Lattice Dynamics of Neon at Two Densities from Coherent Inelastic Neutron Scattering*

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Phonon dispersion relations for two single crystals of neon were measured by inelastic neutron scattering. Growth of the crystals by a high-pressure technique permitted a study of Ne lattice dynamics at densities differing by 4%. Measurements in the principal symmetry directions of the fcc lattice were made at 4.7°K on a crystal with a lattice parameter of 4.462±0.002 Å. These data could be well fitted with a spectrum calculated by self-consistent phonon theory with a Lennard-Jones pair potential. An all-neighbor quasiharmonic calculation with the Lennard-Jones potential also provided a good match after calculated energies were adjusted for a difference in theoretical and experimental lattice parameters. The two models utilized different values for the Lennard-Jones parameters in the calculations. A Born–von Kármán analysis indicated that interatomic forces are short-range and predominantly central. Dispersion curves in the [001] direction were measured for a second sample at 4.7 and 25°K at constant volume (lattice parameter 4.402± 0.002 Å). The temperature shift of the frequencies was small, averaging $(-2.3\pm1.3)\%$ for the transverse and $(2.3\pm2.4)\%$ for the longitudinal mode. A Born–von Kármán analysis of data for this higher-density sample indicated the appearance of significant noncentral forces. Comparison of phonon measurements at 4.7°K for the two samples yielded average quasiharmonic-mode Grüneisen parameters γ_j of 2.9±0.5 and 4.2±0.6, respectively, for the [001] transverse and longitudinal branches.

I. INTRODUCTION

In recent years the theory of the lattice dynamics of the solidified inert gases has received considerable attention.[1–5] Detailed calculations have been made of phonon dispersion curves and anharmonic effects, which may be expected to be large for these elements. Since suitable crystals are not easily grown, however, experimental data for dispersion curves have been published thus far only for helium[6,7] and krypton.[8] In the helium case, the lattice dynamics are dominated by effects arising from large zero-point atomic motion, and for this reason crystalline helium is often referred to as a quantum solid. Krypton, on the other hand, may be taken as an almost ideal example of a simple molecular solid where one can hope to describe the dynamics on a classical model with a minimum number of arbitrary assumptions. Neon represents an intermediate case in which zero-point motion may be expected to play a significant, but not preponderant, role in a dynamical description of the solid.

In the present paper measurements by coherent inelastic neutron scattering of the dispersion curves for two crystals of neon with significantly different densities are described.[9] For one crystal, modes were measured at 4.7°K for all principal symmetry directions. The other crystal grew in an inconvenient orientation in the high-pressure cell, and data were obtainable only for the longitudinal and transverse branches of the [001] direction. The latter measurements were carried out at 4.7 and 25°K with the purpose of determining anharmonic shifts of phonon energies with temperature. Because of the high-pressure technique employed in sample preparation, these measurements were made under the ideal experimental condition of constant volume. Comparison of the 4.7°K data for modes studied in both crystals yielded experimental values for the mode Grüneisen parameters γ_j for these modes. These parameters, defined by $\gamma_j \equiv -d\ln\epsilon_j/d\ln V$ (where ϵ_j is a phonon energy and V is the crystal volume), are related to anharmonicity in the quasiharmonic model.

The experimental dispersion curves have been compared with theoretical curves obtained from the calculations in the harmonic approximation of Grindlay and Howard[1] and with more recent calculations based on the self-consistent phonon approximation, as carried out by Gillis *et al.*[4] and by Werthamer.[5] To facilitate these comparisons, the experimental data were parametrized for presentation in smooth curves by means of a force constant analysis on a Born-von Kármán model. The results of this analysis also have provided useful information on the range and noncentral character of the forces in Ne, and for calculations of elastic

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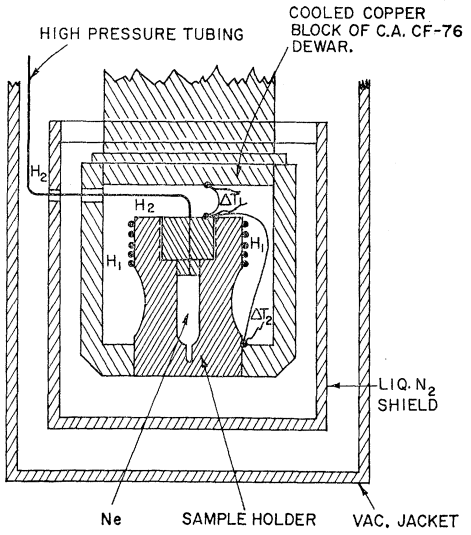

FIG. 1. Cell used in preparation of neon crystals at high pressure.

constants, frequency distribution, heat capacity, and the Debye characteristic temperature.

II. NEON SAMPLES

Crystals were grown from 99.99% pure natural neon, approximately 90% Ne^{20} and 10% Ne^{22}, by a high-pressure technique similar to that used previously to prepare a Kr crystal for inelastic neutron scattering experiments.[8] The technique may be summarized as follows. Fluid neon was introduced through high-pressure steel tubing into an aluminum alloy pressure cell with a minimum wall thickness of about 1.5 cm and an effective sample volume of about 4.5 cm^3. As shown in Fig. 1, the cell was mounted in a temperature-controlled helium cryostat with the bottom of the cell, where there was a nucleation tip, in thermal contact with the control block. A small heater at the top of the cell maintained a slight temperature gradient. Additional heaters were used to prevent blockage by a plug of frozen neon in the tubing linking the cell to an external pressure generating and measuring apparatus. The entire system was allowed to come to equilibrium at some predetermined temperature and pressure, as deduced from the melting curve data of Mills and Grilly.[10] A relatively small increase in pressure at constant temperature was then sufficient to initiate neon crystallization. Additional neon was then pumped very slowly into the cell, maintaining constant pressure as nearly as possible on the sample during its solidification. The actual pressures and temperatures used were 0.7 kbar and 35°K for one of the crystals, Ne(A), and 1.9 kbar and 46°K for the other, Ne(B). It was possible to monitor progressive solidification through the variation of pressure with volume for the combined system of pressure cell and hydraulic pump. After cooling to 4.7°K, the sample pressures were estimated to be very nearly zero for Ne(A) and about 0.6 kbar for Ne(B).

