Low-Temperature Specific Heats of Solid Neon and Solid Xenon*†

H. FENICHEL‡ AND B. SERIN
Rutgers, The State University, New Brunswick, New Jersey
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The specific heats of solid neon and xenon have been measured in the temperature range 1.5 to 24°K, using a calorimeter with a mechanical heat switch. Carbon resistance thermometers were calibrated against a gas thermometer and the helium vapor-pressure scale. The results were analyzed to obtain the temperature dependence of the Debye temperature, $\Theta^c(T)$. In the range $0.020 \lesssim T/\Theta_0^c \lesssim 0.505$, the data were fitted with an expression of the form $\Theta^c(T)=\Theta_0^c+AT^2$, where Θ_0^c is the Debye temperature at 0°K. This procedure gave $\Theta_0^c=74.6\pm1.0$°K for neon and $\Theta_0^c=64.0\pm0.8$°K for xenon. The results for $\Theta^c(T)$ are compared with the calculations of Bernardes, Horton, and Leech, and Barron and Klein, based on Mie-Lennard-Jones potentials for the interaction energy between two atoms. Tables of the following smoothed thermodynamic properties between 1.0 and 24°K are given in Table I: specific heat at constant pressure, specific heat at constant volume, entropy, and enthalpy.

I. INTRODUCTION

THE temperature of the specific heats of the inert-gas solids depends on the details of their lattice dynamics. Although the solids have been analyzed theoretically quite extensively, precise experimental results have become available only in recent years. Specific-heat measurements on inert-gas solids were first performed by Clusius,[1,2] but these show appreciable scatter and do not extend below 11°K. Low-temperature measurements on argon were made by Figgins[3] and Hill,[3] and more recently argon and krypton were measured by Flubacher, Leadbetter, and Morrison,[4] and Beaumont, Chihara, and Morrison.[5] At the time this work was started, no low-temperature data existed for neon and xenon, the two elements situated above and below argon and krypton in the periodic table. It therefore seemed worthwhile to obtain data for the two solids as a step toward obtaining a better understanding of the properties of the solidified rare gases. Neon is of interest because its small mass results in a large energy associated with the zero-point vibrations, whereas in xenon zero-point motion is small. A brief preliminary report on the results for neon has appeared,[6] and more recently, Fagerstroem and Hollis Hallett[7] have also measured the specific heat of neon.

In this paper, we present the results of our investigation of the specific heats of neon and xenon in the temperature range 1.5 to 24°K. The results will be compared with the other data that have been reported, and with the theoretical calculations of Bernardes,[8] Horton and Leech,[9] and Barron and Klein.[10]

II. EXPERIMENTAL

A calorimeter similar in construction to the one described by McConville and Serin[11] was used. It employs a mechanical heat switch which permits the specimen either to be put into thermal contact with the surroundings or isolated from them. A liquid-helium vapor-pressure bulb and a constant-volume helium gas thermometer serve to calibrate the resistance thermometers.

The sample holder was a cylindrical copper vessel (11 cm³) connected to the gas supply via a stainless steel capillary (0.9 mm i.d.). Several copper vanes were soldered into the holder to distribute the heat to the solidified inert gas. The vessel was wound with 200 Ω of heater element (AWG # 38 constantan wire) and coated with a layer of G. E. # 7031 varnish.

Two 0.1-W Allen Bradley carbon resistors cemented to the copper vessel served as working thermometers (56 Ω for work kelow 4.2°K and 220 Ω for higher temperatures). These thermometers were calibrated separately during each run. The calibration points were then fitted to the two constant Clement's equation[12]

$$(\ln R/T^*)^{1/2}=a+b\ln R.$$

A correction curve of $(T-T^*)$ versus T^* was used in order to account for the deviation of T^* from the thermodynamic temperature T. Below 4.2°K the temperatures

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‡ Present address: Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221.

[1] K. Clusius and L. Riccoboni, Z. Physik Chem. **B38**, 81 (1938).

[2] K. Clusius, P. Flubacher, U. Piesbergen, K. Schleich, and A. Sperandio, Z. Naturforsch. **15a**, 1 (1960).

[3] See E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957), for the $\Theta^c(T)$ curve derived from these data.

[4] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1449 (1961).

[5] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1462 (1961).

[6] H. Fenichel and B. Serin, Bull. Am. Phys. Soc. **9**, 455 (1964).

