) measured phonon energies in natural argon (consisting of 99.6%  $^{40}\text{Ar}$ , 0.3%  $^{36}\text{Ar}$ , and 0.1%  $^{38}\text{Ar}$ ) in [100] and [110] directions at 4.2 °K. Recently, Fujii *et al.* (1974) measured phonon dispersion for  $^{36}\text{Ar}$  at 10 °K in all the symmetric directions both using the neutron scattering method. Later results are supposed to be more accurate and much improved than the former as they have taken a pure sample of  $^{36}\text{Ar}$  instead of natural argon. These neutron scattering points have been compared with the theoretical curves computed at 0 °K and zero atmospheric pressure after making proper allowance for the isotopic masses. Our quasiharmonic with TBF curves show excellent agreement with both sets of experimental data. Some measurements of the dispersion curves for  $^{36}\text{Ar}$  have also been made by Batchelder *et al.* (1970) at 4 °K. They have reported that their dispersion curves show a close agreement with the results of Egger *et al.* (1968) after reduction to the isotopic masses. This means that our theoretical results are also in good agreement with those of Batchelder *et al.* (1970).

The inclusion of three-body (Fig. 2) forces as well as anharmonicity increases the frequencies in all the directions. The anharmonic without TBF curves and the quasiharmonic with TBF are approximately the same. It seems that in this case the effect of including TBF is almost the same as that of anharmonicity. It is also seen from the figure that the combined effect of TBF and anharmonicity is very much large.

*Krypton* — The first measurements of the dispersion curves of krypton have been made by Daniels *et al.* (1967). Recently, Skalyo *et al.* (1974) measured more accurate and complete phonon dispersion of krypton at 10 °K with a single crystal having a lattice spacing of 5.646 Å. The comparison of the theoretical curves shows that the experimental points are higher than the theoretical quasiharmonic without TBF, but lower than quasiharmonic with TBF curves. Also the curve-slopes of Skalyo *et al.* (1974) are larger than those of Daniels *et al.* (1967). The divergence seen in the experimental and theoretical results is quite consistent with the recent observations of Batchelder *et al.* (1971) and Leake *et al.* (1969). The studies of Batchelder *et al.* (1971) on an argon crystal at 4 °K and 77 °K, and of Leake *et al.*, on neon crystal at 4.7° K and 25°K suggest a decrease in phonon frequencies with increasing temperature. Brown and Horton (1967) have also suggested that zero temperature and pressure phonon energies should be about 6% larger than those appropriate to the conditions of Daniels *et al.*'s experiment (1967). In this context the agreement of our theoretical

