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Measurements of Lattice Constant, Thermal Expansion, and Isothermal Compressibility of Neon Single Crystals*

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Single crystals of 99.995% purity neon were grown by directional solidification from the liquid, and the x-ray lattice constant was measured by means of a rotating-camera method. The volume coefficient of thermal expansion was determined over the interval 2.5 to 23.9°K with a precision ranging from 5 ppm $°K^{-1}$ at low temperatures to 18 ppm $°K^{-1}$ at the highest temperature. The lattice constant extrapolated to 0°K is 4.46368 ± 0.00009 Å*. Lattice-constant measurements of a crystal under hydrostatic helium pressure gave values of the isothermal compressibility over the temperature range 4.2 to 20.6°K. The compressibility extrapolated to 0°K is $(0.89\pm0.02)\times10^{-10}$ $\text{cm}^2\text{dyn}^{-1}$. This result is compared with the predicted values of several theoretical models. The isothermal compressibility and the volume coefficient of thermal expansion are combined with the heat capacity at constant pressure to determine the temperature variation of the thermal Grüneisen parameter and the caloric Debye characteristic temperature. Existing theoretical treatments of the lattice dynamics of neon appear to be inadequate at finite temperatures.

A SYSTEMATIC study of the noble-gas solids should make a valuable contribution to the understanding of crystal lattices and crystal dynamics. These solids consist of spherically symmetric atoms crystallized into a face-centered cubic lattice that is transparent and nonconducting. These properties make the noble-gas crystals more amenable to theoretical treatment than most other solids, and it should be possible to construct theoretical models which closely approximate the real crystals. Most theoretical studies have used a single model to represent all the solids and have substituted appropriate mass and force constants (or approximate atomic wave functions) to derive the properties of a specific solid. Knowledge of a wide range of physical properties for all the noble-gas solids should facilitate realistic comparison and evaluation of these models. For example, estimates of the relative importance of zero-point vibrations, anharmonicity, and many-body effects have varied considerably.

Neon, with the lightest atomic mass of the noble gases which crystallize under their own vapor pressure, is a particularly interesting solid to study. Extensive review articles[1–4] show that most workers have concentrated their efforts on argon and that few accurate experiments have been performed on solid neon. Neither measurements on single crystals nor attempts to grow them have been reported. In continuation of work on argon,[5] we wish to report extensive x-ray measurements on single crystals of neon. The lattice constant, thermal expansivity, and isothermal compressibility have been measured over a wide temperature range.

X rays were first used in 1930 to determine the structure and lattice constant of solid neon by de Smedt and co-workers[6] who investigated a polycrystalline specimen at 4.2°K. Henshaw[7] performed similar measurements in 1958 using elastic neutron scattering. Curzon and Pawlowicz[8] have shown transmission electron diffraction of solid neon to be possible. Accurate x-ray measurements of the lattice constant between 4.2 and 24°K were made by Bolz and Mauer[9] in 1962. The limitations of their powder diffractometer prevented accurate calculation of the thermal expansivity. The compressibility of solid neon was measured by Stewart[10] at 4.2°K using a piston-displacement technique. His accuracy was limited by the residual friction inherent in the method.

We have used a single-crystal back-reflection x-ray camera of high accuracy (15 ppm in the lattice constant and 7 ppm for relative expansion) to determine the neon lattice constant at different temperatures and pressures. The camera was sufficiently sensitive that above 15°K the accuracy of the expansion measurements was limited by temperature uncertainty (±0.01°K) rather than by possible camera errors. The volume coefficient of thermal expansion has been determined with an accuracy, above 5°K, comparable to or better than that of available heat-capacity mea-

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[1] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).

[2] A. C. Hollis Hallett, in *Argon, Helium and the Rare Gases*, edited by G. A. Cook (Interscience Publishers, Inc., New York, 1961), Vol. I, pp. 313–385.

[3] G. Boato, Cryogenics **4**, 65 (1964).

[4] G. L. Pollack, Rev. Mod. Phys. **36**, 748 (1964).

[5] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

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[7] D. G. Henshaw, Phys. Rev. **111**, 1470 (1958).

[8] A. E. Curzon and A. T. Pawlowicz, Proc. Phys. Soc. (London) **85**, 375 (1965).

[9] L. H. Bolz and F. A. Mauer, in *Advances in X-Ray Analysis*, edited by W. M. Mueller and M. Fay (Plenum Press, Inc., New York, 1963), Vol. 6, pp. 242–249.

[10] J. W. Stewart, Phys. Rev. **97**, 578 (1955); J. Phys. Chem. Solids **1**, 146 (1956).

surements.[11,12] Similar accuracy has been achieved in the determination of the isothermal compressibility at 4.25°K. At higher temperatures the compressibility measurements were less accurate with the error limits reaching 10% at 20.5°K, the limit of our compressibility measurements. These new values permit a greatly improved compilation of those thermodynamic properties which have been predicted from various theoretical models. Specific comparison is made with the calculations of Horton and Leech,[13] Barron and Klein,[14] and Leech and Reissland,[15] and use is made of a model developed by Feldman, Horton, and Lurie.[16] The limitations imposed by the specific interatomic potentials used in the calculations and the inadequate data on the high-temperature compressibility prevent the formulation of a completely clear picture. Indications are, however, that anharmonic models of the neon lattice are more representative of the real crystal than previous theoretical treatments.

I. EXPERIMENTAL METHOD

Neon single crystals were grown using the same techniques which had proved successful in argon crystal growth.[17] Cylindrical specimens (3 mm diam×24 mm) were grown in a Mylar tube by progressive solidification from the melt at growth rates not exceeding 2 mm h^{-1}. To prevent thermal straining, the crystal was separated from its container by evaporation of a few tenths of a millimeter from the crystal surface. The neon gas was supplied by Air Reduction Company with a stated purity greater than 99.995%. Their analysis showed that the only detectable impurity was helium, present in the 30-ppm range.