The above procedure does not always lead to the production of a satisfactory crystal for neutron scattering experiments, and further investigations of this growth technique are desirable. When a large crystal was successfully grown, it was usually found to be considerably larger than any other crystallite detected, but its volume was always rather less than that of the cell. Its orientation did not appear to be related to cell geometry. Thus Ne(A) was found to have a $[\bar{1}\bar{1}2]$ direction about 10° from the Dewar axis and a $[0\bar{1}1]$ direction about 20° from that axis, close to the maximum available tilt of the goniometer head. In Ne(B) the $[\bar{1}20]$ axis was close to the Dewar axis and neither $[\bar{1}10]$ nor $[010]$ could be reached safely.

The perfection of the crystals was studied by Bragg rocking-curve measurements, and in each case mosaic spreads were found to be less than 12 min full width at half-maximum. A careful investigation of Ne(A) revealed that it was twinned on (111). The reciprocal lattices of the two components were oriented so that the equatorial layers perpendicular to $(\bar{1}\bar{1}2)$ were in register. As the major component was six times larger than the minor component, however, phonon measurements in the $[0\bar{1}1]$ zone were not affected.

After alignment of each zone axis, cross-sectional areas of the incident and scattered beams were reduced as much as possible so as to minimize background scattering from the aluminum cell and from the extraneous small crystallites of neon. Careful measurements of the angles of several Bragg maxima yielded a lattice parameter of 4.402 ± 0.002 Å for Ne(B) and 4.462 ± 0.002 Å for Ne(A). The latter is equal within experimental error to the value given by Batchelder *et al.*[11] for the extrapolated lattice parameter at zero pressure and 0°K.

III. PHONON MEASUREMENTS

The phonon dispersion curves were measured on a triple-axis crystal spectrometer at the Brookhaven High Flux Beam Reactor. The energies of the phonons created in the specimen by coherent inelastic scattering of the neutrons were determined using the constant-**Q** technique[12] with fixed incident neutron energies between 20 and 45 meV.

Most of the measurements for Ne(A) were made with the $[\bar{1}\bar{1}2]$ direction vertical. The equatorial layer of reciprocal space for this orientation is shown in Fig. 2(a), with the Brillouin-zone boundaries and symmetry points indicated. The dashed lines denote lines in

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[12] B. N. Brockhouse, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.

reciprocal space along which measurements were taken. All data for Ne(A) were taken at 4.7°K.

As described above, Ne(B) grew in such an orientation that [$\bar{1}$20] was the only useful zone attainable within the limits through which the Dewar could be tilted. Consequently, the only principal symmetry direction accessible was [001]. The paths followed in reciprocal space are shown in Fig. 2(b). The Brillouin-zone boundaries and symmetry points again are indicated. For this crystal, measurements were made at both 4.7 and 25°K.

Some typical neutron groups from both crystals at 4.7°K are shown in Fig. 3, where ζ is the reduced wave-vector coordinate. Figure 4 illustrates two pairs of neutron groups from Ne(B). Each pair shows measurements at 4.7 and 25°K of a phonon with a particular reduced wave vector, the results being superimposed with the vertical scales chosen to make the peak heights approximately equal.

The widths of the neutron groups are of magnitudes to be expected solely from the resolution of the spectrometer. Figure 4 shows no apparent increase in width on raising the temperature from 4.7 to 25°K, and hence any real broadening due to anharmonic effects must be quite small. The measured widths do give information

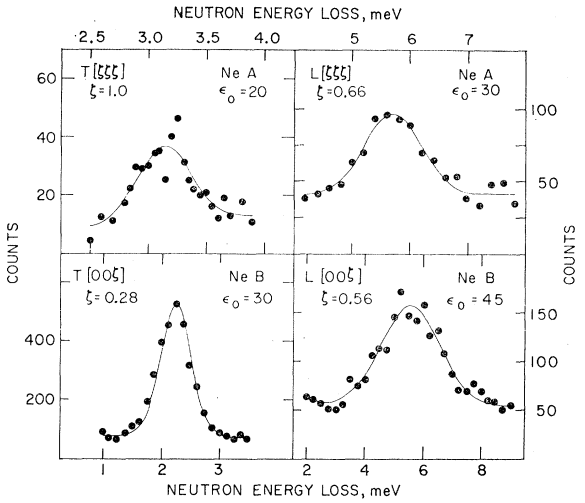


FIG. 3. Typical neutron groups for Ne(A) and Ne(B). ϵ_0 is the incident neutron energy.

on phonon lifetimes, however. For example, the T (0,0,0.28) mode for Ne(B), as shown in Fig. 3, was measured under conditions for which the calculated instrumental width was 0.6 meV, and this is in very good agreement with observation. As the observed curve is a convolution of the instrumental resolution function with the phonon energy surface, and the group width was measured to a precision of 5%, an upper limit of 0.2 meV can be given for the energy width of the phonon. From this a lower limit can be placed on

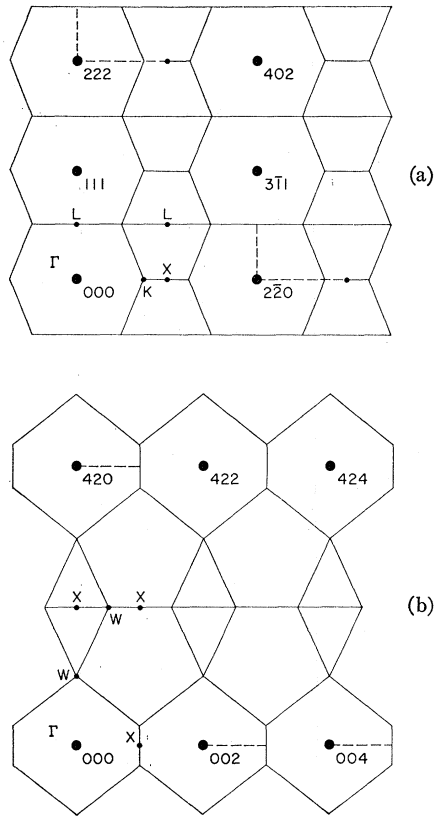


FIG. 2. Planes of the reciprocal lattice showing the Brillouin-zone boundaries and symmetry points. The dashed lines indicate the paths along which the measurements were made (a) perpendicular to [$\bar{1}\bar{1}$2], (b) perpendicular to [$\bar{1}$20].