[7] C. Fagerstroem and A. C. Hollis Hallett, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964* (Plenum Press Inc., New York, 1965).

[8] N. Bernardes, Phys. Rev. **120**, 807 (1960).

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

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

[11] T. McConville and B. Serin, Phys. Rev. **140**, A1169 (1965).

[12] J. R. Clement, *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1955).

were based on the 1958 He^4 vapor-pressure scale.[13] Above 4.2°K, a helium gas thermometer was used and the temperature calculated from the equation of state of the gas following the procedure used by Franck and Martin.[14] For virial coefficients we used the "adopted values" of Keesom.[15]

A separate experiment determined the heat capacity of the sample holder assembly, which at most amounted to 10% of the heat capacity of the sample at the lowest temperatures.

Neon and xenon gas of spectroscopically pure research grade supplied by the Matheson company were used in this investigation. The gases were stored at room temperature in large stainless steel containers at a pressure of about 90 cm of Hg. To condense the gas into the evacuated specimen holder, the latter was stabilized at the normal boiling point of the particular substance and then allowed to cool slowly toward the triple point over a period of about two hours. To prevent premature freezing in the capillary tube during condensation, the tube was electrically insulated from the cryostat and a current was passed through it to heat it. A temperature gradient of a few degrees was maintained across the calorimeter can. The number of moles, n, condensed was determined from measurements of the pressure and temperature of the gas in the storage vessel before and after the sample holder was filled. In various runs, the mass of neon varied between 0.28 and 0.55 moles; and between 0.045 and 0.096 moles of xenon were measured. We estimate the maximum error in n to be 0.5%.

Random errors were estimated to lead to an uncertainty of about 2% in the measurements of specific heat. The data are available on request.[16] Smoothed values of C_p, C_v, and other thermodynamic functions are in Table I.

TABLE I. Summary of smoothed thermodynamic properties. C_p=specific heat at constant pressure; C_v=specific heat at constant volume; S=entropy, H=enthalpy.

T (°K)	C_p (J/mole °K)	C_v (J/mole °K)	S (J/mole °K)	H (J/mole)
		Neon		
1	0.004	0.004	0.00178	0.0002
2	0.039	0.039	0.01336	0.0176
3	0.134	0.134	0.04468	0.0998
4	0.345	0.345	0.1082	0.3260
5	0.760	0.757	0.2269	0.8575
6	1.36	1.35	0.4144	1.883
7	2.13	2.10	0.6769	3.608
8	3.10	3.04	1.020	6.220
9	4.19	4.07	1.446	9.855
10	5.42	5.04	1.949	14.145
11	6.82	6.47	2.530	20.250
12	8.28	7.73	3.184	27.753
13	9.74	8.96	3.904	36.760
14	11.09	10.04	4.675	47.188
15	12.42	11.03	5.486	58.940
16	13.71	11.91	6.328	71.988
17	15.01	12.74	7.197	86.348
18	16.35	13.54	8.092	101.96
19	17.73	14.29	9.012	119.98
20	19.14	14.95	9.955	138.38
21	20.84	15.75	10.830	158.30
22	22.72	16.50	11.842	180.07
23	24.63	17.07	12.891	203.73
24	26.48	17.32	13.986	229.28
		Xenon		
1	0.004	0.004	0.00254	0.0002
2	0.065	0.065	0.02110	0.0250
3	0.238	0.238	0.07458	0.1654
4	0.632	0.632	0.1916	0.5790
5	1.350	1.350	0.4047	1.542
6	2.32	2.32	0.7354	3.345
7	3.54	3.54	1.185	6.215
8	4.94	4.93	1.746	10.630
9	6.40	6.39	2.410	16.098
10	7.84	7.83	3.162	23.230
11	9.28	9.26	3.979	31.790
12	10.62	10.60	4.845	41.745
13	11.83	11.80	5.745	52.970
14	12.98	12.94	6.662	65.383
15	14.01	13.95	7.591	78.885
16	14.90	14.82	8.522	93.348
17	15.66	15.56	9.448	108.64
18	16.36	16.23	10.362	124.68
19	17.03	16.87	11.264	141.36
20	17.68	17.49	12.155	158.70
21	18.30	18.07	13.032	176.69
22	18.85	18.85	13.898	195.30
23	19.28	18.96	14.751	214.36
24	19.67	19.30	15.600	233.96