The special cryostat[18] used in the argon investigations required almost no adaptation for the neon experiments. Temperature measurement was improved by using an encapsulated germanium resistance thermometer over the entire working range. The U. S. National Bureau of Standards calibrated this thermometer on the NBS Provisional Scale 2–20 (1965) between 2 and 20°K.[19] A platinum resistance thermometer, calibrated on the NBS scale, was used as a calibration standard at higher temperatures. A second germanium thermometer was calibrated against the first for use in the compressibility experiments. Helium exchange gas was used in the specimen chamber to minimize any differences between thermometer and crystal temperatures. The resistance of the germanium thermometer was continuously recorded by a potentiometer and dc amplifier system during the lattice-constant measurements. The average temperature of a measurement could be obtained with a precision of 0.001°K by graphical integration of the record, despite fluctuations of up to 0.03°K in some cases. We estimate that our temperature scale represents the crystal temperature to ±0.01°K from 2 to 20°K and to ±0.02°K from 20°K to the triple point. Incident x rays may heat the crystal but a lattice expansion determination near 10°K, using only $\frac{1}{6}$ the usual x-ray power, indicated no measurable irregularity.

Compressibility measurements were made by hydrostatically compressing the crystal with purified helium gas up to pressures of 8 bars. Pressure was measured on a test gauge which had been calibrated to ±0.03 bar by a dead-weight tester.

Lattice constants were determined by an oscillating back-reflection x-ray camera[20] which utilizes a very large specimen-to-film distance (~60 cm) to obtain high sensitivity. Characteristic radiations of Co and

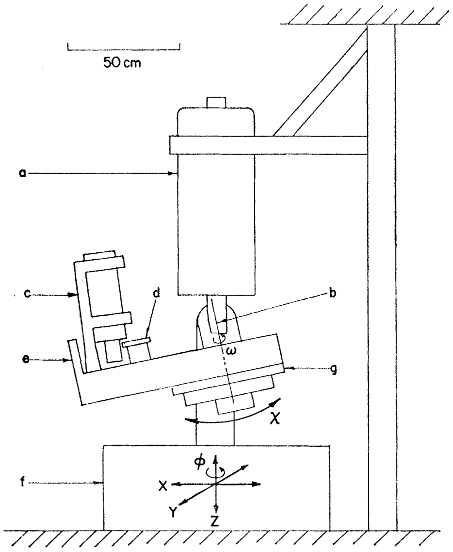

FIG. 1. Schematic diagram of the x-ray camera in operation. The rigid-tail cryostat, a, is used to grow the crystal and retain it fixed at b. X-rays from the tube c are formed into a beam by the collimator d. Diffraction peaks from the crystal at b are recorded on film at e. The camera is positioned by the base f which provides translational motion (x,y,z) as well as rotation about the vertical crystal axis (ϕ). A massive arm inclines the oscillation table g about an axis (χ), perpendicular to the crystal axis. The table g enables the camera to oscillate (ω) at a uniform rate about the diffraction maxima.

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[11] H. Fenichel and B. Serin, Phys. Rev. **142**, 490 (1966).

[12] C. H. Fagerstroem and A. C. H. Hallet, in *Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), Vol. 9, p. 1092. We are indebted to these authors for a table of their smoothed C_p values.

[13] G. K. Horton and J. W. Leech, Proc. Phys. Soc. (London) **82**, 816 (1963).

[14] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) **85**, 533 (1965).

[15] J. W. Leech and J. A. Reissland, Phys. Letters **14**, 304 (1965); Discussions Faraday Soc. **40**, 123 (1966).

[16] J. L. Feldman, G. K. Horton, and J. B. Lurie, J. Phys. Chem. Solids **26**, 1507 (1965).

[17] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, J. Appl. Phys. **36**, 2682 (1965).

[18] O. G. Peterson and R. O. Simmons, Rev. Sci. Instr. **36**, 1316 (1965).

[19] H. H. Plumb and G. Cataland, Science **150**, 155 (1965).

[20] D. N. Batchelder and R. O. Simmons, J. Appl. Phys. **36**, 2864 (1965).

Cu were used with (422) and (440) planes, respectively, to obtain Bragg angles in the range 75.0 to 79.0 deg. Exposure times varied from 10 min at 4.2°K to 45 min in the vicinity of the triple point (24.55°K). Figure 1 shows a general view of the relation between the camera and the cryostat. Angular and linear adjustments of the camera permitted it to be correctly orientated with respect to the crystal, which was never moved during the experiments.

II. RESULTS AND COMPARISONS

A. Lattice Constants

Measurements on five separate neon crystals[21] resulted in a neon lattice constant of 4.46377 Å* at 4.25°K, with small corrections made for absorption and refraction. The root-mean-square (rms) deviation for the five crystals was 0.00008 Å*. Application of our smoothed thermal expansion yields an extrapolated value for the 0°K lattice constant of 4.46368 Å*.

Table I summarizes published values of neon lattice constants at 4.25°K. Our values at all temperatures are in essential agreement with those of Bolz and Mauer,[9] being just outside the substantially larger limits set by ther claimed accuracy. Henshaw's value[7] is smaller than the present work by nearly the same proportion that his argon value[7] is smaller than our argon value,[20] which suggests that his principal error was in his neutron wavelength.

The densities shown in Table II were obtained from the present lattice-constant and expansion measurements, using a value of 20.183 gm mole^{-1} for the molecular weight. The possible difference between the Å* unit[22] and the angstrom is negligible for the purpose of the table.

Table I. Comparison of published values for the neon lattice constant at 4.25°K.

Experiment	Method	Error (Å*)	Lattice constant (Å*)
Present work	Single-crystal x-ray camera	±0.00008	4.46377
Bolz and Mauer[a]	X-ray powder diffractometer	0.001	4.462
Henshaw[b]	Neutron powder diffractometer	0.004	4.429
Curzon and Pawlowicz[c]	Electron diffraction	0.011	4.456
De Smedt *et al.*[d]	X-ray powder camera	...	4.53

[a] Reference 9.
[b] Reference 7.
[c] Reference 8; value corrected from 7°K.
[d] Reference 6.

