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Isotope Effects in the Lattice Constant and Thermal Expansion of ^{20}Ne and ^{22}Ne Single Crystals*

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Single crystals of ^{20}Ne and ^{22}Ne were grown by directional solidification from the liquid, and the x-ray lattice constants were measured by means of a rotating-camera method. The volume coefficients of thermal expansion were determined over the interval 2.5 to 24.3°K with a precision ranging from 5 ppm $°K^{-1}$ at low temperatures to 18 ppm $°K^{-1}$ at the highest temperature. The lattice constants extrapolated to 0°K are 4.46440 Å* for ^{20}Ne and 4.45589 Å* for ^{22}Ne, within an estimated maximum error 0.00008 Å*. Several current lattice-dynamical models adequately describe the isotopic difference in the lattice constant at 0°K, while at finite temperatures the description is unsatisfactory.

As a means of investigating molecular forces, extensive studies of the effects of isotopic substitution upon the properties of molecules in the gas phase have been carried out by many workers, particularly for the case of deuteration of hydrogen-bonded species. Much less work has been published about the properties of condensed phases. These phases possess both added interest and added complication because for them the question of a suitable dynamical model for the structure is added to the question of the molecular forces. Isotope effects in the structural properties of solids were reviewed by Kogan[1] and some features of isotope effects in phase equilibria were reviewed by Bigeleisen.[2] Interpretation of the large effects observed in solid helium has been complicated by difficulties in the preparation of well-characterized crystals.[3]

Of all solids, neon is perhaps the simplest which shows isotope effects which can be studied quantitatively as a function of temperature. The isotopic dependence of the thermodynamic properties of solid neon has been studied in a number of ways. Recent lattice dynamical studies have included this problem in their development and experimental measurements on polycrystalline aggregates of ^{20}Ne and ^{22}Ne have demonstrated an isotopic dependence of the lattice constant,[4,5] heat capacity,[6] and vapor pressure.[7] X-ray lattice constants of ^{20}Ne and ^{22}Ne were first measured with a powder camera at 4°K by Kogan and co-workers.[4] Bolz and Mauer[5] extended the measurements to the triple point; they obtained increased accuracy with a powder diffractometer. They were unable to detect any isotopic dependence in the thermal expansivity, however.

In an extension of work on argon[8] and natural neon[9] we have measured the lattice constant and thermal expansivity of ^{20}Ne and ^{22}Ne single crystals. We have used a single-crystal x-ray camera with an intrinsic accuracy of 15 parts per million (ppm) in the lattice constant and 6 ppm for lattice expansion. The volume coefficients of thermal expansion were determined with an accuracy sufficient to show clearly the small isotopic dependence. The lowest temperature data were extrapolated to obtain the isotopic difference in the lattice constants at 0°K.

We compare our experimental results with the predictions of several lattice-dynamical models within the framework of a quantum-mechanical law of corresponding states. The isotopic difference in the lattice constant at 0°K is adequately described by several current lattice-dynamical models, while at finite temperatures the description is inadequate.

I. EXPERIMENTAL METHOD

Single crystals of ^{20}Ne and ^{22}Ne were grown by progressive solidification from the melt using the techniques developed for argon and neon crystals.[10,11] The resulting cylindrical specimens (3 mm diam×24 mm high) were free-standing and relatively strain free. The ^{20}Ne and ^{22}Ne gases were supplied with stated isotopic purities of 99.0% (0.10% ^{21}Ne, 0.90% ^{22}Ne) and 99.35% (0.30% ^{21}Ne, 0.35% ^{20}Ne), respectively, by the Mound Laboratory of the Monsanto Chemical Co. The gas was

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[3] J. Wilks, *The Properties of Liquid and Solid Helium* (Clarendon Press, Oxford, England, 1967).

[4] V. S. Kogan, B. G. Lazarev, and R. F. Bulatova, Zh. Eksperim. i Teor. Fiz. **40**, 29 (1961) [English transl.: Soviet Phys.—JETP **13**, 19 (1961)].

[5] 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, p. 242.

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

[9] D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. **162**, 767 (1967).

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[11] 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.

Table I. Comparison of published values for the lattice constants of ^{20}Ne and ^{22}Ne at 4.25°K.

Investigators	Method	Error (Å*)	Lattice constant (Å*) ^{20}Ne	Lattice constant (Å*) ^{22}Ne
Batchelder and co-workers[a]	Single crystal x-ray camera	±0.00008	4.46449	4.45598
Bolz and Mauer[b]	X-ray powder diffractometer	0.001	4.462	4.454
Kogan and co-workers[c]	X-ray powder camera	0.004	4.471	4.455

[a] Reference 11.
[b] Reference 5.
[c] Reference 4.

chemically purified immediately before crystal growth by passage through an adsorption purifier at 78°K.

Temperature regulation in the metal cryostat[12] was better than ±0.05°K during crystal growth and ±0.03°K during measurements. Graphical integration of the chart recorder trace enabled the average temperature of a measurement to be determined with a precision of ±0.001°K. The encapsulated strain-free germanium and platinum resistance thermometers were in close proximity to the specimen; they were calibrated by the U. S. National Bureau of Standards on the NBS Provisional Scale 2–20 (1965) and NBS 1955 scale, respectively. Our temperature scale should represent the crystal temperature to ±0.01°K from 2 to 20°K and to ±0.02°K from 20°K to the triple points.