III. TEMPERATURE DEPENDENCE OF $\Theta^c(T)$

We measure the specific heat (C_s) of the solid in equilibrium with its saturated vapor. The specific heat at constant pressure C_p may be obtained using the following thermodynamic expression[17]:

$$C_s=C_p-T\beta v(dP/dT)_s,$$

where β and v are the thermal expansion coefficient and molar volume, respectively, and $(dP/dT)_s$ is the slope of the vapor-pressure curve of the solid. When numerical values are substituted in the equation it is found that C_p-C_s is quite small, being at most of the order of 0.1% of C_p at the triple point of neon, and even less for xenon. We have therefore neglected this difference between C_p and C_s and assumed them to be equal throughout the data analysis.

Theoretical calculations are usually done at constant volume, since the volume can be related quite simply to the lattice parameters. To convert our results from C_p to C_v (the specific heat at constant volume), we used the familiar expression[17]

$$C_p-C_v=\beta^2T/\rho\chi_T, \quad (1)$$

[13] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur. Std. (U. S.), Monograph **10**, (1960).
[14] J. P. Franck and D. L. Martin, Can. J. Phys. **39**, 1320 (1961).
[15] W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942).
[16] Write to: B. Serin, Physics Department, Rutgers, The State University, New Brunswick, New Jersey 08903. The data are also in H. Fenichel, thesis, Rutgers University, 1964 (unpublished).
[17] M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, New York, 1957), 4th ed.

where χ_T is the isothermal compressibility, and ρ is the density of the solid.

For neon, experimental values for β and ρ were taken from Bolz and Mauer,[18] and χ_T from Stewart.[19] The data of Sears and Klug,[20] Pollack,[21] and Packard and Swenson,[22] respectively, were used for the values of β, ρ, and χ_T of xenon.

Stewart reported only the value at 4.2°K for the compressibility of neon. It is rather unlikely that the compressibility remains independent of temperature up to the triple point. In fact, a study of compressibility curves for the other inert-gas solids[21] indicates that χ_T may double or even treble in going from 4.2°K to the triple point of the solids. However the Gruneisen parameter,[17] defined by

$$\gamma=\beta/\chi_T C_v, \tag{2}$$

varies only by about 6% between 10 and 25°K, according to the calculations of Horton and Leech.[9] Thus, eliminating χ_T between Eqs. (1) and (2), we obtain

$$C_v=C_p/(1+\gamma\beta T). \tag{3}$$

Inserting the one compressibility point of Stewart in Eq. (2) gives a value[23] of $\gamma=3.5\pm0.3$ at 4.2°K. This value for γ and Eq. (3) were used to calculate C_v for neon. The foregoing difficulties do not arise in the analysis of the xenon data because $\chi_T(T)$ has been measured.[22] Equation (1) was therefore used to calculate C_v for xenon.

The Debye temperature[24] $\Theta(T)$ is a convenient parameter for comparison of experiments and theory. We converted our C_v data to equivalent $\Theta^c(V,T)$ values, and Figs. 1 and 2 represent typical experimental results for xenon and neon, respectively. It should be noted that while up to ~5°K the two curves for $\Theta^c(T)$ are similar in shape they are noticeably different at higher temperatures. Both curves show an initial approximately parabolic decrease. Beyond 5°K the xenon curve flattens off but rises slightly above 15°K. The neon curve, on the other hand, exhibits an oscillatory behavior. Similar oscillations are evident in the earlier data on argon,[3] but are not present in our $\Theta^c(T)$ curves for xenon nor in Morrison's curves for argon and krypton.[5] Overton[25] has suggested that oscillations in Θ^c can result from anharmonic effects, whereas Feldman

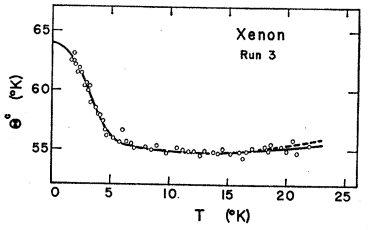

FIG. 1. The experimental temperature dependence of $\Theta^c(V,T)$ for a particular run on xenon. The dashed curve is $\Theta^c(V_0,T)$.

et al.[26] state that the oscillations do not occur in the theoretical model used. We found that the position and size of the oscillations in neon varied from run to run and are also dependent on the data assumed in calculating C_v from C_p. This correction, while only of the order of 2% of C_p for xenon at the highest temperature measured, is ~30% for neon at the highest temperature measured and is very sensitive to the choice of γ. As discussed below, the oscillations may be a consequence of technical difficulties in the experiment. We would say that until more measurements are made and additional compressibility data are available, the true shape of the $\Theta^c(V,T,)$ curve for neon will remain uncertain at temperatures above 9°K.