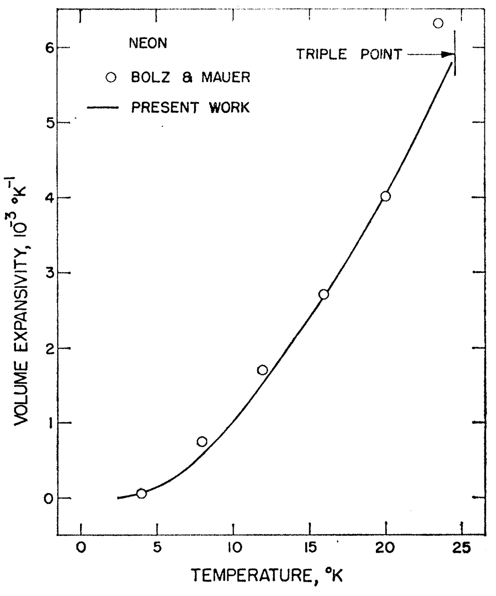

Fig. 2. Volume coefficient of thermal expansion of neon. The values of Bolz and Mauer (Ref. 9) are included for comparison.

B. Thermal Expansion

Table II gives smoothed values of $\Delta a/a_0$, the total relative lattice-constant expansion referred to the value extrapolated to 0°K. These values and the actual data points which appear in the Appendix refer to the neon crystal in equilibrium with its vapor. The measurements were made on one crystal with increasing temperature except for one return to 4.2°K after 10.4°K was attained. No irreversibility was observed in this cycling. The data were all taken within 45 h since substantial migration of specimen material could result from the high vapor pressure if the crystal were maintained at elevated temperatures for longer periods of time. The smoothed values were obtained from least-squares computer fits of the data points to various low-order polynomials. The mean absolute deviation of the individual data points from the final smoothed function was 5 ppm for 35 points below 15°K and 16 ppm for 17 points above 15°K. The increase in the mean deviation above 15°K can be directly related to the uncertainty in temperature.

Values for the coefficient of volume thermal expansion β were obtained from the derivatives of the polynomials used to smooth $\Delta a/a_0$ and are given in Table II. All values in the table apply to neon in equilibrium under its saturated vapor pressure. We note that values for β at zero pressure would be significantly different at high temperatures.

Figure 2 compares the present β with that obtained by Bolz and Mauer.[9] They did not estimate their error; because they quoted their results to only two significant figures, the agreement is somewhat fortuitous. Pollack[4] has reported other values taken from their expansion

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[21] D. N. Batchelder, D. L. Losee, and R. O. Simmons, in *Crystal Growth*, edited by H. S. Peiser (Pergamon Press, Inc., New York, 1967), p. 843.

[22] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

TABLE II. Smoothed values of some thermodynamic functions of crystalline neon versus temperature T. All values apply to solid at the saturated vapor pressure. Linear expansion $\Delta a = a(T) - a_0$, where a_0 is the lattice constant extrapolated to 0°K; x-ray density ρ; coefficient of volume thermal expansion β; isothermal compressibility χ; isobaric heat capacity C_p; entropy corrected to volume at 0°K, S_0; isochoric heat capacity C_V.

T (°K)	$10^4\ \Delta a/a_0$[a]	ρ[a] (gm cm^{-3})	$10^4\ \beta$[a] (°K)$^{-1}$	$10^{10}\ \chi$[a] (cm^2 dyn^{-1})	C_p[b] (J mole^{-1} deg^{-1})	S_0[c] (J mole^{-1} deg^{-1})	C_V[d] (J mole^{-1} deg^{-1})
3	0.01±0.07	1.5072±0.0001	0.18±0.05	...	0.134	0.045	0.134
4	0.13	1.5072	0.60	0.90±0.02	0.347	0.110	0.347
5	0.45	1.5070	1.38	0.90	0.750	0.225	0.749
6	1.08	1.5068	2.46	0.91±0.04	1.355	0.413	1.350
7	2.13	1.5063	3.93	0.92	2.14	0.675	2.13
8	3.74	1.5056	5.73	0.92	3.14	1.020	3.10
9	6.02	1.5045	7.86	0.93±0.06	4.27	1.44	4.19
10	9.02±0.10	1.5032	10.17±0.07	0.94	5.51	1.94	5.36
11	12.91	1.5015	12.69	0.95	6.91	2.50	6.66
12	17.52	1.4994	15.39	0.96±0.08	8.29	3.12	7.89
13	23.13	1.4968	18.18	0.98	9.67	3.77	9.08
14	29.68	1.4939	21.09	1.00	10.95	4.46	10.10
15	37.29±0.15	1.4905	24.09±0.10	1.03±0.10	12.3	5.15	11.1
16	45.84	1.4867	27.00	1.07	13.5	5.87	12.0
17	55.30	1.4825	29.97	1.13±0.12	14.8	6.60	12.9
18	65.77	1.4779	33.12	1.24	16.1	7.37	13.9
19	77.45	1.4728	36.54	1.40	17.5	8.16	15.0
20	90.34	1.4671	40.11±0.14	1.62±0.15	18.9	9.01	15.9
21	104.50	1.4210	43.86	...	20.5	...	...
22	119.97	1.4543	47.64	...	22.3	...	...
23	136.80	1.4470	51.54	...	24.1	...	...
23.5	145.73±0.25	1.4432	...	...	...	...	...

[a] Present x-ray diffraction work. Error in the density is estimated maximum possible systematic error including uncertainties in the x-ray wavelength and in x-ray camera geometry. Error in other quantities is estimated from the scatter in the data points and the uncertainty in temperature measurement.

[b] Data are means of smoothed values from Refs. 11 and 12. These references disagree by amounts up to 4% at certain temperatures. The error in Ref. 11 values is estimated by the authors at ±2%.

[c] Calculated from C_p values, with a further correction to the volume at 0°K, V_0, by the term $3V_0\beta\Delta a a^{-1}\chi^{-1}$. Errors including uncertainty in χ rise to ±0.28 J mole^{-1} deg^{-1} at 20°K.