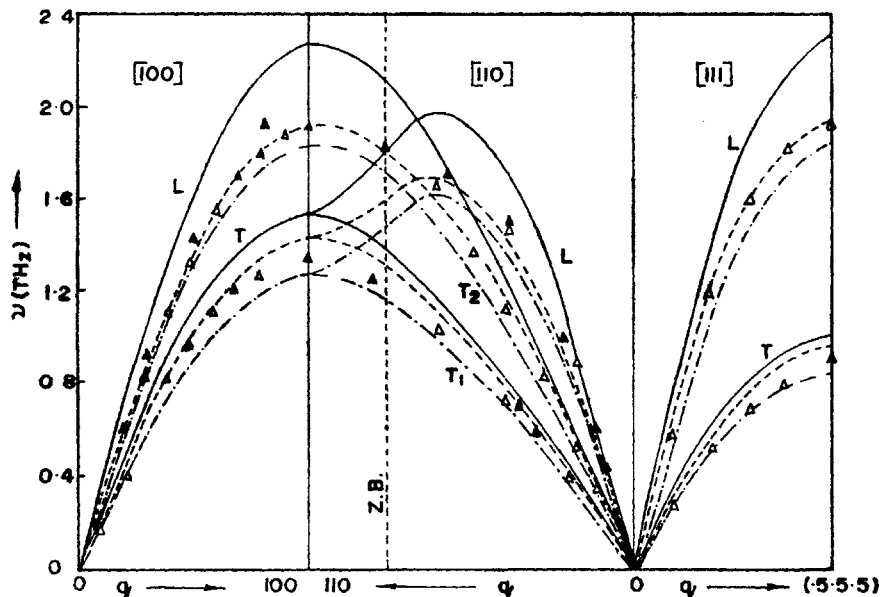


FIG. 2. Phonon dispersion curves for solid argon ; (—) anharmonic with TBF, (---) anharmonic without TBF, (---) quasiharmonic with TBF, and (---) quasiharmonic without TBF, Experimental points : (▲) [Egger *et al.* (1968)] and (△) [Fujii *et al.* (1974)]

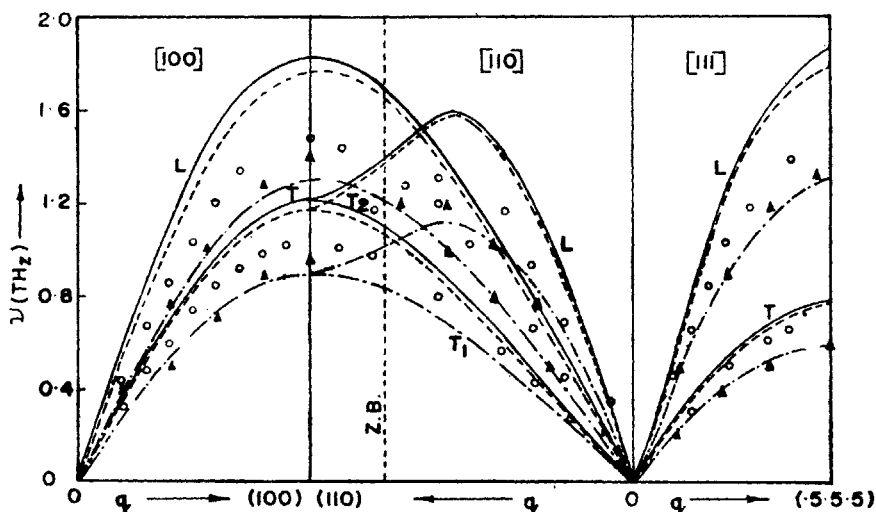


FIG. 3. Phonon dispersion curves for solid krypton : (—) anharmonic with TBF, (---) anharmonic without TBF, (---) quasiharmonic with TBF, and (---) quasiharmonic without TBF Experimental points : (▲) [Daniels *et al.* (1967)] and (○) [Skalyo *et al.* (1974)]

curves without TBF (obtained at 0°K and zero atmospheric pressure) with Daniels *et al.*'s experimental curves (obtained at 79°K and 300 atmospheric pressure) is surprising. However, Brockhouse (1966) is of the view that the dispersion curves with rare