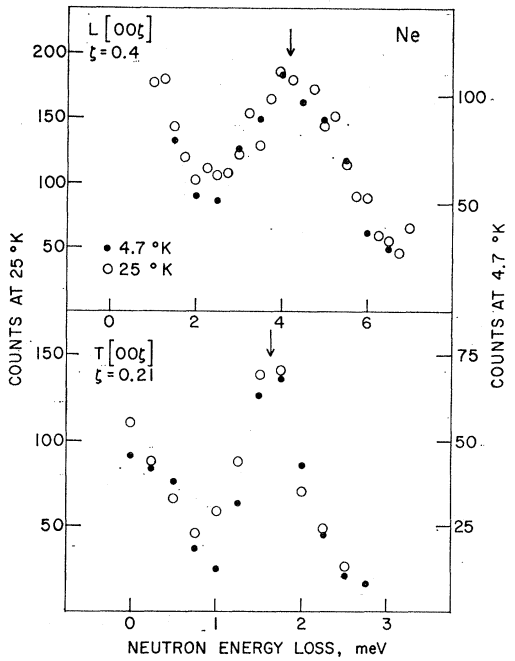


FIG. 4. Neutron groups for two phonons in Ne(B) at 4.7 and 25°K. The times required to reach the preset monitor count were about 7 and 17.5 min for the upper groups and 1.8 and 3.6 min for the lower groups at 4.7 and 25°K, respectively.

TABLE I. Phonon energies (in meV) for the [110] and [111] branches in Ne(A) (a=4.462 Å) at 4.7°K, 4.135 meV=10^{12} Hz.

	[110]T_1		[110]T_2		[110]L	
ζ	ϵ	$\sigma(\epsilon)$	ϵ	$\sigma(\epsilon)$	ϵ	$\sigma(\epsilon)$
0.05	...	...	0.56±0.03		...	...
0.10	...	...	...	...	1.54±0.05	
0.15	1.00±0.05		1.58±0.03		2.34±0.06	
0.20	...	...	...	...	3.14±0.06	
0.30	1.98±0.06		2.98±0.11		4.49±0.08	
0.45	2.81±0.08		...	...	5.71±0.10	
0.55	...	...	5.13±0.07		...	...
0.60	...	...	...	...	5.78±0.08	
0.63	3.71±0.06		...	...	...	...
0.73	...	...	...	...	5.66±0.12	
0.75	4.05±0.06		...	...	...	...
0.85	...	...	...	...	4.91±0.07	
0.88	4.70±0.09		...	...	...	...
1.00	4.72±0.06		7.14±0.16		4.72±0.06	

	[111]T		[111]L	
ζ	ϵ	$\sigma(\epsilon)$	ϵ	$\sigma(\epsilon)$
0.04	0.43±0.03		...	...
0.08	0.80±0.03		1.67±0.04	
0.125	...	...	2.50±0.06	
0.165	1.68±0.06		3.23±0.06	
0.205	...	...	3.90±0.06	
0.245	2.20±0.06		4.61±0.06	
0.285	...	...	5.25±0.11	
0.33	2.78±0.06		5.73±0.07	
0.37	...	...	6.26±0.09	
0.41	3.11±0.05		6.45±0.08	
0.50	3.13±0.03		6.63±0.11	

the phonon lifetime ($t_L=2h/\Delta E$) of 6.6×10^{-12} sec. Since the energy of the phonon is 2.25 meV, it would then be in existence for at least 3.6 oscillations.

The phonon energies are listed in Tables I and II and displayed in Figs. 5(a) and 5(b). The smoothed curves in the figures represent the results of a force constant analysis which will be discussed later. The errors indicated are standard deviations and were calculated following the procedure of Brockhouse *et al.*[13] for deriving standard deviations due to counting statistics. In addition, estimated standard deviations for random errors in the setting of the spectrometer were included. The latter varied from ±0.024 meV at 20-meV incident neutron energy to ±0.088 meV at 45 meV. An alternative method of estimating standard deviations due to counting statistics is provided by fitting a Gaussian curve to the neutron group since there are good reasons for expecting the shape of the group to be approximately Gaussian.[14] This was attempted in a few instances and similar values to those listed were obtained.

IV. ANALYSIS OF DATA AND DISCUSSION

A. Force Constant Analysis

For convenient comparison with theoretical dispersion curves, as well as for other useful information which may be obtained, the experimental data have been represented by smooth curves derived from a force constanta nalysis on a Born–von-Kármán model. The analysis was carried out using a version of the computer program written by Svensson[15] suitably modified and extended for the Brookhaven CDC 6600 system. The principles upon which the linear least-squares fitting is based have been described elsewhere.[16]

In the present work the function minimized was

$$\sum_i w_i(\epsilon_{i0}^2-\epsilon_{ic}^2)^2,$$

where ϵ_{i0} is the measured energy of a phonon, ϵ_{ic} is its calculated energy, and i runs over all phonons studied. The weighting factor w_i was taken as $[\sigma_i\epsilon_{i0}]^{-2}$, where σ_i is the estimated standard deviation of the phonon energy. Since the [001] branches are independent of the $1xy$ force constant, it was necessary to impose an artificial constraint on this constant in order to use the program with the data available for Ne(B). The axially symmetric constraint $1xy=1xx-1zz$ was chosen because it was simple to implement in the program. This has no effect on the final results.

The best values of the interatomic force constants obtained, taking into account up to second nearest neighbors for Ne(B) and up to third nearest neighbors for Ne(A), are shown in Table III. Table IV gives correlation coefficients for the interatomic force constants obtained from the Ne(A) data with the second-nearest-neighbor model. It can be seen that the data available do not permit completely uncorrelated determinations of the five force constants for this model. Table V contains interplanar force constants for Ne(A)

TABLE II. Phonon energies (in meV) for the [001] branches in Ne(A) (a=4.462 Å) at 4.7°K and in Ne(B) (a=4.402 Å) at 4.7 and 25°K.