Lattice constants were determined by an oscillating back-reflection camera[13] which utilizes a large specimen to film distance (~60 cm) to obtain high sensitivity. Characteristic radiations of Co and Cu were used with (422) and (440) planes, respectively, giving Bragg angles in the range of 75° to 79°. Exposure times varied from 10 min near 4°K to 45 min near the triple points.

II. RESULTS AND COMPARISONS

A. Lattice Constants

The results of our lattice constant measurements on ^{20}Ne and ^{22}Ne are shown in Table I. Details of the measurement method and the small correction factors for absorption and refraction are discussed elsewhere.[9,13] Reproducibility of the lattice constants of various natural neon crystals indicated that measurements on single specimens of usual mosaic structure would be sufficient. Application of our smoothed thermal expansions yields extrapolated values for the 0°K lattice constants of 4.46440 Å* for ^{20}Ne and 4.45589 Å* for ^{22}Ne with an estimated maximum possible systematic error of 0.00008 Å*.

Earlier lattice constant measurements on the neon isotopes are also shown in Table I. Our values are in essential agreement with those of Bolz and Mauer,[5] being just outside their substantially larger limits of error.

Table II. Smoothed values of the relative expansion of the lattice constant $\Delta a/a_0$ and of the x-ray coefficient of volume thermal expansion β for crystalline ^{20}Ne and ^{22}Ne. Linear expansion $\Delta a = a(T) - a_0$, where a_0 is the lattice constant extrapolated to 0°K. The β values in the table are for the crystal in equilibrium with its vapor.

T(°K)	$10^4\Delta a/a_0$ ^{20}Ne	$10^4\Delta a/a_0$ ^{22}Ne	$10^4\beta$(°K^{-1}) ^{20}Ne	$10^4\beta$(°K^{-1}) ^{22}Ne
3	0.02±0.07	0.02±0.07	0.18±0.05	0.18±0.05
3.5	0.05	0.05	0.29	0.33
4	0.12	0.13	0.48	0.63
4.5	0.23	0.26	0.83	1.05
5	0.44	0.48	1.29	1.53
6	1.01	1.20	2.42	2.79
7	2.08	2.39	3.96	4.38
8	3.72	4.16	5.91	6.24
9	6.04	6.63	7.97	8.31
10	9.07±0.10	9.78±0.10	10.23±0.07	10.65±0.07
11	12.91	13.72	12.68	13.17
12	17.53	18.54	15.27	15.90
13	23.12	24.33	17.97	18.75
14	29.62	31.11	20.81	21.69
15	37.08±0.15	38.85±0.15	23.67±0.10	24.63±0.10
16	45.50	47.59	26.54	27.63
17	54.84	57.36	29.57	30.66
18	65.29	68.14	32.85	33.72
19	76.91	80.01	36.45	36.99
20	89.79±0.20	93.02±0.20	40.17±0.14	40.47±0.14
21	103.97	107.26	44.13	44.13
22	119.57	122.79	48.39	48.03
23	136.67	139.71	52.92	52.17
24	155.35±0.25	158.09±0.25	57.69±0.18	56.70±0.18
24.5[a]	(165.32)	(167.91)	(60.09)	(59.16)

[a] Extrapolated values.

B. Thermal Expansivity

Smoothed values of $\Delta a/a_0$, the total relative expansion referred to the value of the lattice constant extrapolated to 0°K, are listed in Table II. The data are presented in the Appendix. The ^{22}Ne measurements were made with increasing temperature with one return to 4.2°K after 14°K was reached. With ^{20}Ne, one return was made at 14°K and another at 22°K. No irreversibility in the x-ray lattice expansion was observed during this thermal cycling. The smoothed values of $\Delta a/a_0$ were obtained from least-squares computer fits of the data points to various low-order polynomials. For ^{22}Ne the mean absolute deviation of the individual data points from the final smoothed function was 4 ppm for 34 points below 15°K and 11ppm for 19 points above 15°K. The corresponding values for ^{20}Ne are 4 ppm for 21 points and 13 ppm for 17 points. The increase in the scatter above 15°K can be directly related to the uncertainty of the temperature together with the larger coefficient of thermal expansion.

Values for the coefficients of volume thermal expansion, $^{22}\beta$ and $^{20}\beta$, 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 refer to the crystal

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

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

in equilibrium with its own saturated vapor. The values of β at zero pressure should be significantly higher above 20°K. There may also be an appreciable difference between the present x-ray determinations of β and the bulk values near the triple points due to the creation of vacant atomic sites.[14]

III. DISCUSSION

The thermodynamic properties of the solidified noble gases are often discussed in the framework of a quantum-mechanical law of corresponding states. De Boer[15] has shown that such a law is valid if the atoms in the solid interact through a two-body potential of the form

$$\phi(r)=\epsilon f(r/\sigma)\,, \tag{1}$$

where r is the interatomic separation. The parameters ϵ and σ describe the depth and range of the interatomic potential; the values are usually fixed by comparison of a theoretical model with two or more experimentally determined properties. In this formulation the equation of state can be written in a reduced form which is applicable to all the noble gas solids,

$$P^*=P^*(V^*,T^*,\Lambda^*)\,. \tag{2}$$

The reduced properties are defined by

$$P^*=P\sigma^3/\epsilon\,,\quad V^*=V/N\sigma^3\,,\quad T^*=kT/\epsilon\,,\quad \Lambda^*=h/\sigma(m\epsilon)^{1/2}\,, \tag{3}$$

where N is the Avogadro number (6.023×10^{23} mole^{-1}) and m is the atomic mass. The parameter Λ^* is a measure of the importance of quantum-mechanical effects and the equation of state is often expanded in powers of Λ^*.[16]