The dashed curve in Figs. 1 and 2 represent $\Theta^c(V_0,T)$, the Debye temperature with the volume reduced to V_0 (the volume of the solid at $T=0$°K). This further correction is necessary for comparison of the results with the theoretical calculations which are done for a fixed volume. We reduced our data to the equivalent $\Theta^c(V_0,T)$ values at constant volume V_0, using the equation[27]

$$\Theta(V_0,T)=\Theta(V,T)[\rho(0)/\rho(T)]^\gamma. \tag{4}$$

Note that this equation depends on the value of γ. Hence the uncertainties discussed earlier concerning the choice of γ for neon apply to this expression as well. For xenon we calculated $\gamma(T)$ below 20°K from our data for C_v and the other data quoted; the γ values of Packard and Swenson[22] were used at higher temperatures. The change from $\Theta^c(V,T)$ to $\Theta^c(V_0,T)$ is much more pronounced in neon than in xenon. It also has the effect of flattening the oscillations in neon.

In Fig. 3, the data shown in Fig. 1 are replotted. We see that at low temperatures they are reasonably well

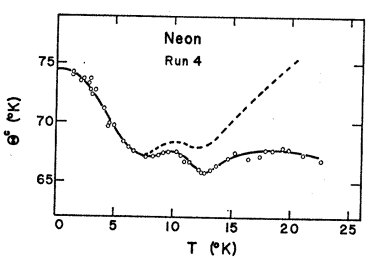

FIG. 2. The experimental temperature dependence of $\Theta^c(V,T)$ for a particular run on neon. The dashed curve is $\Theta^c(V_0,T)$.

[18] L. H. Bolz and F. A. Mauer, Advan. X-Ray Anal. **6**, 242 (1963).
[19] J. W. Stewart, Phys. Rev. **97**, 578 (1955).
[20] D. R. Sears and H. P. Klug, J. Chem. Phys. **37**, 3002 (1962).
[21] G. L. Pollack, Rev. Mod. Phys. **36**, 748 (1964).
[22] J. R. Packard and C. A. Swenson, J. Phys. Chem. Solids **24**, 1405 (1963).
[23] Horton and Leech (Ref. 9) calculate $\gamma=3.2$ for neon at this temperature.
[24] See, e. g., C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, New York, 1956), 2nd ed. To find Θ^c from C_v we used the tables of J. A. Beattie, J. Math. Phys. **6**, 1 (1926).
[25] W. C. Overton, Jr., in *Lattice Dynamics, Proceedings of the International Conference, Copenhagen, Denmark, 1963* (Pergamon Press, Inc., Oxford, 1964).
[26] J. L. Feldman, G. K. Horton, and J. B. Lurie, Bull. Am. Phys Soc. **10**, 434 (1965). Also, J. Chem. Phys. Solids **26**, 1507 (1965)
[27] G. K. Horton, Proc. Roy. Soc. (London) **A252**, 551 (1959)

represented by the relation

$$\Theta^c=\Theta_0^c+AT^2, \quad (5)$$

where A is a constant. As a result, we fitted the low-temperature data by the method of least squares to this equation to find A and Θ_0^c, the Debye temperature at 0°K. The values obtained for these parameters for neon and xenon are shown in Table II. Also shown are values obtained from the data for argon[4] and krypton.[5] This procedure gave essentially the same values of Θ_0^c as the one commonly used[5] in which C_v/T^3 is plotted as a function of T^2 to obtain the limiting value of Θ^c at 0°K.

Equation (5) corresponds to taking terms up to T^5 in the expansion of C_v. Barron and Morrison[28] have pointed out that terms up to T^7 can be expected to contribute to C_v in the temperature region $T>\Theta_0^c/25$. Our data are not accurate enough to enable us meaningfully to evaluate the term in T^7. Neglect of this term probably does not affect the values obtained for Θ_0^c within the stated errors. However, the values of A may be somewhat doubtful.