	Ne(A) 4.7°K		Ne(B) 4.7°K		Ne(B) 25°K	
ζ	ϵ	$\sigma(\epsilon)$	ϵ	$\sigma(\epsilon)$	ϵ	$\sigma(\epsilon)$
			[001]T			
0.14	...	...	1.21±0.05		1.17±0.05	
0.21	...	...	1.69±0.05		1.61±0.05	
0.245	...	...	1.96±0.05		1.99±0.06	
0.28	1.84±0.06		2.25±0.05		2.37±0.13	
0.35	...	...	2.70±0.06		...	...
0.40	...	...	3.17±0.10		3.02±0.09	
0.56	3.50±0.06		4.03±0.09		3.99±0.11	
0.77	4.37±0.07		4.76±0.10		...	...
1.00	4.72±0.06		5.24±0.10		...	...
			[001]L			
0.21	1.88±0.06		2.38±0.11		...	...
0.28	2.67±0.06		3.11±0.13		3.64±0.22	
0.40	3.64±0.06		4.32±0.11		4.44±0.11	
0.56	...	...	5.59±0.10		...	...
0.77	5.83±0.14		7.42±0.25		...	...
1.00	7.14±0.16		8.07±0.14		8.11±0.17	

[13] B. N. Brockhouse, T. Arase, G. Caglioto, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962). For an extension to the case of an appreciable background, see R. Lechner and G. Quittner, Phys. Rev. Letters **17**, 1259 (1966).

[14] M. J. Cooper and R. Nathans, Acta Cryst. **23**, 357 (1967).

[15] We are indebted to Professor B. N. Brockhouse for sending a card deck and listing of this program.

[16] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967).

TABLE III. Experimental interatomic force constants for neon in 10^2 dyn cm^{-1}. Quantities in parentheses are values of interatomic force constants calculated from the pair potential energy function $\varphi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. The values $\epsilon=48.7\times10^{-16}$ erg, $\sigma=2.85$ Å have been used in this calculation.

	Ne(A) at 4.7°K		
Force constant	1 Neighbor fit	2 Neighbor fit	3 Neighbor fit
$1xx$	2.02±0.04	2.18±0.08	2.20±0.08 (2.23)
$1zz$	0.10±0.06	−0.08±0.09	−0.03±0.09 (−0.05)
$1xy$	2.21±0.04	2.19±0.04	2.30±0.06 (2.28)
$2xx$	··· ···	−0.30±0.10	−0.23±0.14 (−0.21)
$2yy$	··· ···	0.07±0.04	0.07±0.08 (0.03)
$3xx$	··· ···	··· ···	−0.03±0.04 (−0.032)
$3yy$	··· ···	··· ···	−0.01±0.03 (−0.002)
$3yz$	··· ···	··· ···	0.02±0.03 (−0.010)
$3xz$	··· ···	··· ···	−0.04±0.02 (−0.020)

	Ne(B)			
Force constant	4.7°K 1 Neighbor	25°K 1 Neighbor	4.7°K 2 Neighbor	25°K 2 Neighbor
$1xx$	2.75±0.08	3.00±0.12	3.04±0.10	3.16±0.17 (2.89)
$1zz$	−0.12±0.10	−0.41±0.15	−0.45±0.12	−0.59±0.38 (−0.13)
$1xy$	[a]	[a]	[a]	[a] (3.02)
$2xx$	··· ···	··· ···	−0.76±0.20	−0.47±0.36 (−0.23)
$2yy$	··· ···	··· ···	0.05±0.06	0.02±0.22 (0.04)

[a] Undetermined. The force constant between the atom at the origin and the atom at $\frac{1}{2}a(u,v,w)$, $u\geq v\geq w\geq 0$, is given by the tensor whose indices are

$$\begin{matrix} nxx & nxy & nxz, \\ nxy & nyy & nyz, \\ nxz & nyz & nzz, \end{matrix}$$

where n denotes the shell of neighbors in which the reference atom occurs. For general forces the symmetry requires $1yy=1xx$, $1yz=1xz=0$; $2zz=2yy$, $2yz=2xz=2xy=0$; and $3zz=3yy$, $3xy=3xz$.

For forces sometimes referred to as central, $1zz=0$, $1xx=1xy$, $2yy=0$, $3yy=3yz=\frac{1}{4}(3xx)$, and $3xz=\frac{1}{2}(3xx)$.

For axially symmetric forces, $1xx=1zz+1xy$, $3xx=3yy+3(3yz)$, and $2(3xx)=2(3yy)+3(3xz)$.

and Ne(B), as calculated from the appropriate linear combinations of interatomic force constants.[17]

In examining the results of the Ne(A) analysis, it was found by the statistical F test that the inclusion of second-nearest-neighbor forces was significant at the 2.5% level ($F_{2,42}=4.5$). With addition of third nearest neighbors, however, the results were not significant at a 10% level ($F_{4,38}=1.7$). Consequently, subsequent discussion involving the force constant analysis will be based for the most part on the results of models including up to three nearest neighbors. The smooth "experimental" curves shown in Figs. 5 and 6, for example, were calculated on a three-neighbor model.