Intercomparison between theoretical models which predict reduced equations of state may be difficult since the reduced properties are strongly dependent upon the choice of ϵ and σ. For example, if ϵ and σ are chosen for a particular model on the basis of solid-state or other data then the use of these parameters in another model produces comparisons of dubious value.[17] This particular difficulty can be substantially eliminated if the thermodynamic properties of different isotopes of the same element can be measured. With ϵ and σ fitted to the properties of one isotope, a change in the atomic mass in the model will predict the properties of a different isotope. In this way, models which have different (but, for each, self-consistent) values of ϵ and σ may be compared both with each other and with experiment. The use of a simple central potential with only two parameters is rather unrealistic; it may have the advantage, however, of showing possible essential distinctions between different dynamical models for the crystal. The problem of the appropriate molecular potential is thus somewhat separable from the dynamical problem.[18]

TABLE III. Intermolecular potential parameters used in several models discussed in the text. σ and ϵ are defined in Eq. (4) by $\phi(0)$ and by the well depth, respectively.

Author, model	σ(Å)	$10^{16}\epsilon$(erg)
Hillier, Islam, and Walkley,[a] cell	2.78	50.53
Brown,[b] AN quasiharmonic	2.774	48.73
AN anharmonic	2.788	50.64
1N quasiharmonic	2.691	68.83
1N anharmonic	2.701	72.09
Bernardes,[c] cell	2.74	50

[a] See Ref. 19.
[b] See Ref. 24.
[c] See Ref. 16.

Our experimental results for the isotopic dependence of the lattice constant and thermal expansivity of neon are compared with predictions which have been made for Einstein, Grüneisen, Born–von Kármán, and self-consistent phonon models. Values of the potential parameters used in these models are given in Table III. Most of the theoretical work has been limited to zero-point properties but there are some calculations for finite temperatures. Our comparisons are confined to those models which have been published in reduced form or for which explicit calculation of the ^{20}Ne and ^{22}Ne properties has been made.

A. Lattice Constants

1. *Values at 0°K*

The present extrapolated value of the relative difference in the isotopic lattice constants is compared to the predictions of several lattice dynamical models in Table IV. Qualitatively we expect ^{20}Ne to have the larger lattice constant since it has a smaller mass and thus larger lattice-wave frequencies and ground-state energy. Two-body Mie–Lennard-Jones interatomic potentials of the type

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

where r is the internuclear separation, were used in the calculations. The values of the parameters ϵ and σ were fixed for most models by comparison of the experimental and predicted values of the lattice constant and the heat of sublimation at 0°K of the natural isotopic mixture. Internal consistency is thus achieved for such a model although each model in Table IV uses different values of ϵ and σ.

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

[15] J. de Boer, Physica **14**, 139 (1948).

[16] N. Bernardes and C. A. Swenson, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Co., New York, 1963), p. 101. Bernardes gives an explicit $V^*(\Lambda^*)$ relation, his Eq. (5-36), which yields isotopic volume differences similar to those of the more detailed calculations of Ref. 22.

[17] We will return to this point in connection with some of the results in Refs. 27 and 28.

[18] Various model potentials are listed in the review by G. K. Horton, Am. J. Phys. **36**, 93 (1968).

TABLE IV. Relative difference in the lattice constants a of ^{20}Ne and ^{22}Ne at 0°K. The present extrapolated experimental value is compared with the predictions of several lattice-dynamical models. The models all use a Mie–Lennard-Jones 12-6 pair potential; for the first two, the parameters ϵ and σ were fitted to 0°K experimental data on natural neon.

Model		$10^3(^{20}a-^{22}a)/(^{22}a)$ Prediction	Experiment
Einstein[a]	Cell model	2.0	1.91±0.03
Born–von Kármán[b]	AN quasiharmonic	1.92	
	AN anharmonic	1.59	
	1N quasiharmonic	2.04	
	1N anharmonic	1.87	
Self-consistent phonon[c]	Even-order anharmonic	2.1	

[a] See Ref. 19.

[b] See Ref. 23. AN and 1N refer to all-neighbor and to nearest-neighbor models, respectively, for the static and harmonic interactions. The values given are smaller than those appearing in Ref. 23 by a factor $^{22}a/a$(static), where a(static) is the lattice constant for the particular model in the absence of ground-state vibrations.

[c] See Ref. 27.

Hillier and co-workers[19] have represented the noble gas crystals by a single-particle anharmonic Einstein model. Correlations in the atomic motion were thus ignored and the spherically symmetric potential was developed according to the cell theory of Lennard-Jones and Devonshire. In this model the motion of a single particle is considered in the spherically symmetrical cell potential,

$$\Phi(u/\sigma)=\Phi_0+\epsilon W(u/\sigma,z_i,\alpha_i)\,, \tag{5}$$

where u is the particle displacement from the center of the cell, Φ_0 is the static lattice potential, z_i is the coordination number of the ith shell of atoms at distance α_i/σ in the fcc structure, and W is a sum over shells of a polynomial. Only the three smallest shells were included. The radial part of the Schrödinger equation with this potential was solved by the WKB method.