TABLE II. Average values of the Debye temperature at 0°K, Θ_0^c, and the coefficient A of Eq. (5) as calculated from the data are given. For Ar, the data of Flubacher *et al.* (Ref. 4) were used; and for Kr we used those of Beaumont *et al.* (Ref. 5). The numbers of data points between $1.5°K<T\lesssim 0.055\ \Theta_0^c$ used in the calculation are listed.

Solid	Θ_0^c(°K)	$-A$(°K)$^{-1}$	No. of data points
Ne	74.6±1.0	0.24±0.04	63
Ar	93.1±0.5	0.23±0.02	26
Kr	72.1±0.5	0.26±0.02	14
Xe	64.0±0.8	0.35±0.08	51

The values for Θ_0^c obtained from some of the runs differed from each other by about 0.5°K. We found that the small deviations between different runs in Θ_0^c were also reflected in the $\Theta^c(T)$ curves which were shifted vertically with respect to each other by an amount about equal to the difference in the Debye temperatures at 0°K. These differences were not obvious in the values of $C_p(T)$ obtained in the various runs. Recent work in this laboratory by Buchanan has shown that such systematic deviations and even nonmonotonic behavior of $\Theta^c(T)$ can occur in metal specimens of poor thermal conductivity, unless extreme care is taken to heat them uniformly. Since in this experiment we have no way of knowing the nature of the thermal contact between the solid and the copper container, it is possible that the observed systematic deviations and perhaps the oscillations in $\Theta^c(T)$ arose from nonuniform distribution of heat.

[28] T. H. K. Barron and J. A. Morrison, Can. J. Phys. **35**, 799 (1957).

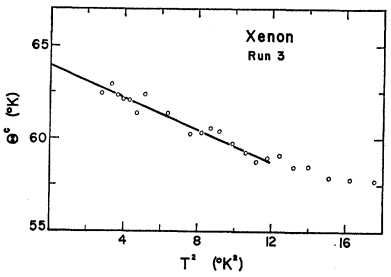

FIG. 3. The experimental Debye temperature as a function of T^2 for the data in Fig. 1.

We must also note that recent studies of the crystal structure of neon films[29] and solid argon[30] indicate that traces of hexagonal-close-packed phase, probably with a high density of stacking faults, can be embedded within the fcc structure of the inert-gas solids. Theoretical calculations by Feldman[31] show that the Debye temperature Θ_0^c for the fcc inert-gas crystal and for the corresponding hcp, may differ from each other by as much as 2%. The possibility that the structure of the solid could be different in the various runs also contributes to the over-all uncertainty of parameters deduced from the data.

The final error limits for the average quantities for neon and xenon listed in Table II are twice the calculated average deviations.

In our opinion, the uncertainties do not affect the conclusions discussed in Sec. IV. Fagerstroem and Hollis Hallett[7] give only $\Theta_0^c=75$°K and $\Theta^c=65.7$°K at 9.5°K for neon. Our specific-heat results agree, within their probable errors, with these values, and also with those of Clusius[1,2] in the range from 9 to 15°K. At higher temperatures, Clusius' results are consistently lower than ours by up to 3% for xenon and 5% for neon.

IV. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

A. Debye Temperature at 0°K

In Fig. 4 the reduced Debye temperature at 0°K, Θ_0^* for the inert-gas solids is compared with theoretical

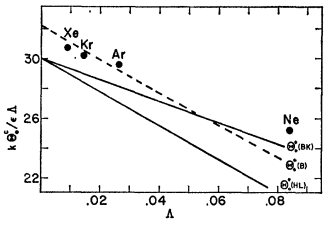

FIG. 4. Reduced Debye characteristic temperature $\Theta_0^*=k\Theta_0^c/\epsilon\Lambda$ for a 6–12 potential all-neighbor (AN) model plotted against Λ. The initials in the parentheses after Θ_0^* refer to the calculations of Barron and Klein (Ref. 10) (BK), Bernardes (Ref. 8) (B), and Horton and Leech (Ref. 9) (HL).

[29] M. J. Goringe and U. Valdre, Phil. Mag. **9**, 897 (1964).
[30] L. Meyer, C. S. Barrett, and P. Haasen, J. Chem. Phys. **40**, 2744 (1964).
[31] C. Feldman, Proc. Phys. Soc. (London) **86**, 865 (1965).