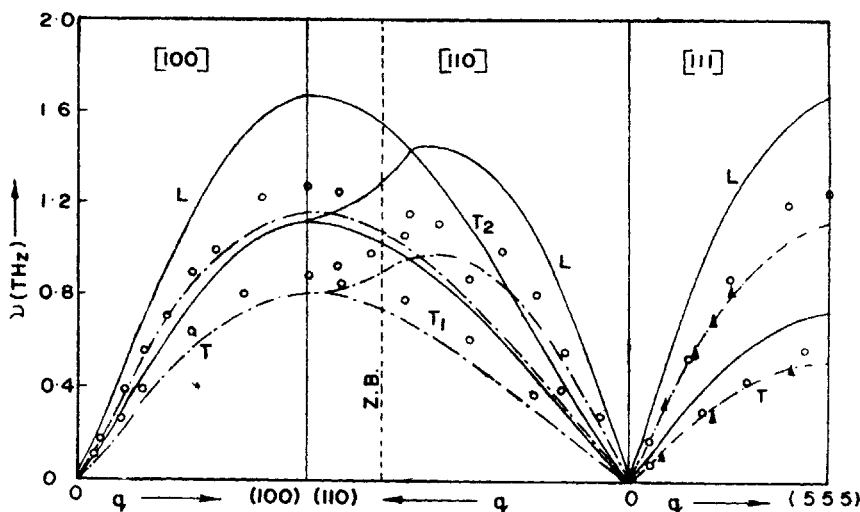


FIG. 4. Phonon dispersion curves for solid xenon : (—) anharmonic with TBF, (---) anharmonic without TBF, (-.-) quasiharmonic with TBF, and (....) quasiharmonic without TBF. Experimental points : (▲) [Palmer *et al.* (1973)] and (○) [Lurie *et al.* (1974)]

exception (Cowley, 1964) are not strongly temperature dependent. As long as the temperature difference is only of the order of 10% of the melting temperature, the results are substantially equivalent to results for 0 °K.

It is seen (Fig. 3) that while addition of three-body forces has improved the results the zero-point anharmonic effects have not contributed much to the results. As such the difference in the quasiharmonic and the anharmonic curves is negligibly small.

*Xenon*—Palmer *et al.* (1973) first determined phonon frequencies in xenon crystals using the techniques of Batchelder *et al.* (1971). Dispersion curves were obtained for phonons in [111] direction at 4 °K and 77 °K. Recently, Lurie *et al.* (1974) used the same technique to measure the low-frequency phonon dispersion relations for a single crystal of xenon at 159.6 °K, 111 °K, and 10 °K. The agreement of our quasiharmonic curves with those of Palmer *et al.* (1973) at 4 °K is reasonably good while the slopes of the experimental curves of Lurie *et al.* (1974) in all the directions are higher than those of our quasiharmonic without TBF curves, but lower than the quasiharmonic with TBF. Here also the results may be said to be in good agreement with the experiments following the observations of Batchelder *et al.* (1971) and Leake *et al.* (1969).

It is seen (Fig. 4) that in this case also the difference between quasiharmonic and anharmonic curves is negligibly small showing the insignificance of anharmonicity in solid xenon. The three-body forces have contributed much to the results.

#### CONCLUDING REMARKS

In general, the effect of inclusion of three-body forces on the phonon dispersion is seen in the increase of slopes of all the branches at low wave-vectors. The three-body effect seems to be larger in krypton and xenon than in neon and argon. This may be due to the fact that the three-body forces represented by the expression (11) are

governed by the triplet interaction coefficient  $\Omega$  which is maximum for xenon and minimum for neon (Table I) because of the value of polarizability (Table II) which increases from neon to xenon. On the other hand, the effect of inclusion of anharmonicity is also of the same nature, but here the effect is maximum in neon decreasing gradually through argon and krypton to minimum in xenon. This is quite consistent with the positions which these solids occupy in the periodic table. Neon, being closest to the quantum solid helium, must possess the largest anharmonic effect. The modification introduced in the quasiharmonic results is also in accordance with the nature of this class of solids. As the slopes of the dispersion curves for quite small  $q$ 's indicate the velocity of sound waves in crystals in the appropriate crystallographic directions the uniform increase in slopes suggests increase in the macroscopic sound velocity by TBF and anharmonicity. However, unfortunately the accurate ultrasonic data (Brockhouse, 1966) for these solids the correctness of the slopes of the dispersion curves cannot be tested, and as such no further comments may be made on this point.