The resulting eigenvalues $\lambda_{L,n}$, which depend upon the atomic mass m, were put in a partition function Z which was used to calculate thermodynamic properties. For example, the expression for the pressure,

$$P=kT\left(\frac{\partial\ln Z}{\partial\ln V}\right)_T=kT\frac{\sqrt{2}}{3\alpha^2}\left(\frac{\partial\ln Z}{\partial\alpha}\right)_T\approx 0\,, \tag{6}$$

yields a form of Eq. (2) to determine the equilibrium volume V^*. The latent heat of sublimation at $T=0$°K, L_0, is

$$-L_0=N\lambda_{0,0}+\Phi_0\,. \tag{7}$$

For the ground state $\lambda_{0,0}=\epsilon\lambda_{0,0}^*$ and Eq. (6) can be written as

$$\frac{\partial\lambda_{0,0}^*}{\partial V^*}+\left(\frac{\partial\Phi^*}{\partial V^*}\right)=0\,. \tag{8}$$

For comparison with experiment, Eqs. (7) and (8) were first used to give ϵ and σ in Eq. (4) from experimental data for L_0 and a_0. Then Eq. (8) gave a relation $V_0^*=V_0^*(\Lambda^*)$ which is displayed in Fig. 3 of these authors.[19]

We have used these results to obtain the prediction for the relative isotopic lattice constant difference of ^{20}Ne and ^{22}Ne given in our Table IV. This Einstein model predicts a value which is only 5% high, a result which indicates that correlation effects may be quite small for scalar properties of the ground state of neon and that the effect of possible many-body forces could be largely contained in the empirical potential constants ϵ and σ. Comparison between the work of Mullen[20] on neon, which included an account of correlation, and the work of Bernardes,[16] which did not, also indicates that correlation effects are small for the properties of the ground state that they considered.

Born–von Kármán lattice dynamics have been applied in the harmonic approximation to models of the noble gas crystals by Horton and Leech[21] and Barron and Klein.[22] The former evaluated the lattice vibrational modes directly while the latter calculated moments of the frequency spectrum. To display isotopic dependences Brown and Feldman[23] have written

$$-L_0=\Phi_0+\Lambda^*E_0+\Lambda^{*2}(F_3(0)+F_4(0)) \tag{9}$$

and Eq. (2) as

$$-P=\left(\frac{d\Phi_0}{dV}\right)_T+\Lambda^*\left(\frac{dE_0}{dV}\right)_T+\Lambda^{*2}\left(\frac{dF_3(0)}{dV}+\frac{dF_4(0)}{dV}\right)_T\approx 0\,. \tag{10}$$

Here one has

$$\Lambda^*E_0=\tfrac{1}{2}\hbar\sum_{\mathbf{q}=1}^{N}\tilde{\omega}_{\mathbf{q}}(0)\,, \tag{11}$$

where $\tilde{\omega}_{\mathbf{q}}$ are the quasiharmonic phonon frequencies obtained by a Born–von Kármán lattice-wave treatment, and $\Lambda^{*2}F_3(0)$ and $\Lambda^{*2}F_4(0)$ are cubic and quartic contributions, respectively, to the ground-state energy. Experimental values for L_0 and a_0 for natural neon were used in Eqs. (9) and (10) to determine the potential parameters in Eq. (4) in these cases[24]: (a) quasiharmonic approximation (terms including Λ^*), and (b) anharmonic approximation (terms including Λ^{*2}). Then in each case a_0 for ^{20}Ne and ^{22}Ne could be calculated from Eq. (10) by using the appropriate value of Λ^*.

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[19] J. H. Hillier, M. S. Islam, and J. Walkley, J. Chem. Phys. **43**, 3705 (1965).

[20] W. J. Mullin, Phys. Rev. **134**, 1249 (1964).

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

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

[23] J. S. Brown and J. L. Feldman, Proc. Phys. Soc. (London) **89**, 993 (1966).

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

In this way Brown and Feldman[23] have used the model of Horton and Leech [case (a)] to calculate the harmonic values of the isotopic lattice constant differences for nearest-neighbor (1N) and all-neighbor (AN) interactions. These values, listed in Table IV, are essentially the same as those that can be obtained from Tables 2 and 3 of Barron and Klein.[22] In addition, the anharmonic values [case (b)] in Table IV were predicted by Brown and Feldman. For this they used the results of Feldman and Horton[25] who calculated the anharmonic contributions $F_3(0)$ and $F_4(0)$ to the free energy in a 1N interaction model.

For the Born–von Kármán lattice dynamics, agreement with experiment is very good for the AN harmonic and the 1N anharmonic models. Fenichel and Serin[26] have plotted the reduced Debye characteristic temperatures for the noble gas solids as a function of Λ^*. They also concluded that the 1N anharmonic model fitted the experimental data better than the AN anharmonic model. This further success of the physically unrealistic 1N model reemphasizes our lack of understanding of the interatomic potential in the noble gas solids.