[d] Calculated from the relation $C_V = C_p - \beta^2 T \rho^{-1} \chi^{-1}$. Errors including the uncertainty in β and χ rise to ±1.6 J mole^{-1} deg^{-1} at 20°K.

data which differ considerably from our results. We note that the error limits for our results are too small to be shown clearly in the figure.

C. Compressibility

A value for the isothermal compressibility χ of neon at 4.25°K resulted from 24 different lattice-constant measurements taken between 0 and 8 bars. Most measurements were taken with decreasing pressure but recycling twice to high pressure reproduced the original data within the expected experimental scatter. Figure 3 displays the data and a straight line which was fitted to the points by a least-squares method. The isothermal compressibility calculated from this slope is $(0.899 \pm 0.010) \times 10^{-10}$ cm^2 dyn^{-1}, where the error is the standard deviation of the slope. The extrapolated value of Stewart[10] at 4.2°K lies just outside the combined limits of possible systematic error and is not in serious disagreement.

We note that all lattice parameter values shown in Fig. 3 refer to a crystal in contact with helium, and, further, that this lattice constant extrapolated to zero pressure is about 0.00018 Å* larger than the mean value for five crystals never exposed to helium.[21] However, the data of Fig. 3 were obtained from a crystal of high perfection (Spec. 8 of Ref. 21) which apparently had a lattice constant larger than the mean. The existence of a helium effect as observed in argon[5] and krypton[23] is therefore in doubt. Such a possible effect on the lattice parameter, if present, is very small, and we suppose that any effect of helium on the compressibility is also small.

Above 4.25°K, temperature instabilities prevented an isothermal type of measurement, but we found it possible to measure the isobaric thermal expansion at approximately 8 bars, up to a temperature 20.6°K.

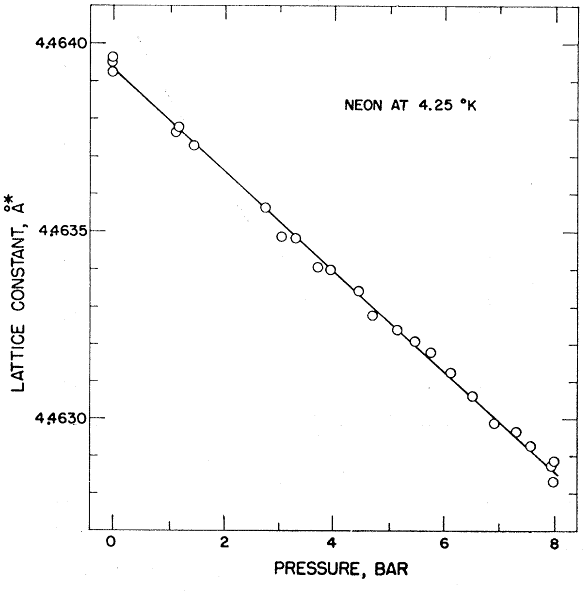

FIG. 3. Pressure variation of the lattice constant of neon at 4.25°K. The straight line was least-squares fitted to the data and corresponds to a volume compressibility of 0.90×10^{-10} cm^2 dyn^{-1}.

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[23] A. O. Urvas, D. L. Losee, and R. O. Simmons, J. Phys. Chem. Solids (to be published).

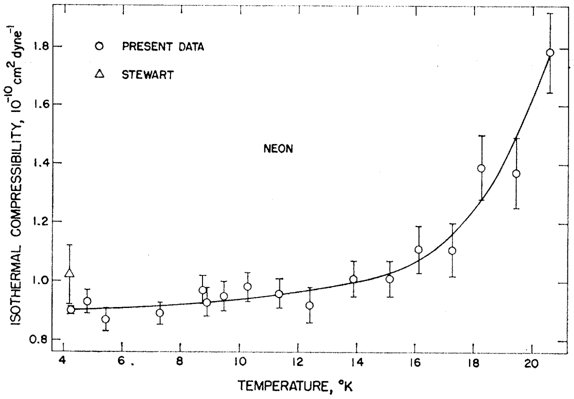

FIG. 4. Temperature dependence of the isothermal compressibility of neon. The single value of Stewart (Ref. 10) at 4.2°K was obtained by extrapolation from high pressure. The bars show the estimated possible systematic error.

Individual expansion values were then compared with the smoothed thermal-expansion results at zero pressure to obtain $\chi(T)$. We assumed that any helium contact effect was temperature- and pressure-independent. Figure 4 shows the data and a smoothed curve. A slight temperature dependence of χ is apparent at 4.25°K; an extrapolated value of $(0.89\pm0.02)\times10^{-10}$ cm^2 dyn^{-1} at 0°K is reasonable.

D. Elastic Wave Velocities

Fenichel and Serin[11] give the value (74.6±1.0)°K for the characteristic temperature at 0°K,

$$\Theta=\frac{h}{k}\left[\frac{4\pi V}{9N}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\right]^{-1/3}, \qquad (1)$$

where v_l and v_t may be regarded as longitudinal and transverse elastic wave velocities, respectively, in polycrystalline material. For such material, the relation

$$\chi(0)^{-1}=\rho(v_l^2-4v_t^2/3), \qquad (2)$$

where ρ is the density, together with our extrapolated value given above, then yields values at 0°K for these velocities of $v_l=(1131\pm14)$ m sec^{-1} and $v_t=(633\pm9)$ m sec^{-1}. The corresponding Poisson ratio is 0.27 ± 0.01 for such an assumed isotropic material.

III. DISCUSSION

The lattice dynamics of the face-centered cubic lattice has been extensively developed for the case in which the atoms interact with a central two-body potential. Applications of the pair-potential lattice models to noble-gas solids have had some success,[13,14] notably in predicting the compressibility at 0°K and the relative temperature variation of the caloric Debye characteristic temperature for argon.[5] Crystalline neon should be a more stringent test for the model, since the amplitudes of atomic vibrations are substantially larger.