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#### REFERENCES

- Axilrod, B. M. (1949). The triple-dipole interaction between atoms and cohesion in crystal of rare gases. *J. chem. Phys.*, **17**, 1349.
- (1951). Triple-dipole interaction theory. *J. chem. Phys.*, **19**, 719–729.
- Barker, J. A., Bobetio, M. V., and Klein, M. L. (1971). Lattice dynamics of solid krypton. *Phys. Lett.*, **A**, **34**, 415–416.
- Barker, J. A., Fisher, R. A., and Watts, R. O. (1971). Liquid argon: Monte-Carlo and molecular dynamics calculations. *Mol. Phys.*, **21**, 657.
- Batchelder, D. N., Collins, M. F., Haywood, B. C. G., and Sidy, G. R. (1970). *Lattice dynamics of argon at 4°K.* *J. Phys.*, **C**, **3**, 249.
- Batchelder, D. N., Haywood, B. C. G., and Saunderson, D. H. (1971). Temperature dependence of phonon frequencies in Ar by inelastic scattering. *J. Phys.*, **C**, **4**, 910–915.
- Batchelder, D. N., Losec, D. L., and Simmons, R. O. (1967). Measurement of lattice constant, thermal expansion and isothermal compressibility of neon single crystal. *Phys. Rev.*, **162**, 767–775.
- Boato, G. (1964). The solidified inert gases. *Cryogenics*, **4**, 65–75.
- Bobetic, M. V., Barker, J. A., and Klein, M. L. (1972). Lattice dynamics with three-body forces, II. Krypton. *Phys. Rev.*, **B**, **5**, 3185–3189.
- Brockhouse, B. N. (1966). *Phonons* (ED. R. H. W. Stevenson), p. 110, Oliver & Boyd, London.
- Brown, J. S., and Horton, G. K. (1967). Model potentials and the dispersion law in solid Krypton. *Phys. Rev. Lett.*, **18**, 647.
- Cavallini, M., Gallinaro, G., Meneghetti, L., Scoles, G., and Valbusa U. (1970). Rainbow scattering and the intermolecular potential of argon. *Chem. Phys. Lett.*, **7**, 303.
- Chell, G. G., and Zucker, I. J. (1968). Effect of long range 3-body-forces on the zero-point-energy of inert gas solids. *J. Phys.*, **C**, **1**, 35–41.