Finally, the self-consistent phonon approximation has been applied to neon isotope crystals by Gillis, Werthamer, and Koehler.[27] In this recently devised model, the equilibrium state is regarded as given by phonons whose frequencies are determined self-consistently. In contrast to the previous theories there is no assumption made of smallness of the amplitude u of individual atomic vibrations. An effective trial Hamiltonian of harmonic oscillator form is assumed,

$$H=-\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2+\tfrac{1}{2}\sum_{i,j=1}^{N}(\mathbf{u}_i-\mathbf{u}_j)\cdot\mathbf{\Phi}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j), \qquad (12)$$

where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the dynamical displacement variables. The parameters $\mathbf{\Phi}_{ij}$ are determined variationally by inserting this operator H in a trial free energy F and minimizing F with respect to variations in $\mathbf{\Phi}_{ij}$ and in the displacement-displacement correlation $\mathbf{D}_{ij}=\langle(\mathbf{u}_i-\mathbf{u}_j)(\mathbf{u}_i-\mathbf{u}_j)\rangle$. Iterative numerical analysis yields the self-consistent frequencies $\omega_\mathbf{q}$ and polarization vectors. The procedure as carried out[27] (a) used a pair potential, Eq. (4), with values of the parameters taken from different work,[16] and (b) summed all the even-derivative terms in the crystal potential energy.

Values predicted for the neon isotope lattice constant difference in this model are also listed in Table IV. The agreement with experiment is fairly good. We note that on account of the choice of potential parameters,[16,17] the lattice constants themselves are not correctly given. Possibly, the predicted isotopic difference would be nearer the present experimental value if an internally consistent choice of σ, ϵ were to be used.

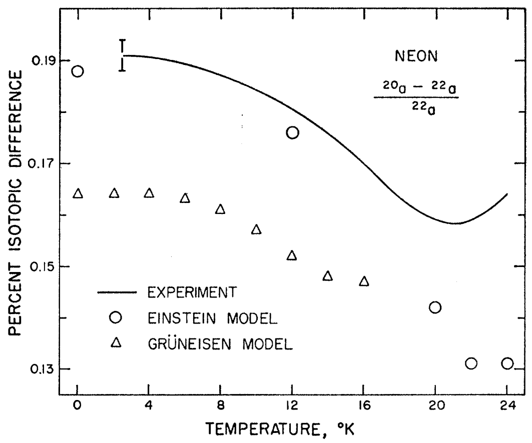

FIG. 1. Temperature dependence of the relative difference in the lattice constants of ^{20}Ne and ^{22}Ne. The present experimental values are compared with the theoretical predictions of Einstein and Grüneisen models, Refs. 28 and 32, respectively.

2. *Values at Finite Temperature*

We show the experimental value of the relative difference in the isotopic lattice constants plotted as a function of temperature in Fig. 1. Previous experiments on simple crystals (excluding helium) have failed to reveal any temperature variation of such a difference.[1,5] Qualitatively, we expect that as the temperature increases quantum effects should become less important. At some high-temperature limit the quantum-mechanical law of corresponding states should go over to a classical law. Since the classical law is mass-independent, isotopic properties should become identical. Thus, as the temperature increases, we expect the difference in the isotopic lattice constants to decrease. Figure 1 shows that the experimental lattice constants of ^{20}Ne and ^{22}Ne follow this behavior up to 21°K.

The reason for the increase at higher temperatures is not clear; possibly it is associated with the generation of thermal equilibrium vacancies.[14] Some confidence in the present data is justified, although the measurements were made on just one specimen of each isotope, because previous natural neon data[9] (91% ^{20}Ne) lie smoothly near the present ^{20}Ne data.

To study the temperature variation of neon isotope properties, Johns[28] followed the method of Henkel, an anharmonic Einstein model, which employs the spherically symmetric cell potential

$$\Phi(u_x^2,u_y^2,u_z^2)=\Phi_0+P_2(u_x^2+u_y^2+u_z^2)+P_4(u_x^4+u_y^4+u_z^4), \qquad (13)$$

where $\mathbf{u}$ is the atomic displacement from the center of the cell. P_2 and P_4 involve fcc lattice sums and are

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[25] J. L. Feldman and G. K. Horton, Proc. Phys. Soc. (London) **92**, 227 (1967).

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

[27] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. **165**, 951 (1968).

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

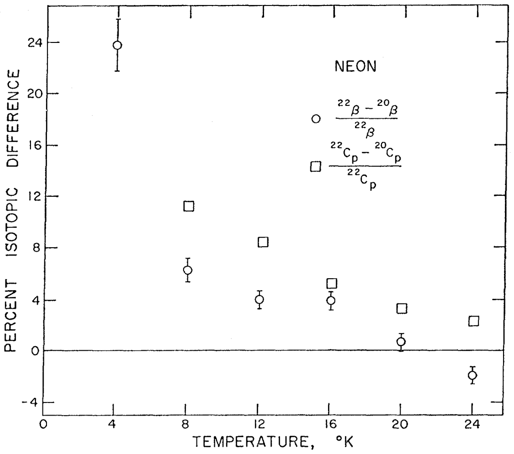

FIG. 2. Comparison of the temperature dependences of the relative isotopic differences in the present values of β and the C_P values of Clusius and co-workers (Ref. 6) for ^{20}Ne and ^{22}Ne.

analytical functions of the arguments indicated. The single-particle Schrödinger equation is thus separable and the terms in P_4 are treated by perturbation theory. The remaining steps are like those described immediately before Eq. (6).