This comparison is limited, unfortunately, by insufficient knowledge of the interatomic potential. The long-range part of the attractive interaction for low atomic density has been established,[24] but no model-independent determination of the potential has been made at distances characteristic of nearest-neighbor atoms in the solid. Furthermore, it is possible that many-body forces play a significant role in the crystal.[25] The potential which has been frequently used is the Lennard-Jones *m-n* type,

$$\phi(r)=\frac{\epsilon}{n-m}\left[m\left(\frac{r_0}{r}\right)^n-n\left(\frac{r_0}{r}\right)^m\right] \quad (n>m), \qquad (3)$$

where r is the internuclear distance and ϵ and r_0 are parameters usually fixed by experimental quantities. This potential has the virtue of being relatively easy to use in lattice calculations, even though its resemblance to the interaction between noble-gas atoms is still uncertain.[25–27]

Many calculations on models specifically representing solid neon at 0°K [14,28–31] or at finite temperature[13,32,33] have been published. Where they employ potential parameters ϵ and r_0 fixed only from gas-phase data or from early lattice-constant measurements, we prefer not to make a detailed comparison between their quantitative predictions and the present measurements. It may be worthwhile to recompute the results of such treatments, with redetermined parameters, but we have not done so. Instead we will consider the most recent calculations, primarily of the temperature dependences of some thermodynamic functions for neon, and the evidence they give about lattice anharmonicity.

Lattice dynamical treatments of the pair-potential lattice model generally expand the Hamiltonian in powers of coordinates u, the displacements of the atoms from their equilibrium positions. If only terms to u^2 are kept, then the atomic motions may be resolved into noninteracting normal modes of vibration and the model is "harmonic." Thermal expansion and other properties of the real crystal are included by using the "quasi-harmonic" approximation in which vibrations are still harmonic, but the frequencies of normal modes are allowed to be volume-dependent. Strictly speaking, this is an anharmonic effect, but we will reserve the

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[24] For references see E. A. Mason, R. J. Munn, and F. J. Smith, Discussions Faraday Soc. **40**, 27 (1966).

[25] D. L. Losee and R. O. Simmons, Phys. Rev. Letters **18**, 451 (1967).

[26] Various views form the content of Discussions Faraday Soc. **40**, (1965).

[27] Mie-Grüneisen theory also suggests that the simple potential, Eq. (3), is inadequate for solid neon. The relation $E(T)V(0)\times[V(T)-V(0)]^{-1}=Q-bE(T)$, where $E(T)=\int_0^T C_V dT$, accurately describes the neon data between 6 and 20°K, with $Q=5.44$ kJ mole^{-1} and $b=7.2$. But the resulting $m+n=(6b-3)$ of 40 is far larger than the conventional 6+12.

[28] N. Bernardes, Phys. Rev. **112**, 1534 (1958).

[29] L. H. Nosanow and G. L. Shaw, Phys. Rev. **128**, 546 (1962).

[30] W. J. Mullin, Phys. Rev. **134**, A1249 (1964).

[31] T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966).

[32] I. J. Zucker, J. Chem. Phys. **25**, 915 (1956); W. I. Jenkins and J. Walkley, *ibid.* **43**, 3721 (1965).

[33] T. F. Johns, Phil. Mag. **3**, 229 (1958).

word "anharmonic" to describe models which include terms in the Hamiltonian of u^3 and higher orders.

Horton and Leech[13] carried out extensive machine calculations on the pair-potential lattice model for a variety of 6-n potentials and differing numbers of interacting neighbors. Normal-mode dispersion curves were obtained in the harmonic approximation and used to calculate the temperature variation at constant volume of the caloric Debye characteristic temperature Θ^c and the Grüneisen parameter γ.

The thermodynamic properties of a lattice can often be related to moments of the lattice-frequency spectrum. The even moments can be calculated from traces of the harmonic dynamical matrix without recourse to calculating the normal modes. Barron[34] followed this procedure to calculate the temperature dependence of the Grüneisen parameter for the pair-potential lattice model with nearest-neighbor interactions. Barron and Klein[14] extended this type of calculation to nearest-neighbor (1N) and to all-neighbor (AN) models with a 6-12 potential at 0°K. They calculated the strain dependence of the first few even moments and used the results to obtain the elastic constants in the quasiharmonic approximation.

Leech and Reissland[15] also used a 6-12 potential in extending the model of Horton and Leech to the anharmonic approximation. Their Hamiltonian included terms in u^3 and u^4 which were calculated to second and first order in perturbation theory, respectively. They calculated the anharmonic contribution to the free energy and the heat capacity at constant volume. In addition, they were able to establish several points of contact between their mode treatment and the moments approach of Barron and Klein.

The application of the pair-potential lattice model can be made to neon only when appropriate potential parameters have been chosen, for example, for Eq. (3). For $n=12$, the alternative parameter $\sigma=2^{-1/6}r_0$ is convenient. Leech and Reissland[15] and Brown[35] have obtained the two parameters for the harmonic, quasiharmonic, and anharmonic cases by equating the experimental and model values of the lattice constant and heat of sublimation L_0 at 0°K. Their values are given in Table III. For contrast, Table III also shows several other values obtained by investigators who did not necessarily depend on lattice constants to fix their potential parameters. For the latter, some variability is evident, although the resulting de Boer parameters Λ appear less sensitive to differences between fitting schemes.

TABLE III. Lennard-Jones potential parameters for Eq. (3) of text with $n=12$, as obtained by various investigators. The de Boer parameter Λ is $\hbar/\sigma(\sqrt{M}\epsilon)^{1/2}$, where M is the atomic mass.

Investigators	Method	$-\epsilon/k$ (°K)	σ (Å)	Λ
a	Anharmonic model fit to a_0, L_0	36.8	3.144	0.082
a, b	Quasiharmonic model fit to a_0, L_0	35.29	3.113	0.084
c	Corresponding-states law fitted to vapor-pressure ratio of isotopic liquids	37.1	2.67	0.085
d	Fit to L_0, V/V_0 versus p of Stewart	37.4	2.75	0.082
e	Anharmonic model fit to a_0, L_0	36.9	3.129	0.082

[a] Reference 15.
[b] Reference 35.
[c] G. Boato and G. Casanova, Physica **27**, 571 (1961).
[d] Reference 30.
[e] Reference 35.