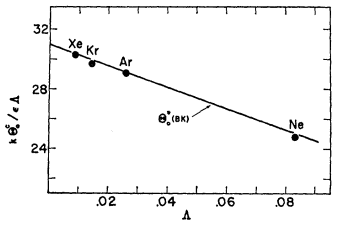

FIG. 5. Reduced Debye characteristic temperature Θ_0^* for a 6–13 all-neighbor (AN) model plotted against Λ.

predictions. The theoretical calculations are based on the Mie-Lennard-Jones 6-m potential energy of interaction between two atoms of mass M,

$$\phi(r) = -\epsilon[(r_0/r)^m - 2(r_0/r)^6], \tag{6}$$

where ϵ is the depth of the potential well and r_0 is the position at which the potential has a minimum. The reduced Debye temperature $\Theta_0^* = k\Theta_0^c/\epsilon\Lambda$, where k is Boltzmann's constant and Λ is the deBoer parameter defined as $\Lambda = \hbar/r_0(M\epsilon)^{1/2}$. The lowest curve [labeled Θ_0^*(HL)] was obtained using the Horton and Leech[9] quasiharmonic model, while the curve Θ_0^*(BK) includes anharmonic effects as calculated by Barron and Klein.[10] The dashed curve, Θ_0^*(B), is due to Bernardes.[8] The potential parameters for neon and xenon were derived by Brown[32] from recent x-ray measurements of the lattice constants. The argon and krypton parameters were taken from Horton and Leech. All the calculations shown in Fig. 4 are based on the (6–12) potential.

Although Θ_0^*(B) agrees with the results for solids of small Λ, when we consider the point for neon it seems clear that Θ_0^*(B) has too steep a slope. It appears that the slope of Θ_0^*(BK) is close to that of a line through the experimental points despite the disagreement in magnitude. From the nature of the variables plotted it is evident that Θ_0^*(BK) and the experimental points can be brought closer to each other by a slight adjustment of the potential parameters. In fact, this can be done by choosing a 6–13 rather than a 6–12 potential. If it is assumed that the anharmonic contribution to the frequency spectrum is the same in the 6–13 as in the 6–12 potential then Θ_0^*(BK) for a 6–13 potential will be parallel to Θ_0^*(BK) in Fig. 4 but raised by an amount proportional to the potential parameters. At the same time the 6–13 parameters will lower the experimental points. In Fig. 5 we plot Θ_0^*(BK) and the experimental points using the 6–13 potential. The agreement is now reasonable. This tends to show that the Lennard-Jones 6–12 potential well is too shallow, since the 6–13 potential is deeper and somewhat steeper, indicating that the atomic forces are of a shorter range than the 6–12.

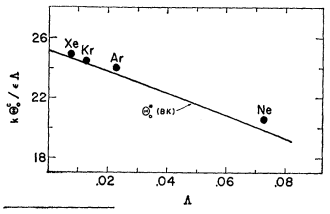

FIG. 6. Reduced Debye characteristic temperature Θ_0^* for a 6–12 potential nearest-neighbor (IN) mode plotted against Λ.

[32] J. S. Brown, Proc. Phys. Soc. (London) 85, 394 (1965).

Another way of effectively deepening the 6–12 potential is to assume only nearest-neighbor interaction in the theoretical calculations. Such a model abruptly cuts off the potential at a given distance from the atom. In Fig. 6 we present the results of a 6–12 nearest-neighbor-model calculation. The agreement is about as good as in Fig. 5. As will be discussed in the next section the temperature dependence of $\Theta^c(T)$ is also in reasonable agreement with the 6–12 nearest-neighbor-model calculation.

B. Temperature Dependence of Θ^c(T)

No detailed anharmonic calculations on the temperature dependence of Θ^c are currently available. We can only compare the experiments with the quasiharmonic theory of Horton and Leech.[9] The anharmonic calculations of Barron and Klein[10] discussed earlier apply only to the properties of the solid at 0°K. However, they have shown that while the anharmonic contribution to Θ_0^c for neon is 16% it is only ~1% for xenon. It is therefore quite appropriate to compare the experimental results for xenon with the quasiharmonic calculations of Horton and Leech.

