In the low range, all the highly reduced samples show a maximum in the extra specific heat and a large magnetic specific heat. For the Ti-powder–reduced sample, the magnetic specific heats in fields of 6200 and 4450 Oe, and the paramagnetic susceptibility all agree with a model of a two-level paramagnetic system which has a level separation increasing with the square of the field strength and a spin splitting of the individual levels proportional to the field strength. The hydrogen-reduced samples show indications of interactions between the paramagnetic ions which change the paramagnetic susceptibility and specific-heat behaviors. It was speculated that the interaction is ferromagnetic, but it was not possible to derive a model which completely describes the low-range specific heat and magnetic susceptibility of hydrogen-reduced rutile. This type of paramagnetic ion is not present to any large extent in the vacuum-reduced sample; however, the donor level does split in a magnetic field to yield a magnetic specific heat.

The various centers present, then, are a function of the amount and method of reduction. The vacuum reduction, with its relatively high oxygen partial pressure, results mainly in an impurity-related center, while the main centers introduced by the reductions at low oxygen partial pressure are too numerous to be impurity related. If hydrogen is used in the reduction process, the center responsible for electrons in the band is modified so that there is no activation energy into the band. The hydrogen in the lattice may also contribute to the interactions between the paramagnetic ions.

## ACKNOWLEDGMENTS

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# Low-Temperature Heat Capacities of Solid Argon and Krypton*

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The specific heats of high-purity argon and krypton have been measured between 0.4 and 12°K, permitting a reliable extrapolation to 0°K. The higher-temperature results are in agreement with those of Morrison *et al.*, but for argon the extrapolation to 0°K is not. At the lowest temperatures the heat capacities are represented by $C=(12/5)\pi^4R(T/\Theta_0)^3$, with $\Theta_0=92.0$°K for argon and 71.9°K for krypton. The apparatus and techniques are described, and the results are compared with theoretical estimates.

## INTRODUCTION

THE noble-gas solids, with their relatively simple van der Waals attractive forces, are one of the best experimental systems for testing theories of lattice dynamics. A measure of current interest in the field is the number of recent review articles: Since Dobbs and Jones's review[1] of a decade ago, Pollack,[2] Boato,[3] Horton,[4] and Simmons[5] have also reviewed the field. Although these reviews treat mainly the perfect crystalline state, there is also now an interest, both theoretical and experimental, in various defect states of the noble-gas solids (see, e.g., Hartmann and Elliott[6] and Maradudin[7]). In general, the theories are at their best with the heavier noble gases (argon, krypton, and xenon) where one does not have the large zero-point energy effects of helium and neon, and where at the lowest temperatures thermal vibrations are of small amplitude. The Debye characteristic temperature $\Theta$ and Grüneisen "constant,"[8] and their values $\Theta_0$ and $\gamma_0$ at 0°K, are convenient parameters for describing experimental or theoretical results.

The comparison between theories and experimental results of the lowest-temperature properties of the heavier noble solidified gases has been much improved during recent years due to the following advances: The

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

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

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

[4] G. K. Horton, Am. J. Phys. 36, 93 (1968).

[5] R. O. Simmons, Solid State Phys. (to be published).

[6] W. M. Hartmann and R. J. Elliott, Proc. Phys. Soc. (London) 91 187 (1967).

[7] A. A. Maradudin, Solid State Phys. 18, 273 (1966); 19, 1 (1966).

[8] See, e.g., C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1966), Chap. 6.

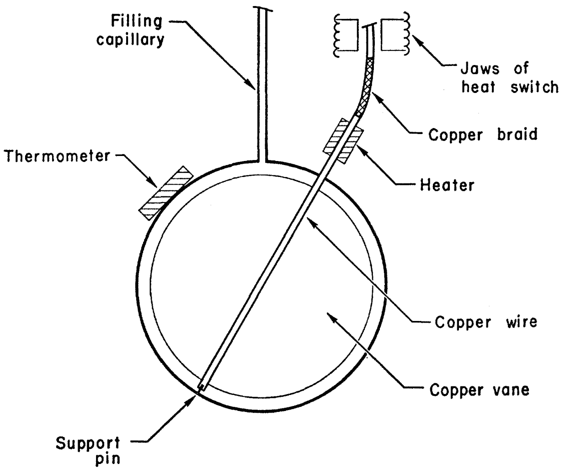

FIG. 1. Calorimeter.