If the anharmonic approximation best represents the crystal, then it follows that the anharmonic potential parameters most closely represent the actual interatomic potential in the solid, within the restriction of the form of Eq. (3). We will assume therefore that the use of anharmonic-potential parameters in the quasiharmonic model should be a better approximation to the solid than the use of quasiharmonic potential parameters. This may be true in spite of the fact that the model thereby loses some of its self-consistency.

The following sections compare, where possible, the present experimental results with the thermodynamic properties calculated for the pair-potential lattice model in the harmonic, quasiharmonic, and anharmonic approximations. In addition we have investigated the empirical model for anharmonicity proposed by Feldman and co-workers[16] as an alternative approximation to those employed by Leech and Reissland.[15] This model, based on work by Barron,[36] assumes that anharmonic effects can be explained by a relative shift in the frequency of each lattice mode which is proportional to the total quasiharmonic vibrational energy of the lattice e, that is,

$$\Delta\nu/\nu=Ae, \tag{4}$$

where e is in units of $3Nk$, N being Avogadro's number and k the Boltzmann constant. The particular value of A which is appropriate depends upon the thermodynamic function being considered. Unless otherwise noted, A refers below to the entropy frequency shift.

A. Debye Characteristic Temperature

The experimental heat capacity at constant volume for neon may be calculated from existing measurements of the heat capacity at the saturated vapor pressure[11,12] and the present values of β and χ. Smoothed average values are included in Table II. Figure 5 shows the resulting temperature dependence of the caloric Debye temperature Θ^c, which has been corrected to the volume at 0°K using the relation[37]

$$\Theta(V_0)=\Theta(V_T)(\rho_0/\rho_T)^\gamma, \tag{5}$$

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[34] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[35] J. S. Brown, Proc. Phys. Soc. (London) **89**, 987 (1966).

[36] T. H. K. Barron, Discussions Faraday Soc. **40**, 69 (1966); in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 247.

[37] A. Paskin, Acta Cryst. **10**, 667 (1957).

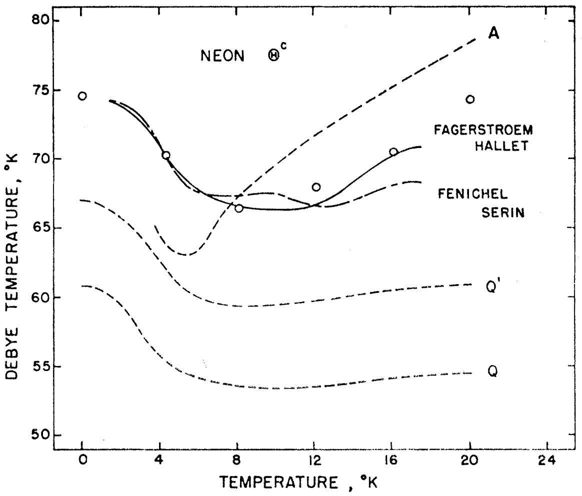

FIG. 5. Temperature dependence of the Debye characteristic temperature obtained from the heat capacity at constant volume. All values have been referred to the crystal volume at 0°K. The experimental curve was calculated from the present results and the measurements of References 11 and 12. The theoretical curves were predicted by Leech and Reissland (Ref. 15); Q, quasiharmonic model with quasiharmonic potential constants; Q′, quasiharmonic model with anharmonic potential constants; A, anharmonic model (Ref. 38). Circles are values calculated on the basis of the model of Feldman and co-workers (Ref. 16), with the leading anharmonic coefficient near 5×10^{-3} deg^{-1}.

where γ is the thermodynamic Grüneisen parameter. We note that there is some apparent disagreement between the measurements of Fenichel and Serin[11] and of Fagerstroem and Hollis Hallet.[12] The possible difference, however, lies very near the sum of the estimated errors of these authors. We have terminated the curves at 18°K because above this temperature the volume correction, Eq. (5), becomes increasingly uncertain.

The dashed lines in Fig. 5 show the results of the 6-12 pair-potential calculations by Leech and Reissland[15,38] for different approximations: The curve marked Q is their quasiharmonic model with their quasiharmonic potential parameters given in Table III; the curve Q' is the same model with their anharmonic parameters. Curves A and Q' may be extrapolated below 4°K to a value at 0°K determined by the parameters of Leech and Reissland in the models of Barron and Klein.[14] (The latter authors showed that to first order in perturbation theory the elastic Debye temperature at 0°K, Θ_0^{el}, which they calculated in the quasiharmonic approximation, was equal to Θ_0^c in the anharmonic approximation.)

There are three points to note from the curves. First, Θ^c for the quasiharmonic model is much closer to the experimental results when anharmonic potential parameters are used. Second, the shape of the experimental Θ^c is very similar to that of the quasiharmonic model. This is in striking agreement with the prediction of Barron[36] that thermodynamic properties of even very anharmonic lattices should exhibit approximately the same temperature dependence as a quasiharmonic model over a temperature region, where the thermal vibrational energy is much less than the zero-point energy. This is a consequence of interpreting anharmonic effects in terms of a shift in the frequency spectrum. Third, while agreement for the anharmonic model (using Barron and Klein's model) is excellent at 0°K, the finite-temperature anharmonic calculations appear to underestimate the anharmonic contribution below 8°K and to overestimate it at higher temperatures. Since Leech and Reissland found fair agreement for the same model with experimental results for argon, this disagreement may indicate that the model needs to be calculated more accurately to obtain similar agreement with neon experiments.

One may pursue the above second point a bit further in order to estimate a value for A, the leading anharmonic coefficient which appears in Eq. (4). Unfortunately this estimate is sensitive to the particular form of the potential chosen, but with this reservation in mind some consideration of the resulting values is nevertheless worth while.