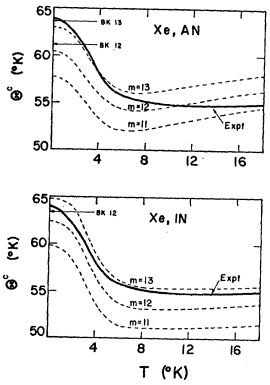

FIG. 7. $\Theta^c(T)$ curve showing variation with number of interacting neighbors and with m value. The dashed curves are from Horton and Leech (Ref. 9). The solid curves are the experimental values. The arrows point to Θ_0^c(BK) calculated by Barron and Klein (Ref. 10).

In Fig. 7 we reproduce a number of curves from Horton and Leech together with the experimental results. The theoretical curves based on the interaction of only nearest neighbors (IN) show a decrease of 14% between Θ_0^c and the flat portion of the curve beyond 8°K. The all-neighbor (AN) results, on the other hand, show a decrease of only 8%. These latter curves also have a definite minimum at 7°K. We observe that the $m=13$ nearest-neighbor model appears to fit the experimental data best in both shape and magnitude. We have also included in Fig. 7 the anharmonic results of Barron and Klein for Θ_0^c. Assuming that the anharmonic contribution to $\Theta^c(T)$ is constant over the entire temperature range in question (and furthermore, independent of the choice of m in the 6-m potential), we can raise each of the theoretical curves in Fig. 7 by approximately 1°K. A best fit to the data for xenon

would then be the 6–12 nearest-neighbor-model. Horton and Leech[9] also concluded that near-neighbor calculations best fit the data for argon and krypton.

A nearest-neighbor model is physically unrealistic. It assumes that the potential vanishes abruptly at a distance quite close to the potential well. One would expect a meaningful theoretical model to incorporate all neighbor interactions. As pointed out by Guggenheim and McGlashan,[33] the Lennard-Jones potential exaggerages the effect of distant neighbors and is inadequate for predicting the thermal properties of the solids. What is required is a deeper and shorter range potential. In this connection, Leech and Reissland[34] have added an intermediate-range attractive term $1/r^8$ (i.e., the next term in the expansion of the Van der Waal's potential) to the Lennard-Jones 6-12 potential. The agreement of their specific-heat calculations with Morrison's argon data[5] was not significantly better than the Horton and Leech 6–12 (AN) results. However, a $1/r^9$ term[35] considerably improved the agreement with the argon experiments. The effect of this term is to deepen the potential well and hence decrease the effect of all but the nearest neighbors. It would be interesting to see how well theoretical calculations of the specific heat, with this new term in the potential, compare with our xenon and neon data.

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[35] J. W. Leech and J. A. Reissland, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964* (Plenum Press, Inc., New York, 1965).

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Unified Approach to Interacting Phonon Problems*

PHILIP C. KWOK† AND PAUL C. MARTIN
Lyman Laboratory of Physics, Harvard Univessity, Cambridge, Massachusetts

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A unified treatment of the behavior of a system of interacting phonons is presented. This treatment is based on the physically measurable atomic-displacement correlation function or structure function. The perturbation treatment of its high-frequency behavior is briefly summarized. Its more complex behavior at low frequencies is studied in detail. Using a simple model of longitudinal phonons with cubic anharmonic interactions and without umklapp processes, two modes, representing damped first and second sound, are obtained. The parameters which occur in the calculated correlation function are shown to agree with those expected more generally from a phenomenological analysis which is also presented. The paper clarifies certain paradoxes relating to the difference between phonon, ordinary sound, and second sound, by showing that there is no fundamental distinction between these concepts in the only physical quantity, the displacement correlation function.

I. INTRODUCTION

As is by now well known, inelastic neutron scattering and Brillouin scattering measure the distribution in energy of density fluctuations of an atomic system. At high frequencies when these fluctuations have a wavelength short compared to an average mean free path this continuous energy spectrum has a well-defined peak. The position and width of this peak correspond to the natural frequency and damping of the phonon or the ordinary sound mode. The collision rate $1/\tau$ which corresponds to this mean free path is approximately equal to the damping of thermal frequency phonons. When the fluctuations have a wavelength long compared with the mean free path or $\omega\tau \ll 1$, a hydrodynamic description applies. In this limit, there appears a second peak with a smaller weight. It describes the thermal conduction mode or under certain circum-

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† Present address: IBM Watson Research Center, Yorktown Heights, New York.