The predictions of this model are shown in Fig. 1. The agreement in magnitude with the present experiments for $({}^{20}a-{}^{22}a)/{}^{22}a$ is probably fortuitous. The numerical values of Johns give this difference only to about 15 % accuracy. The model was fitted at 0°K to a lattice parameter 1.7% larger than experiment, and thermal expansion of the model is only $\frac{1}{2}$ to $\frac{1}{3}$ of present experimental values in the range 12 to 24°K. Instead of the repulsive exponent 12 of Eq. (4) the model uses 14. Finally, the approximations which are made in this model are probably invalid for neon,[29] but the continuous decrease in the isotopic difference does suggest that the experimental *increase* above 21°K is not due to purely anharmonic effects in the crystal.

The Einstein model of Jenkins and Walkley,[30] Eqs. (5)-(8), was fitted to the Bolz and Mauer[5] natural neon lattice parameter at 0°K and predicts the observed thermal expansion within about 10% at the higher temperatures. However, no prediction was made of a difference between the thermal expansions of the isotopes.

No predictions of the temperature dependence of isotopic differences have been published for Born-von Kármán models. We note that the thermal expansion of the harmonic model for neon is nearly twice that of the real crystal.[31]

London proposed a Grüneisen model for isotope effects.[32] In this model the equilibrium volume, Eq. (2), is given by

$$-P=\frac{d\Phi_0}{dV}+\frac{\gamma}{V}\sum_{\mathbf{q}=1}^{N}\hbar\omega_{\mathbf{q}}\frac{d}{d(\hbar\omega_{\mathbf{q}}/kT)}\times\left[\frac{1}{2}\frac{\hbar\omega_{\mathbf{q}}}{kT}+\ln(1-e^{-\hbar\omega_{\mathbf{q}}/kT})\right]\approx 0, \quad (14)$$

where $\gamma=-d\ln\omega_{\mathbf{q}}/d\ln V$ is assumed the same for all modes $\mathbf{q}$ and for the different isotopes. When the isotopic mass is introduced as an independent variable, Eq. (14) becomes in the present case

$$\frac{{}^{20}a-{}^{22}a}{{}^{22}a}=\frac{\gamma}{6BV}(E_z+E_T-TC_V)\left(\frac{{}^{22}m-{}^{20}m}{{}^{22}m}\right). \quad (15)$$

In evaluating this equation, we have used experimental values for the isothermal bulk modulus B and molar volume V[9] and for the thermal energy E_T and isochoric heat capacity C_V.[6,9,26] A theoretical value for the ground-state vibrational energy E_z was taken from Feldman and Horton.[25] We have used a mean value of 2.8 for the parameter γ over the range 4–16°K where the thermal Grüneisen parameter βBVC_V^{-1} is reasonably independent of temperature.[9] The results are shown in Fig. 1. We see that this semiempirical model gives fair agreement with experiment over the temperature range where the approximations of the model are likely to be valid.

Recent isochoric calorimetry on solid helium isotopes[33] indicates that γ is isotopically invariant, as London assumed. On the other hand, London pointed out that his other assumption, that γ was the same for all modes, was not exact. The different Grüneisen parameters for sound velocities in neon crystal directions of high symmetry, as well as their temperature dependences, have been calculated in the self-consistent phonon model.[27] However, the detailed applicability of these calculations to the actual solid is presently uncertain because no single-crystal elastic data are available. We note that this particular model exhibits only $\frac{2}{3}$ of the total measured thermal expansion of neon, together with a rather small temperature variation of the bulk modulus.

B. Thermal Expansivity

The relative difference in the volume coefficients of thermal expansion β of ^{20}Ne and ^{22}Ne as found in this experiment is shown in Fig. 2. Clusius and co-workers[6] found that the temperature dependence of the relative isotopic difference in the specific heat was nearly the same and we show their experimental values. This similarity also suggests that the Grüneisen parameter is approximately isotopically invariant. Unfortunately

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[29] E. A. Guggenheim and M. L. McGlashan, Mol. Phys. 3, 563 (1960).

[30] W. I. Jenkins and J. Walkley, J. Chem. Phys. 43, 3721 (1965).

[31] J. W. Leech, C. J. Peachey, and J. A. Reissland, Phys. Letters **10**, 69 (1964).

[32] H. London, Z. Physik. Chem. **16**, Simon-Gedenkheft, 302 (1958).

[33] H. H. Sample and C. A. Swenson, Phys. Rev. **158**, 188 (1967).

TABLE V. Quantities adopted for examining the low-temperature ratio of coefficients of thermal expansion. (^{n}Ne means natural Ne.)

Substance	$V(0)$ (cm^3 mole^{-1})	$\theta(0)$ (°K)	$B(0)$ (kbar)
^{20}Ne	13.397[a]	75.0	...
^{n}Ne	13.391[b]	74.6[c]	11.2[b]
^{22}Ne	13.321[a]	71.5	...

[a] Present measurements.
[b] Reference 9.
[c] Reference 26.

for a more detailed comparison, the specific-heat data are of limited accuracy and cover only part of the entire temperature range.