To obtain an estimate of A, one may compare the experimental value of $\Theta_0^c = 74.6$°K [11] with that predicted by the quasiharmonic model using the Leech and Reissland anharmonic potential constants [$\Theta_0(L) = 67.0$°K, in the notation of Barron and Klein].[14] In the low-temperature limit, the anharmonic (i.e., experimental) characteristic temperature is given by

$$\Theta_0^c = \Theta_0^s = \Theta_0^a \cong \Theta_0(L)(1+\tfrac{3}{8}A\Theta_\infty), \qquad (6)$$

where the Debye approximation has been used for the zero-point energy.[36] We take the appropriate high-temperature limit for the quasiharmonic characteristic temperature from the Q' curve on Fig. 5, $\Theta_\infty = 61.0$°K. The resulting A is 5×10^{-3} deg^{-1}.

Other values of A follow from the comparison of other models with experiment. The range of values thus obtained gives some idea of present uncertainty in the value of A. On the one hand, Fenichel and Serin[11] have shown that improved agreement of reduced values $\Theta_0^* = k\Theta_0^c/\epsilon\Lambda$ versus Λ relations for all noble-gas solids is given by the use of 6-12 (1N) or 6-13 (AN) models. Such models have not been numerically calculated for present experimental data. However, an estimate of the changes to be expected from 6-12 (AN) calculations may be made by scrutiny of the extensive work of Horton and Leech,[13] who treated the various models. The resulting values of A in both cases are about 4×10^{-3} deg^{-1}. On the other hand, a value of A near 10^{-2} deg^{-1} follows from a comparison to the curve Q of Fig. 5 using Eq. (6).

Feldman and Horton[39] have recently evaluated A by calculating the anharmonic contribution to the free energy in the high-temperature limit. They include a

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[38] J. W. Leech and J. A. Reissland (private communication). The results of Ref. 15 have been slightly modified by the inclusion of new potential parameters which are based on the present lattice-constant data.

[39] J. L. Feldman and G. K. Horton (unpublished).

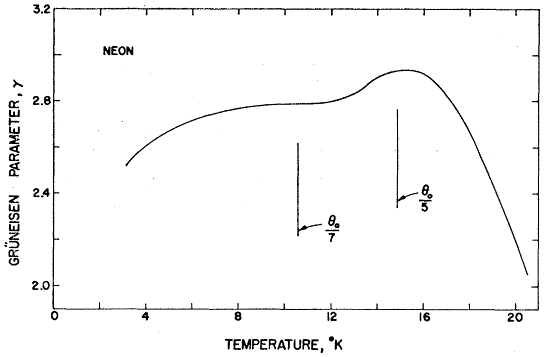

FIG. 6. Grüneisen's thermal parameter, $\gamma=\beta\rho^{-1}C_V^{-1}\chi_T^{-1}$, for solid neon. Error limits are discussed in the text, Sec. II C.

critical analysis of the A values predicted by other models.

To summarize, an uncertainty in A of up to a factor of 2 in either direction seems present, within the framework of existing theoretical models and experimental uncertainty increasing above 18°K.

The relation, Eq. (4), for the frequency shifts leads to an expression for the anharmonic specific heat,[16]

$$C_V^a(T)=C_V^h\left(\frac{T}{1+Ae}\right)[(1+Ae-AcT)(1+Ae)^{-1}]. \quad (7)$$

A given value of A and a quasiharmonic model, as represented for example by curve Q′ in Fig. 5, can then be used to generate anharmonic values of Θ as a function of temperature. Such values are shown in Fig. 5, generated using $A=4.8\times10^{-3}$ deg^{-1}, plotted as circles. Ironically, the results indicate that for such an anharmonic lattice the simple model of Eq. (4) is not a good approximation to the extensive numerical calculation of Leech and Reissland, but in fact does represent the crystal more accurately.

Any conclusions must still be tempered, of course, by the uncertainty of the interatomic potential. We note, for example, that 6-12 (1N) and 6-13 (AN) models (giving $A\sim4\times10^{-3}$ deg^{-1}) might yield somewhat better Θ^c values at higher temperatures when Eq. (7) is applied. Such models also seemed somewhat better than a 6-12 (AN) model to Fenichel and Serin.[11] However, their analysis assumed a law of corresponding states and hence a domination by two-body central forces for all the noble-gas solids, an assumption which has not yet been independently tested in any decisive manner.

B. Compressibility at 0°K

Table 2 of Barron and Klein[14] has been used to obtain values of χ in the harmonic and quasiharmonic approximations, $\chi_0(L)$ and $\chi_0(1)$, respectively, with both quasiharmonic and anharmonic potential constants. Interpolation from the table was made using the experimental value of the reduced volume at 0°K. The various values of χ_0 are tabulated in Table IV to be compared with the present experimental value. The anharmonic potential constants bring the prediction of the quasiharmonic model into excellent agreement with experiment.

TABLE IV. Compressibility of solid neon at 0°K. A comparison of the extrapolated experimental value with lattice dynamical theory. Units are 10^{-10} cm^2 dyn^{-1}.

Model	Potential parameters[a] Quasiharmonic	Anharmonic
Harmonic[b]	1.92	1.40
Quasiharmonic[b]	1.08	0.93
Anharmonic[c]	1.03	0.88
Experiment	0.89±0.02	

[a] Obtained from Ref. 15 for the Lennard-Jones 6-12 potential.
[b] Obtained by interpolation from Table II of Ref. 14.
[c] Correction derived on the basis of the model of Ref. 16.