availability of high-speed computing machines has allowed the theoretician to test the validity of the mathematical approximations which are necessary to reduce the problem to manageable proportions, and also to compute more accurate results. On the experimental side, large single crystals of neon, argon, and krypton have been grown[9,10]—though at the expense of great effort. Dispersion curves for solid neon and krypton have been measured under pressure by Daniels and his associates.[10,11] Improved experimental techniques, of exceedingly high accuracy in the case of the x-ray work, have determined the Grüneisen $\gamma$ at zero pressures and temperatures which are effectively 0°K.

The lattice parameter (and hence the density $\rho$), the coefficient of thermal expansion $\alpha$, and the isothermal compressibility $\kappa$ have been measured for neon[12] and argon[13] by Simmons and his associates, who have also measured $\alpha$ and $\kappa$ for krypton.[14] The specific heat at constant pressure, $C_P$, has been measured for neon and xenon by Fenichel and Serin[15] and by Fagerstroem and Hollis Hallett.[16] Excellent specific-heat measurements for argon from 2 to 86°K, and for krypton from 2 to 115°K were made by Flubacher, Leadbetter, and Morrison[17] and Beaumont, Chihara, and Morrison.[18] To establish $\Theta_0$ well, however, one must have measurements at temperatures below $\Theta_0/50$, and preferably[19] below $\Theta_0/100$, i.e., at below 2°K for argon and krypton. Hence it was decided to measure the heat capacities of argon and krypton to 0.4°K in a helium-3 cryostat, and to overlap the higher-temperature measurements of Morrison *et al.*[17,18] for comparison purposes. Below 0.4°K, the heat capacities of solid argon and krypton are so small that they are difficult to measure. However, it is considered that the measurements presented in this paper are of more than sufficient accuracy in $\Theta_0$ for existing theories.

## EXPERIMENTAL PROCEDURES

The present experimental methods differ from those of Morrison *et al.* in the following chief particulars: The apparatus was designed to give good specific-heat results in the lowest-temperature range, whereas that of Morrison *et al.* was designed to cover the range 2–300°K and also to measure vapor pressures. At the lower temperatures, the careful adiabatic shielding, which is required for heat-capacity measurements at high temperatures, is not necessary. Advantage was taken of the availability of stable germanium resistance thermometers of high reproducibility,[20] usable to 0.3°K,[21,22] thus avoiding the problems of calibration shifts which Morrison *et al.* experienced[17] with carbon resistance thermometers. The samples of argon and krypton used were larger than those of Morrison *et al.* (2.1 moles of argon compared with 0.16 to 0.24 moles; 1.6 moles of krypton compared with 0.11 to 0.16 moles), so that the unavoidable "background," due to the calorimeter, would not be excessive even at the lowest temperatures. The thermal diffusivity of the samples was not expected to get appreciably worse at temperatures below 1°K.

### Calorimeter Vessel

Since the specific-heat measurements were to be extended to the lowest possible temperature, it was important to choose a calorimeter material with a low heat capacity. Since the heat capacity of the sample varies approximately as $T^3$, a metal calorimeter, with an electronic heat capacity falling only as $T$, would appear at first sight to be not as good a choice as a nonmetallic calorimeter. A study was made of possible materials, including glass, polymethyl methacrylate,[23] and beryllium, which has a high $\Theta$ and low electronic specific heat. A glass calorimeter was actually con-

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[9] 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.

[10] W. B. Daniels, G. Shirane, B. C. Frazer, H. Umebayashi, and J. A. Leake, Phys. Rev. Letters **18**, 548 (1967).

[11] W. B. Daniels, G. Shirane, B. C. Frazer, J. A. Leake, J. Skalyo, and Y. Yamada, Bull. Am. Phys. Soc. **12**, 1063 (1967).

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

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

[14] A. O. Urvas, D. L. Losee, and R. O. Simmons, J. Phys. Chem. Solids **28**, 2269 (1967).

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

[16] C.-H. Fagerstroem and A. C. Hollis Hallett, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 1092.

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

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

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

[20] G. Cataland and H. H. Plumb, J. Res. Natl. Bur. Std. (U. S.) **70A**, 243 (1966).