By the same qualitative reasoning used in considering the lattice constant difference, we expect the isotopic difference in β to decrease with increasing temperature. The value of $^{22}\beta$ should be larger than $^{20}\beta$ in order that the lattice constant difference should also decrease. The experimental results can be explained qualitatively on this basis up to 21°K. Above this temperature $^{20}\beta > {}^{22}\beta$ and such a simple argument fails. This effect is obviously closely related to the increase in the isotopic lattice constant difference.

An indication of the extent to which the expansivities of noble gas solids deviate from a classical law of corresponding states can be found in Fig. 3. The reduced volume expansivitity β^* is plotted as a function of the reduced temperature T^*. Expansion coefficients for argon[8] and for krypton[34] are from precise x-ray data while those for xenon are from bulk data.[35] The reducing factors are given by $T^* = T/T_{\text{tr}}$ and $\beta = \beta T_{\text{tr}}$, where T_{tr} are the triple-point temperatures. The values of T_{tr} have been used as a reducing factor in preference to ϵ/k since they are independent of the form of the interatomic potential.[36] For this choice of reducing factors, β^* for the neon isotopes approaches a common value near $T/T_{\text{tr}} = 1$.

We expect that this classical scaling procedure would not be valid at the lower temperatures, $T < \Theta$, or for the lighter substances, because of the increasing importance of quantum effects. Examination of Fig. 3 indeed verifies that β^* for each substance falls below the common curve for temperatures below a characteristic Θ for the substance. This deviation from the classical law increases with decreasing temperature and for the neon isotopes increases with decreasing atomic mass. This behavior is consistent with our qualitative account of the temperature dependence of the isotopic differences in a and β.

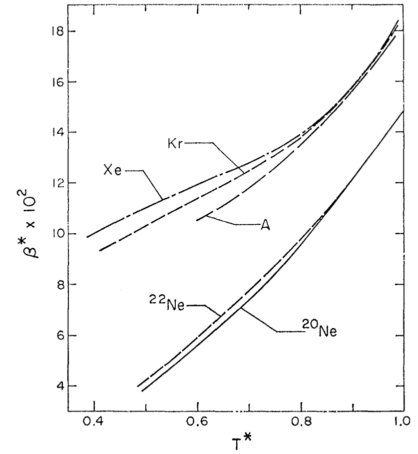

FIG. 3. Classical reduced coefficient of volume thermal expansion, $\beta^* = \beta T_{\text{tr}}$, versus reduced temperature, $T^* = T/T_{\text{tr}}$, from x-ray measurements on krypton, argon, and neon crystals and from bulk measurements on solid xenon. The respective Debye temperatures occur at T^* values of about 0.4 (xenon), 0.6 (krypton), 1.0 (argon), and 3 (neon).

Elsewhere[34] we have examined the proposal by Manzhelii and co-workers[35] that at sufficiently low temperatures the ratios of coefficients of thermal expansion of noble gas solids follow the relation

$$\beta_1/\beta_2 = (C_{V_1}/C_{V_2})\gamma_1 V_2 B_2/\gamma_2 V_1 B_1. \qquad (16)$$

This ratio is considered at common reduced temperatures T/Θ_0, where Θ_0 is the low-temperature limit of the Debye characteristic temperature for the specific heat. Equation (16) is apparently well-satisfied by natural neon, argon, and krypton up to about $T/\Theta_0 \sim 0.2$.

For the neon isotopes the present work gives precise β and V values in this temperature range. Further, calorimetric data,[6] which we may correct to C_V by means of the factor $(1+2.8\beta T)^{-1}$ for each isotope, are available in the range above $T/\Theta_0 \simeq 0.12$. We may use these data after assuming suitable Θ_0 values for each isotope, in order to make a test of Eq. (16). The test can be regarded as essentially that for a consistency relation between the properties concerned, on the assumption that the neon isotopes have identical $\gamma(T/\Theta_0)$ relations.

In the absence of calorimetric data on the isotopes at low temperatures one may construct suitable Θ_0 values by noting that the combination $\omega_q{}^2 m$ appears in the equations used to determine the frequencies ω_q, whether the theory is of single-particle, Born–von Kármán, or self-consistent phonon type. Θ_0 is then obtained from an appropriate average ω in the case of the latter two types of theory, even for an anharmonic crystal such as neon. Our choices of $\Theta_0 \sim m^{-1/2}$ for ^{20}Ne and ^{22}Ne are listed in Table V, together with other data. For these Θ_0 values adopted, the measured specific heat ratio[6] $^{20}C_V/^{22}C_V$ is unity within experimental error, although there is a tendency for it to exceed unity by a few

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[34] D. L. Losee and R. O. Simmons, Phys. Rev. **172**, 944 (1968).

[35] V. G. Manzhelii, V. G. Gavrilko, and E. I. Voitovich, Fiz. Tverd. Tela **9**, 1483 (1967) [English transl.: Soviet Phys.—Solid State **9**, 1157 (1967)].

[36] The values of ϵ determined for a given model in Refs. 22 and 24 give $kT_{\text{tr}}/\epsilon = 0.700 \pm 0.005$ for four noble gas solids, so that the two scaling procedures give essentially the same results, except for the neon isotopes. For ^{20}Ne, $T_{\text{tr}} = 24.577$°K, and for ^{22}Ne, $T_{\text{tr}} = 24.727$°K, according to J. Bigeleisen and E. Roth [J. Chem. Phys. **35**, 68 (1961)].