Table IV also includes anharmonic values of χ_0 which are based on the model of Barron[36] and of Feldman and co-workers.[16] Anharmonic corrections to the quasiharmonic χ_0 are calculated from frequency shifts in the free energy which are assumed to be half as large as those for the entropy used to calculate Θ^c.[16] In this approximation, at $T=0$°K, the free energy is given by

$$F^a(0)=F^h(0)+\tfrac{3}{2}NkAe_z^2, \quad (8)$$

where e_z is the zero-point energy. Assuming a Grüneisen solid we find the anharmonic correction to the bulk modulus is given by

$$(\chi_0^a)^{-1}-(\chi_0^h)^{-1}=3ANke_z^2V_0^{-1}\gamma(2\gamma+1), \quad (9)$$

where A is the same as in Eq. (4), V is the molar volume at 0°K, and γ is an appropriate Grüneisen parameter. This correction term is relatively small so the approximation used to calculate it should not be very important. The effect of this correction to χ_0 is much less than that of using anharmonic potential constants and does not significantly improve the agreement with experiment. Anharmonic corrections to χ_0 have also been considered for 6-m(1N) potential models.[40]

C. Grüneisen Parameter

Another useful thermodynamic quantity for making comparisons with theoretical models is the Grüneisen parameter, $\gamma=\beta VC_V^{-1}\chi_T^{-1}$. We have combined the results of the present measurements with the smoothed heat-capacity measurements listed in Table II to produce the temperature variation of γ shown in Fig. 6. The uncertainty in γ is approximately 6% at 6°K, rises gradually to 12% at 20°K, and rises to 25% at 3°K. The increase at high temperatures is due to uncertainty in χ and at low temperatures to uncertainty in β. The rather sharp drop in γ above Θ/5 is greater than experimental uncertainty but further experimental study will be necessary to determine accurately the magnitude of the decrease.

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[40] J. S. Brown and G. K. Horton, Can. J. Phys. (to be published).

Barron[34] and Horton and Leech[13] have used the pair-potential lattice model in the quasiharmonic approximation to predict the temperature variation of γ at constant volume. The 6-12 (1N) model of Barron predicts a universal curve for the noble-gas solids but the approximations were only expected to be valid for the heavier noble gases. In the high- and low-temperature limits Barron predicted $\gamma_\infty=3.00$ and $\gamma_0=2.85$, respectively, with the principal variation occurring near $\Theta/5$. The present curve, Fig. 6, follows this behavior between $\Theta/5$ and $\Theta/7$ but departs substantially from the prediction outside this narrow region.

The more detailed calculation of Horton and Leech[13] predicts a similar temperature dependence but with γ for neon about 10% higher than for the other noble-gas solids. A comparison of the present γ with that for argon[5] shows this predicted difference in the neighborhood of $\Theta_0/5$, but the uncertainty in γ is nearly as large as the difference. As in the case of argon[5] the value of $m=11$ in the potential of Eq. (3) gives the best agreement for the magnitude of γ between $\Theta_0/5$ and $\Theta_0/7$. We note, however, that such a 6-11 (AN) adjustment of the potential is inconsistent with the 6-12 (1N) and 6-13 (AN) adjustments discussed above in Sec. III B.

None of the harmonic-model variations used by Horton and Leech predicted the decrease in γ for $T>15$°K. No anharmonic calculations have yet been published for neon nor have the anharmonic parameters of neon calculated by Leech and Reissland[15] been used as yet in the quasiharmonic model. A correction to such a quasiharmonic γ^h could be made to obtain γ^a, the anharmonic γ, using the procedure of Feldman and co-workers[16] in the same way that C_V was corrected in Sec. III A. For the correction, with $\gamma=-(V/\nu)d\nu/dV$ and the volume dependence of the vibrational energy given by[41] $de/dV=\gamma(cT-e)/V$, we obtain

$$\frac{\gamma^a-\gamma^h}{\gamma^h}=\frac{Ae-AcT}{1+Ae}, \tag{10}$$

where c is the heat capacity at constant volume in units of $3Nk$. For a constant γ^h this will cause γ^a to decrease with temperature, but if we assume that A is the same as for the entropy frequency shifts, then the decrease would be much less than that observed in the experimental curve. It does not appear that correction of this type can explain the observed temperature dependence of γ. Other effects, for example, explicit strain dependences,[42,43] are probably more important at high temperatures.

IV. CONCLUSION

Comparison of the present experimental results with detailed lattice dynamical calculations shows good agreement with simple models in the low-temperature limit provided anharmonicity is taken into account. At higher temperatures, there are indications that a more exact calculation of the caloric properties is necessary for neon. Experimental and theoretical work on the elastic constants needs to be extended to higher temperatures for a more detailed comparison.

The inadequacy of our present knowledge of the interatomic potential is to be emphasized. Indeed, the use of only a two-body interatomic potential may be questioned. For example, Losee and Simmons[25] measured the equilibrium vacancy concentration in solid krypton and concluded that up to 20% of the total potential energy might be contributed by many-body forces.

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APPENDIX

The x-ray lattice expansion data listed in Table V were obtained for a crystal in equilibrium with its saturated vapor.

TABLE V. Complete thermal-expansion data for natural neon where $\Delta a/a_0$ is the fractional change in lattice constant referred to the extrapolated value at 0°K.

T(°K)	$10^4\ \Delta a/a_0$	T(°K)	$10^4\ \Delta a/a_0$	T(°K)	$10^4\ \Delta a/a_0$
2.51	−0.034	6.580	1.648	15.503	41.632
2.78	0.014	7.172	2.447	16.065	46.438
3.09	0.005	7.545	2.873	16.626	51.880
3.13	0.016	7.951	3.574	17.159	57.162
3.53	0.018	8.412	4.678	17.800	63.434
3.73	0.025	8.841	5.556	18.672	73.388
3.90	0.126	9.320	6.834	19.063	78.001
4.10	0.083	9.924	8.870	19.677	85.755
4.25	0.126	10.456	10.600	19.803	87.363
4.26	0.263	10.928	12.657	20.458	96.812
4.27	0.166	11.551	15.393	20.965	104.098
4.28	0.181	12.076	17.836	21.468	111.715
4.825	0.409	12.858	22.294	21.888	118.237
5.019	0.460	13.274	24.710	22.590	130.036
5.135	0.606	13.538	26.483	23.075	138.071
5.650	0.880	14.203	31.105	23.560	146.617
6.080	1.089	14.611	34.180	23.930	155.100
6.377	1.394	15.061	37.840		

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[41] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (University Press, Oxford, England, 1956), 2nd ed., p. 50.

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