[21] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. **38**, 159 (1967).

[22] N. E. Phillips *et al.* (to be published).

[23] Common trade names for this plastic are "Plexiglas," "Lucite," and "Perspex."

structed, but was considered to be too fragile for use. Polymethyl methacrylate and beryllium presented construction problems, especially in their attachment to a gas input capillary of low thermal conductivity, and beryllium is also toxic, requiring special precautions in machining. Finally, it was decided to make the calorimeter of gold-plated copper.

The calorimeter walls were made as thin as possible (0.004-in.) consistent with adequate strength, and a spherical shape was chosen (see Fig. 1) for minimum weight and reasonably good heat-transfer characteristics. Two spun hemispheres, 2 in. diam, were hard-soldered together; at the (lap) joint were soldered three equally spaced loops of copper wire, to which were later attached cotton threads. To improve thermal contact with the sample inside, a set of eight semicircular vanes at 45° intervals was mounted concentrically with, but not directly touching, the sphere. At their mutual line of contact, the vanes were silver-soldered to each other and to a straight copper wire of 0.040-in. diam. This wire, which was then a diameter of the sphere, was held in position at its lower end by a short concentric stainless steel pin of 0.005-in. diam. The upper part of the wire emerged from the sphere through a 0.005-in.-thick stainless-steel collar; to the portion of the wire outside the sphere was attached the heater for specific-heat measurements. The outermost end of the 0.040-in.-diam wire was silver-soldered to one end of a 2-in. length of flexible copper braid, of roughly equal cross-sectional area. To the upper end of the braid was silver-soldered $\frac{1}{2}$ in. of gold-plated 0.063-in.-diam copper wire, which lay between the jaws of the mechanical heat switch by means of which the calorimeter was cooled. The copper braid prevented damage to the fragile calorimeter from stresses due to the operation of the heat switch. The germanium resistance thermometer was attached to the outer surface of the sphere by a copper foil cemented with "7031" varnish,[24] and the electrical leads to the thermometer were also thermally anchored to the surface of the sphere with the same varnish. It is well known, for example, from ultrasonic measurements,[25,26] that the large volume contraction on cooling a noble-gas solid is enough to considerably weaken the fragile van der Waals bond of the solid to the walls of its container, and the construction just described was chosen because (a) the large contact areas would improve thermal contact to the argon, and (b) the heat pulse from the heater would be delivered more directly to the sample, minimizing the undetected heat loss through the gas-input capillary, electrical leads and supports that would result from superheating of the calorimeter wall. The calorimeter was suspended by the gas input capillary (stainless-steel 0.050-in.-o.d.×0.006-in. wall). Lateral motion was prevented by cotton threads and small wedges of expanded polystyrene foam (which had previously been found useful in specific-heat work down to 0.1°K[27]). The heater was wound from 0.0009-in. diameter, 9%-tungsten-91%-platinum-alloy wire[28] and was of 1744.8 Ω effective resistance at 4°K. Each end of the heater wire was connected to a length of fine copper wire, wound round the 0.040-in.-diam copper wire which was connected to the vanes inside the calorimeter as a thermal anchor. The other ends of these fine copper wires were attached to one end of a free-standing spiral lead of the same wire used in the heater, which provided thermal insulation. The other ends of the spiral leads were each attached to two copper wires, thermally anchored to the cage surrounding the calorimeter, which were ultimately connected to a current source and a potentiometer. For this conventional arrangement, the usual approximation was made that half of the total resistance (here half of 53.2 Ω) of the 9%-W-91%-Pt spiral leads was added to the actual heater resistance to provide the effective-heater resistance.[29]

The thermometer was an encapsulated doped germanium resistance thermometer,[30] series MHSP-IV, resistance at 4°K of 27 Ω. The four leads were each attached to 9%-W-91%-Pt wire spirals. The thermometer was calibrated from 0.3 to 25°K by a combination of magnetic, gas, and vapor-pressure thermometry in this laboratory.[22]