B. Comparison with Theoretical Dispersion Curves

In analyzing the results of the present study, it is of major interest to compare the experimental dispersion curves with those predicted theoretically. Comparisons are made in this section with the calculations in the harmonic approximation of Grindlay and Howard,[1] and with more recent calculations based on the self-consistent phonon approximation, as carried out by Gillis, Werthamer, and Koehler.[4,5] Calculations of the latter type take into account effects due to zero-point and thermal motion of the atoms, and may be

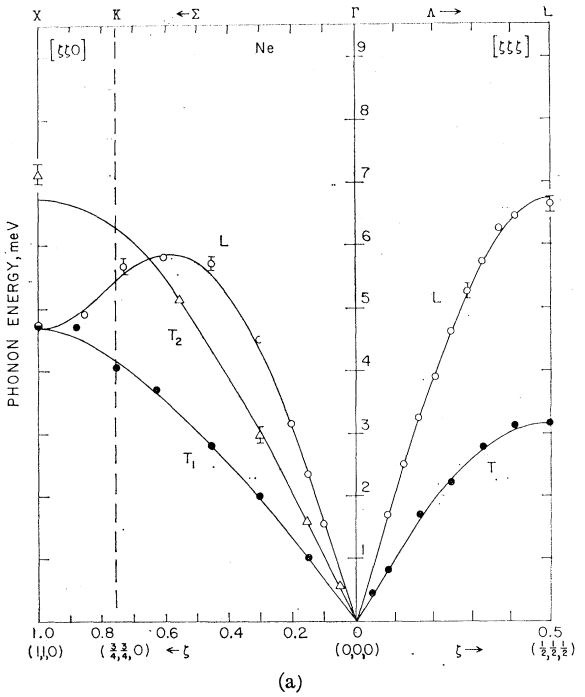
[17] See, for example, Table V of Ref. 13.

TABLE IV. Correlation coefficients for interatomic force constants from the second-nearest-neighbor model.

	(Ne)(A)				
	$1xx$	$1zz$	$1xy$	$2xx$	$2yy$
$1xx$	1				
$1zz$	−0.922	1			
$1xy$	−0.082	0.076	1		
$2xx$	−0.816	0.735	0.224	1	
$2yy$	−0.032	−0.148	0.146	−0.335	1

TABLE V. Interplanar force constants for neon (in 10^2 dyn cm^{-1}) from the second-nearest-neighbor model.

	Branch	Φ_1 $\sigma(\Phi_1)$	Φ_2 $\sigma(\Phi_2)$
Ne(A)	[001]T	8.40±0.13	0.14±0.07
	[001]L	17.42±0.64	−0.59±0.21
	[111]T	3.84±0.08	··· ···
	[111]L	17.01±0.23	··· ···
	[110]T_2	17.42±0.64	0.11±0.21
	[110]T_1	8.40±0.13	−0.49±0.09
	[110]L	8.40±0.13	8.29±0.15
Ne(B) 4.7°K	[001]T	10.33±0.31	0.11±0.13
	[001]L	24.30±0.76	−1.51±0.40
Ne(B) 25°K	[001]T	10.28±1.34	0.03±0.45
	[001]L	25.29±1.37	−0.94±0.71



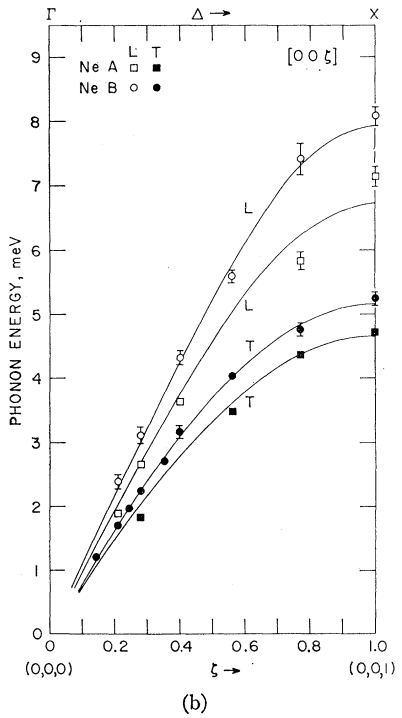


FIG. 5. Observed dispersion curves for neon. (a) The [110] and [111] directions for Ne(A) at 4.7°K. (b) The [001] direction in Ne(A) and Ne(B) at 4.7°K. The smoothed curves for Ne(A) are derived from the force constant analysis using a third-nearest-neighbor model. The data for Ne(B) at 25°K would fall very close to those at 4.7°K and so are not shown.

compared directly with experimental data without arbitrary scaling.

The calculations of Grindlay and Howard[1] (GH) have been scaled to give a best least-squares fit with the experimental data, it being assumed that all branches could be scaled by the same factor. This factor can be related to physically meaningful parameters for neon if one assumes that the reduced phonon energies (e_0), given by the GH calculations at 0°K and at a lattice parameter $a_0=1.542\ \sigma$, can be converted to energies (e_a) appropriate to the conditions of the present experiment by a quasiharmonic shift:

$$e_a=\frac{1}{\pi a_0}\left(\frac{8\epsilon}{M}\right)^{1/2}\left(\frac{a_0}{a}\right)^{3\Gamma}e_0,$$

where a is the experimental lattice constant, M is the mass of a neon atom, and Γ is a Grüneisen constant. The quantities σ and ϵ are the distance parameter and the potential well depth, respectively, for the Lennard-Jones 6-12 interatomic pair potential:

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}].$$

A range of estimates for the value of ϵ exists in the literature. A typical value of $\epsilon=48.7\times10^{-16}$ erg was assumed in calculating quasiharmonic shifts. Γ was taken to be the same for all modes and was set equal to the macroscopic thermodynamic Grüneisen constant obtained by Batchelder *et al.*,[11] from whose results an average value of 2.8 was taken rather than the actual value at 4.7°K. Then for the experimental lattice constant of $a=4.462$ Å, the least-squares scale factor gives a value of $\sigma=2.85$ Å. This is a reasonable value, but it is somewhat larger than values one usually finds in the literature (ranging from 2.67–2.80 Å).[11] To the extent that this may be significant, an explanation could be that the zero-point motion gives the neon atom an effective size larger than its true size.

The scaled GH curves are compared with the smoothed experimental data in Fig. 6. The over-all

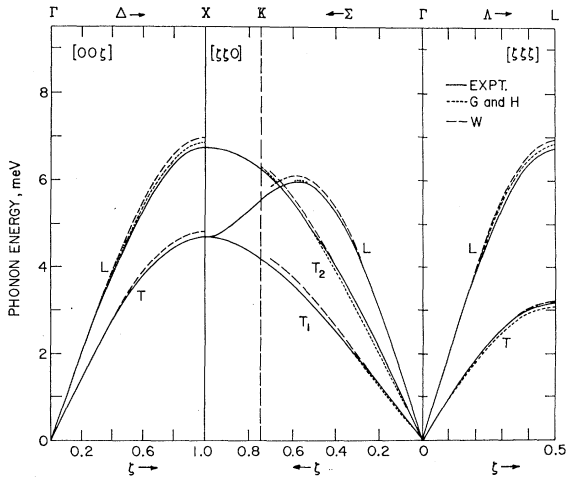


FIG. 6. Theoretical and experimental dispersion curves for Ne(A).

agreement between the experimental and the scaled theoretical curves, especially with regard to curve shapes, is seen to be very good.