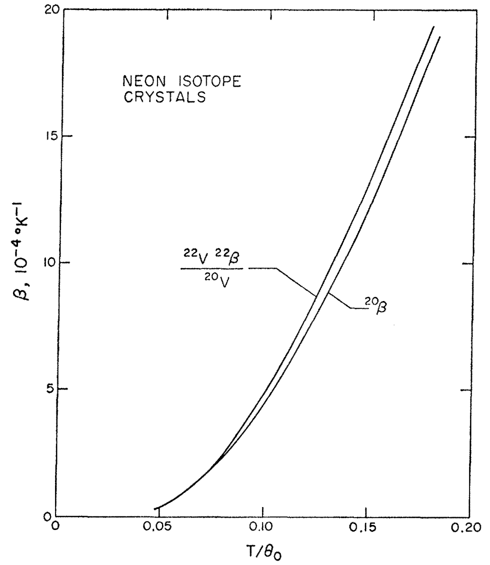

FIG. 4. Low-temperature coefficients of thermal expansion of neon isotope crystals, as discussed in the text, Sec. III B.

percent in the range of reduced temperature from 0.12 to 0.15.

In Fig. 4 we show $^{22}V^{22}\beta/^{20}V$ and $^{20}\beta$ as functions of the reduced temperatures. Over the temperature range the ratio is essentially constant at 1.07. From the arguments and assumptions above, including Eq. (16), one might therefore guess that $^{20}B/^{22}B\simeq 1.07$. No explicit predictions for a difference in the bulk moduli have been published, although it is implicit in several of the papers previously cited. On working out this ratio for the models of Bernardes[16] and of London[32] one finds $^{20}B/^{22}B\simeq 1.03$. We conclude that either such models are inadequate or that one or more of the earlier arguments and assumptions used are incorrect. The present discussion is sufficient to emphasize several reasons why accurate calorimetric data on the isotopes at low temperatures will be useful.

IV. CONCLUSION

The isotopic dependence of the lattice constants of ^{20}Ne and ^{22}Ne at 0°K can be adequately explained by various current lattice-dynamical models. For a 12-6 Mie–Lennard-Jones interaction, AN harmonic and 1N anharmonic Born–von Kármán models give the best agreement with experiment. We note that these models give a poor account of the coefficient of T^3 in the low-temperature specific heat of natural neon, however.[9] Cell models, of course, do not even exhibit T^3 behavior. At finite temperatures the theoretical predictions for relative differences between the isotope lattice constants are less extensive but are in qualitative agreement with the experimental results up to 15°K. The thermal expansions *themselves* are not well represented, however.

Above 21°K the isotopic difference in the lattice constants apparently increases with increasing temperature. Further experimental data will be needed to show if the effect is caused by generation of thermal equilibrium defects. More theoretical calculations could show whether or not the effect can be explained by lattice dynamics.

APPENDIX

In Tables VI and VII we give our data for x-ray lattice expansion of ^{20}Ne and ^{22}Ne crystals at their respective saturated vapor pressures.

TABLE VI. Complete thermal expansion data for ^{20}Ne, where $\Delta a/a_0$ is the fractional change in the lattice constant referred to the extrapolated value at 0°K, $^{20}a_0=4.46440\pm0.00008$ Å*.

T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$
2.57	0.014	5.893	0.907	17.049	55.575
2.77	0.000	6.451	1.345	18.040	65.493
2.98	−0.040	7.332	2.543	18.983	76.579
3.25	0.025	8.061	3.874	20.030	90.284
3.51	0.112	9.040	6.166	21.045	104.786
3.81	0.108	10.126	9.607	21.980	119.373
4.00	0.099	11.262	14.013	21.990	119.341
4.229	0.144	11.993	17.532	22.920	135.139
4.243	0.049	13.010	23.128	23.350	142.828
4.244	0.184	14.045	29.886	23.360	143.244
4.250	0.155	15.003	37.125	23.770	150.770
4.259	0.209	15.039	37.499	24.230	159.813
4.696	0.384	15.068	37.686	24.240	160.397
5.306	0.597	16.059	45.885	···	···

TABLE VII. Complete thermal expansion data for ^{22}Ne, where $\Delta a/a_0$ is the fractional change in lattice constant referred to the extrapolated value at 0°K, $^{22}a_0=4.45589\pm0.00008$ Å*.

T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$
2.57	0.000	7.069	2.453	16.056	48.131
2.77	0.027	7.461	3.087	16.569	53.085
3.00	−0.002	8.011	4.236	17.076	58.088
3.24	−0.029	8.545	5.379	17.647	64.164
3.51	0.043	9.020	6.672	17.871	66.678
3.76	0.119	9.549	8.365	18.344	72.113
4.015	0.115	10.037	9.771	19.019	80.471
4.214	0.216	10.506	11.743	19.566	87.091
4.245	0.205	10.968	13.580	20.078	93.714
4.246	0.243	11.478	15.923	20.855	105.454
4.260	0.265	12.088	19.049	21.407	113.626
4.519	0.232	12.523	21.464	21.960	122.175
4.734	0.346	13.070	24.783	22.537	131.572
5.207	0.621	13.590	28.073	22.023	140.012
5.624	0.933	14.036	31.430	23.500	148.534
5.784	0.951	14.526	35.156	24.048	158.963
6.169	1.390	15.038	39.161	24.270	163.524
6.622	1.785	15.587	43.858	···	···