- Copeland, D. A., and Kestner, N. R. (1968). Accurate effective inter-molecular pair potential in gaseous argon. *J. chem. Phys.*, **49**, 5214–5222.
- Daniels, W. B., Shirane, G., Frazer, B. C., Umebayshi, H., and Leake, J. A. (1967). *Phys. Lett.*, **18**, 548–550.
- Dolling, G., and Woods, A. D. B. (1965). *Thermal Neutron Scattering* (ED. P. A. Egelstaff), p. 193. Pergamon Press, London.
- Doran, M. B., and Zucker, I. J. (1971). Higher Order multipole three-body van der Waals interactions and stability of rare gas solids. *J. Phys.*, C, **4**, 307–312.
- Endoh, Y., Shirane, G. and Skalyo, J. Jr. (1975). Lattice dynamics of solid neon at 6.5 and 23.7K. *Phys. Rev.*, B, **11**, 1681–1688.
- Egger, H. A., Gsanger, M., Luscher, E., and Dorner, B. (1968). *Phys. Lett.* **28**, 433–434.
- Fenichell, H., and Sarin, B. (1966). Low temperature specific heats of solid neon and solid xenon. *Phys. Rev.*, **142**, 490.
- Fisher, R. A., and Watts, R. O. (1972). The friction coefficient formalism in the statistical mechanics of transport processes. *Mol. Phys.*, **23**, 1051.
- Fujii, Y., Lurie, N. A., Pynn, R., and Shirane, G. (1974). Inelastic neutron scattering from solids <sup>38</sup>Argon. *Phys. Rev.*, B, **10**, 3647–3659.
- Gewurtz, S., and Stoicheff, B. P. (1974). Elastic constants of argon single crystal determined by Brillouin Scattering. *Phys. Rev.*, B, **10**, 3487–3499.
- Guggenheim, E. A., and Mc Glashan, M. L. (1960). Interaction between argon atoms. *Proc. R. Soc.*, A, **255**, 456.
- Gupta, N. P., and Dayal, B. (1966). Effect of zero-point energy on the specific heats of solid neon and xenon. *Phys. Stat. Solidi*, **18**, 731–736.
- Horton, G. K. (1968). Ideal rare gas crystals. *Am. J. Phys.*, **36**, 93–119.
- Huller, A. (1971a). High precision calculation of three and many-body lattice sums. *Z. Phys.*, **241**, 340–347.
- (1971b). Many-body forces and elastic constants of rare-gas crystals. *Z. Phys.*, **245**, 324.
- Horton, G. K., and Leech, J. W. (1963). On the statistical mechanics of the ideal inert gas solids. *Proc. phys. Soc.*, **82**, 816–854.
- Jansen, L. (1964). Stability of crystals of rare gas atoms and alkali halides in terms of three-body. *Phys. Rev.*, A, **135**, 1292.
- Klein, M. L., and Venables, J. A. (1976). *Rare Gas Solids*, 1. Academic Press, London.
- Klein, M. L., Horton, G. K., and Feldman, J. L. (1969). Thermodynamic properties of solid Ar, Kr, and Xe based upon a short-range central force and the conventional perturbation expansion of the partition function. *Phys. Rev.*, **184**, 968–978.
- Leake, J. A., Daniels W. B., Skalyo, J. Jr., Frazer, B. C., and Shirane, G. (1969). Lattice dynamics of neon at two densities from coherent inelastic neutron scattering. *Phys. Rev.*, **181**, 1251–1260.
- Lurie, N.A., and Skalyo, J. Jr. (1974). On the importance of many-body forces in Xenon. *Phys. Lett.*, A, **46**, 357.
- Lurie, N. A., Shirane, G., and Skalyo, J. (1974). Temperature dependence of the zero-sound elastic constants of crystalline xenon. *Phys. Rev. B*, **9**, 2661–2669.
- Losee, D. L., and Simmons, R. O. (1968). Thermal expansion measurements and thermodynamics of solid krypton. *Phys. Rev.*, **172**, 944–957.
- Margenau, H. (1939). Van der Waal's forces. *Rev. mod. Phys.*, **11**, 1.
- Parson, J. M., Siska, P. E., and Lee, Y. T. (1972). Inter-molecular potentials from crossed-beam differential elastic scattering measurements : IV Ar + Ar. *J. chem. Phys.*, **56**, 1511–1516.
- Pollack, G. L. (1964). The solid state of rare gases. *Rev. mod. phys.* **36**, 748–791.
- Palmer, B. J., Saunderson D. H., and Batchelder D. N. (1973). Phonon frequencies in xenon by inelastic neutron scattering. *J. Phys.*, C **6**, L 313–315.

- Peterson, O. G., Batchelder D. N., and Simmons, R. O. (1967). Measurements of X-ray lattice constant, thermal expansivity and isothermal compressibility of argon crystals. *Phys. Rev.*, **150**, 703.
- Sears, D. R., and Klug H.P. (1962). Density and expansivity of solid xenon. *J. chem. Phys.*, **37**, 3002.
- Skalyo, J. Jr., Endoh, Y., and Shirane G. (1974). Inelastic neutron scattering from solid Kr at 10°K. *Phys. Rev.*, **B 9**, 1797-1803.
- Tanaka, Y., and Yoshino K. (1970). Absorption spectrum of the Argon molecule in vacuum-UV region. *J. chem. Phys.*, **53**, 2012-2030.
- Tricky, S. B., and Green F. R. (1973). One electron theory of bulk properties of crystalline Ar, Kr, and Xe. *Phys. Rev.*, **B, 8** 4822-4832.
- Urvas, A. O., Losee, D. L., and Simmons, R. O. (1967). *J. Phys. Chem. Solids*, **28**, 2269-2281.
- Zucker, I. J., and Chell, G. G. (1968). Effect of long range Three-body forces on the elastic constants of rare gas crystals at 0°K. *J. Phys.*, **C 1**, 1505-1514.