Figure 6 also includes a comparison with theoretical dispersion curves derived from calculations based on the self-consistent phonon approximation.[5] This comparison is of particular interest since it may be made directly without an arbitrary scaling procedure. The calculations take into account effects due to zero-point and thermal motion of the atoms. The curves shown are those predicted for Ne^{20} at 4.7°K by Gillis, Werthamer, and Koehler.[4,5] A 6-12 potential was employed with the parameter values $\epsilon=50\times10^{-16}$ erg and $\sigma=2.74$ Å (from Bernardes[18]). Again, the agreement with experiment is good and would be expected to improve if a correction were made for the 1% mass difference between Ne^{20} and naturally abundant neon.

There are additional comparisons which can be made between experimental and theoretical results. For example, it is possible to make a detailed comparison of the "experimental" interatomic force constants with those which may be calculated directly from a pair potential energy function. Force constants obtained in this way exhibit the symmetry of "axially symmetric" forces, as discussed by Lehman *et al.*[19] Such a comparison has been made using the 6-12 potential with the same parameters given above in the discussion of the GH scaling ($\epsilon=48.7\times10^{-16}$ erg and $\sigma=2.85$ Å). The results, as shown in Table III, reveal essential agreement for Ne(A) on the basis of either a two- or a three-neighbor fit to the data, although the match is somewhat better in the three-neighbor case. For the compressed Ne(B) crystal there are unfortunately insufficient data for very quantitative conclusions. It would appear, however, that the interatomic force constant $1zz$ has a larger negative value than can be accounted for using a Lennard-Jones potential. This constant is closely associated with explicitly noncentral interactions. This may be taken as an indication that deformation of the outer electron wave functions of the neon atoms in a compressed crystal is causing a significant appearance of noncentral forces. Further experiments on higher density crystals should be of interest.

C. Phonon Energy Shifts

Because of the magnitude of higher-order terms in the expansion of the 6-12 potential appropriate for neon, anharmonic effects might be expected to contribute significantly to the lattice dynamics. One set of measurements bearing directly on this point has already been considered in Sec. III, where the temperature dependence at constant volume of a neutron group width was discussed. In the present section attention is given to other constant-volume measurements in which phonon energy shifts were examined over the temperature range 4.7–25°K. In addition, by comparing phonon measurements at 4.7°K for Ne(A) and Ne(B), where the sample densities differ by about 4%, average quasiharmonic mode Grüneisen parameters are obtained for the [001] transverse and longitudinal branches.

(*1*) *Temperature effects.* It has been predicted that significant changes should occur in phonon energy for neon as the temperature is increased at constant volume.[20,21] Estimates of shift magnitudes for a temperature increase from 4.7–25°K range from +3–+13%. The calculations of Gillis, Werthamer, and Koehler,[4,5] for example, predict for these temperatures a shift of +5% for phonons in the [001]L branch and +4% for those in the [001]T branch.

The neutron results for phonons on the [001] branches in Ne(B) show that the shifts must, in fact, be smaller than present theory would indicate. Some typical data are displayed in Fig. 4. For the longitudinal branch the average shift on increasing the temperature from 4.7–25°K (approximately $\frac{1}{5}\Theta_D$) for three phonons measured at both temperatures and at the same settings of the spectrometer was (2.3 ± 2.4)%, while for five transverse phonons so measured it was (-2.3 ± 1.3)%. The standard deviations quoted were calculated by assigning to the individual phonons weights which did not allow for possible systematic errors. Systematic errors should have been similar for both phonons in each pair, however, unless the volume of the specimen changed. Measurements showed that the lattice parameter at 4.7°K was equal to that at 25°K to within 1 part in 2000. The quasiharmonic energy change generated by a proportional lattice parameter change of this magnitude would alter the above percentages by 0.8.

It is of interest that a small *decrease* in the [001]T-mode energies is observed with increasing temperature, while all theoretical estimates predict an *increase* in both the transverse- and longitudinal-mode energies. Since all theoretical estimates have been based on a central, two-body intermolecular potential, such a discrepancy may lie either with the potential form or with the anharmonic models used.

The changes in neutron counting rates on going from 4.7–25°K, as reflected in the data shown in Fig. 4, are consistent with the expected temperature dependence of the scattering cross section due to phonon population and Debye-Waller corrections. Calculating the latter with a Debye temperature of 70°K, one finds rms vibration amplitudes of 0.16 Å at 4.7°K and 0.20 Å at 25°K, or 5.1 and 6.5% of the nearest-neighbor separation, respectively. The amplitude magnitudes and the smallness of the change indicate the importance of the zero-point motion at both temperatures. Here

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[19] G. W. Lehman, T. Wolfram, and R. E. deWames, Phys. Rev. **128**, 1593 (1962).
[20] See, for example, discussions in Refs. 4 and 11.
[21] J. L. Feldman and G. K. Horton, Proc. Phys. Soc. (London) **92**, 227 (1967).

TABLE VI. Elastic constants for neon (in 10^{10} dyn cm^{-2}) from the second-nearest-neighbor model.

	Ne(A)	Ne(B) (4.7°K)	Ne(B) (25°K)
c_{11}	1.69±0.05	2.07±0.12	2.45±0.24
c_{12}	0.97±0.04	[a]	[a]
c_{44}	1.00±0.03	1.22±0.03	1.18±0.07
B	1.21±0.04[b]	··· ···	··· ···

[a] c_{12} cannot be deduced from [001] data.
[b] $B=\frac{1}{3}(c_{11}+2c_{12})$.

it should be recalled that the de Boer parameter for neon, $\Lambda=h/\sigma(m\epsilon)^{1/2}$, is 0.59, as compared to 2.7 for He[4] and 0.10 for Kr. The ratio of thermal vibrational energy to total vibrational energy rises from 0.3% at 4.7°K to about 20% at 25°K.

(2) *Volume effects.* As shown by the data displayed in Fig. 5(b), there are pronounced shifts in phonon energies as the unit cell volume of neon is changed at constant temperature from that of Ne(A) to that of Ne(B). By comparing phonon energies with the same values of ζ at 4.7°K, it is possible to determine directly from experimental data values of the microscopic Grüneisen parameters γ_j[22,23] for the [001]T and [001]L branches, assuming the parameters to be constant for each branch. These "mode gammas," which were introduced as anharmonicity parameters in the quasiharmonic theory of the temperature-dependent equation of state for solids, bear the following relation to the Grüneisen gamma:

$$\Gamma_G(T)\equiv\alpha B_T V/C_v=\sum\gamma_j C_{vj}/\sum C_{vj}.$$

In this equation the sums extend over all modes, C_{vj} is the Einstein heat capacity of the jth mode at the observation temperature T, α is the volume coefficient of thermal expansion, B_T is the bulk modulus, and C_v/V is the heat capacity per unit volume of the crystal.

The results obtained in the present investigation are: $\gamma=2.9\pm0.5$ for [001]T and $\gamma=4.2\pm0.6$ for [001]L. Although the difference between these values does not have a high level of statistical significance, the ratio of γ[001]L to γ[001]T should be independent of systematic errors in the lattice parameter. The observed ratio of 1.4±0.3 may be compared with the value of 1.21 predicted by Gillis *et al.*[4]

It is not possible to make a comparison of the mode gammas obtained for only two phonon branches with the thermodynamic Grüneisen parameter unless additional assumptions are introduced. One assumption which could be used is that *all* transverse modes had the value $\gamma_T=2.9$ and *all* longitudinal modes had the value $\gamma_L=4.2$. This would lead to a high-temperature limit of the Grüneisen parameter $\Gamma_\infty=\frac{2}{3}\gamma_T+\frac{1}{3}\gamma_L=3.3$, which can be compared with a maximum of about 2.9 found by Batchelder *et al.*[11] for the thermodynamic Grüneisen parameter. In their work the maximum appeared at $T/\theta\sim0.2$ and Γ dropped precipitously at temperatures above this. This anomalous decrease was apparently related to an abnormally large decrease in the value of the bulk modulus at temperatures higher than $T/\theta\sim0.2$.

D. Miscellaneous Calculations

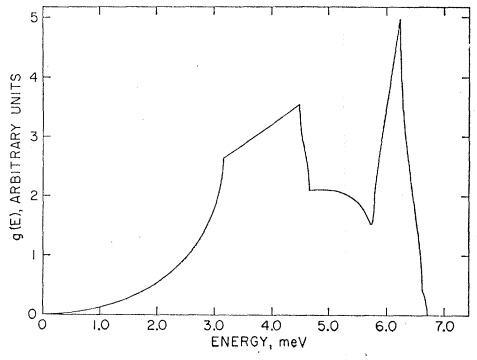
The results of the force constant analysis discussed above in Sec. IV A can be used as a basis for calculating various quantities used in describing the physical properties of neon. Some calculations carried out in the present investigation are discussed briefly here.

By considering the long-wavelength limit the "neutron" elastic constants can be derived from the interplanar force constants. Table VI shows the results for Ne(A) at 4.7°K and for Ne(B) at both observation temperatures. The limited data for Ne(B) did not permit determination of C_{12} and also the accuracy of the values obtained for C_{11} and C_{44} is not high. For Ne(A) it may be noted that $C_{12}\sim C_{44}$. For a static lattice with purely central forces and no applied stresses, this equality would be exact. Although the "neutron" elastic constants are likely to be different from either the isothermal or adiabatic elastic constants,[24] it is of interest to compare the neutron compressibility, $B^{-1}=0.83\times10^{-10}$ cm^2 dyn^{-1}, with the isothermal value obtained by Batchelder *et al.*,[11] 0.90×10^{-10} cm^2 dyn^{-1}. Using the results of the third-nearest-neighbor mode leads to a neutron compressibility, $B^{-1}=0.89\times10^{-10}$ cm^2 dyn^{-1}, in Ne(A).

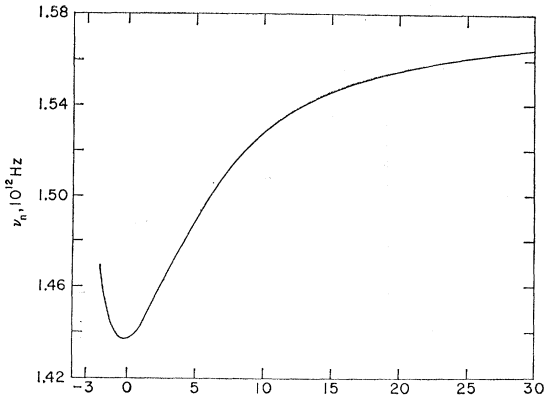
The phonon density of states in energy was obtained from the force constants by employing the method of Gilat and Raubenheimer.[25] The curve for the second-nearest-neighbor model is shown in Fig. 7(a). The smooth curve was obtained from a histogram based on a channel width of 10^9 Hz and the number of mesh points in the irreducible zone was 10 007.

Stedman *et al.*[26] have shown experimentally that the process of Gilat and Raubenheimer can be inadequate when the interatomic force constants are determined from dispersion curves only along symmetry directions. This is especially true when the number of force constants necessary to fit the data is large; hence, large correlations exist between the parameters. In such a case, the good fit obtained along the symmetry directions may belie a spurious behavior which obtains in off-symmetry directions. In the present instance, note may be made of the fact that $g(E)$ contains Van-Hove-type singularities[27] at 4.49 and 6.24 meV, which are paramountly determined at points in the zone where

[22] T. H. K. Barron, Ann. Phys. (N. Y.) **1**, 77 (1957); Phil. Mag. **46**, 729 (1955).
[23] W. B. Daniels, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 273.
[24] R. A. Cowley, Proc. Phys. Soc. (London) **90**, 1127 (1967).
[25] G. Gilat and L. J. Raubenheimer, Phys. Rev. **144**, 390 (1966); Oak Ridge National Laboratory Report No. TM1425 (unpublished).
[26] R. Stedman, L. Almqvist, and G. Nilsson, Phys. Rev. **162**, 549 (1967).
[27] L. Van Hove, Phys. Rev. **89**, 1189 (1953).



(a)



(b)

FIG. 7. (a) Density of states in energy for phonons in neon based on the second-nearest-neighbor model using the data from Ne(A). (b) Debye frequencies derived from the nth moment of the frequency distribution obtained from the same model.

no measurements were made. The singularity at 4.49 meV is in fact the W_2' mode,[28] while that at 6.24 meV is due to the highest-energy surface at (0.8, 0.26, 0.26). In retrospect, measurements at these two points would have solidified the $g(E)$ curve.

The moments M_n, and associated Debye frequencies ν_n,[29] of the frequency distribution, have been calculated for $-3<n\leq 30$ from

$$M_n=\int \nu^n g(\nu)d\nu, \qquad n>-3$$

$$\nu_n=[\tfrac{1}{3}(n+3)M_n]^{1/n}, \quad n\neq 0 \text{ or } -3$$

$$\nu_0=\exp\left[\frac{1}{3}+\int g(\nu)\ln\nu d\nu\right],$$

$$\nu_{-3}=(k_B/h)\Theta_D(0°\text{K})=(3/a)^{1/3},$$

[28] Notation after L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[29] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).

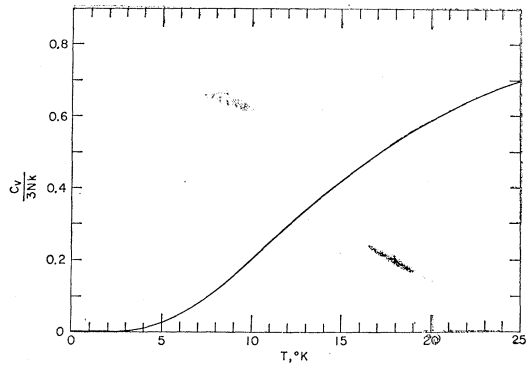


FIG. 8. Lattice specific heat for neon, based on the same model as Fig. 7.

where a is the coefficient of ν^2 in the expansion of $g(\nu)$ at low frequencies. The values of ν_n for the second-nearest-neighbor model are displayed in Fig. 7(b).

The lattice specific heat $C_V(T)$ was calculated from the expression

$$\frac{C_V(T)}{3Nk}=\int_0^\infty \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} g(\nu)d\nu$$

and the corresponding Debye temperature $\Theta_D(T)=h\nu_m/k$ was obtained by equating this value of $C_V(T)$ to the Debye expression

$$\frac{C_V(T)}{3Nk}=\frac{3}{\nu_m{}^3}\int_0^{\nu_m} \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\nu^2 d\nu,$$

ν_m being the value of the Debye cutoff frequency. The results are shown in Figs. 8 and 9. Debye temperatures can also be calculated by equating other thermodynamic functions to those of an ideal Debye solid or obtained from the Debye-Waller factor through the mean-square displacement of the atoms. These methods depend on

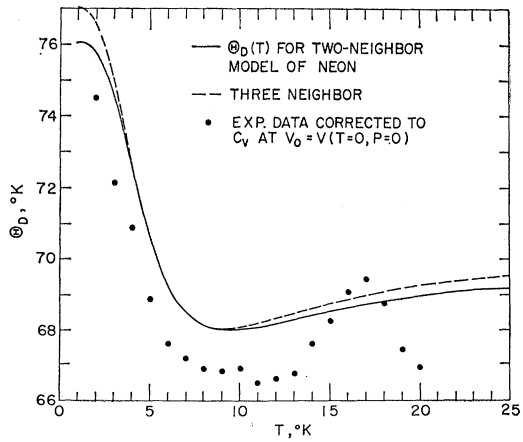


FIG. 9. Heat-capacity Debye temperatures from dispersion curves and averaged heat-capacity (C_p) measurements by Fenichel and Serin (Ref. 31) and by Fagerstroem and Hollis Hallett (Ref. 30).

differently weighted sums over the density of states and so give different values of $\Theta_D(T)$. Figure 9 also shows the values of $\Theta_D(T)$ based on experimental heat-capacity data obtained by Fagerstroem and Hollis Hallett[30] and by Fenichel and Serin[31] after correction to conditions appropriate to Ne(A) by a quasiharmonic shift (cf. Ref. 11).

V. CONCLUDING REMARKS

The results of the neutron scattering experiments on crystalline neon have shown that the lattice dynamics can generally be explained quite well in terms of short-range two-body forces. There were indications in the Ne(B) data that noncentral forces may contribute significantly to the dynamical behavior in compressed crystals, although further investigation would be required for this to be well established. Zero-point motion clearly plays a significant but not a preponderant role in the dynamics. Comparison of data collected at the same temperature but at different densities permitted the determination of microscopic Grüneisen parameters directly from experimental data. The accuracy was not high, but the values obtained were quite reasonable. With the high resolution available in the experiments, it had been hoped that quantitative information might be obtained on phonon lifetimes through observation of broadening of neutron group widths on raising the temperature from 4.7 to 25°K. Since no broadening was observable, it was possible only to place a lower limit on lifetimes. Recent calculations of phonon lifetimes in rare gases[32,33] indicate that values measurable by neutrons should occur only near zone boundaries. An experimental determination of these lifetimes as a function of temperature will be forthcoming. The results least expected in the neutron study were in the phonon shifts with temperature at constant volume. These not only disagree numerically with existing theory, but the sign is opposite to that of all theoretical estimates in the case of the [001] transverse mode energies. Molecular dynamic calculations utilizing the Lennard-Jones potential have recently been made on neon which reportedly demonstrate the importance of anharmonicity and give dispersion results in agreement with the present experiment.[34] A full report of this work is not yet available.

ACKNOWLEDGMENTS

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