### Filling of Calorimeter

Ideally, one would like to make measurements on perfect single crystals of the solidified noble gases, but they are extremely difficult to prepare. Fortunately, for the measurement of a bulk quantity like the specific heat, polycrystalline samples are adequate and at low temperatures the effect of vacancies in at least solid argon[31] and krypton[32] should be negligible. Liquid argon (not quite enough to fill the calorimeter), was condensed into the calorimeter and then frozen, keeping the input capillary warm enough by electrical heating so that no liquid would condense in it. (The capillary was conveniently self-heated by passing an electric current along its length.[33]) During freezing, the internal vanes of the calorimeter were connected to the mechanical heat switch, and hence to the refrigerant in the cryostat, so that the sample would preferentially freeze to the vanes before freezing to the spherical surface of the calorimeter. In this way, thermal contact to the sample heater would be preserved as the sample was cooled to liquid-helium temperatures. The thermometer

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[24] General Electric Co., Schenectady, N. Y.

[25] J. R. Barker and E. R. Dobbs, Phil. Mag. **46**, 1069 (1955).

[26] L. Finegold, Ph.D. thesis, University of London, 1959 (unpublished).

[27] L. Finegold, Phys. Rev. Letters **13**, 233 (1964).

[28] J. C. Ho and N. E. Phillips, Rev. Sci. Instr. **36**, 1382 (1965).

[29] J. E. Neighbor, Rev. Sci. Instr. **37**, 497 (1966).

[30] This thermometer was made in 1964 by Honeywell, Inc., Riviera Beach, Fla.

[31] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phil. Mag. **12**, 1193 (1965).

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

[33] This idea is due to Professor Bernard Serin.

response during the actual specific-heat measurements showed that the thermal contact of the sample was quite satisfactory. As soon as the sample was completely frozen, as shown by a change in the resistance of the sample thermometer, the heating of the capillary was reduced, and the whole sample cooled further. Care was taken, by the addition of a heater to the capillary near the calorimeter, that the capillary would remain unblocked until the vapor pressure of the solid sample was low enough. The quantity of gas left in the capillary tubing and the filling system was then negligible.

Although the calorimeter, being spherical, had maximum strength for its mass, it was necessary to keep the filling pressure to below 2 atm for fear of bursting it. The liquid range from the triple point to one atmosphere pressure is only 3.5°K for argon and 4.0°K for krypton. Hence it was convenient to have an automatic pressure regulator to allow the (large amounts of) gas to condense at reasonable rates at pressures from 0 to 2 atm. To control the temperature of the calorimeter during condensation of the gas, it was easiest to fill the "helium" Dewar surrounding the apparatus with a suitable liquid refrigerant, and to adjust the temperature of the refrigerant by means of the same vapor-pressure controller which was later used to control the liquid-helium temperature. For argon, the liquid refrigerant was liquid oxygen. For krypton, carbon tetrafluoride (commercial Freon 14) was used. The gases were high purity cylinder gases.[34] The supplier's batch analysis of impurities, in parts per million, was as follows:

Argon: $O_2$, 1; $N_2$, 1; $H_2O$, 0.4; hydrocarbons, $<1$; $H_2$, $<1$.

Krypton: $O_2$, 2.4; $N_2$, $<50$; $H_2O$, 9.2; hydrocarbons, $<1$; Xe, $<10$.

At the end of the measurements, the gases were stored in large metal cylinders at $\approx 2$ atm. Samples were later analyzed on a mass spectrometer[35] and the following impurities (ppm) detected:

Argon: $N_2$ (or CO), $26_{-10}^{+0}$; $H_2O$, $10_{-5}^{+0}$; $C_2H_4$, $15_{-5}^{+0}$; $C_2H_2$, $11_{-3}^{+0}$; $CH_4$, $10_{-5}^{+0}$; $H_2$, $110_{-10}^{+0}$.

Krypton: $O_2$, $1\pm1$; $N_2$, $<25$; $H_2O$, $<16$; $CH_4$, $15\pm3$; $C_2H_2$, $\leq 5$; $C_2H_4$, $\leq 20$; $C_2H_6$, $\leq 8$; $H_2$, $98\pm6$; CO, $\leq 15$; $CO_2$, $10\pm3$.

(The limits on undetected impurities are, in general, less than 5 ppm for any single impurity. Owing to low sensitivity, the limit on detection of helium is 10 ppm and that of neon is 40 ppm. Note that neon must be determined on mass 22, which isotope is only 10% abundant.) It is likely that much of these impurities were desorbed from the walls of the metal storage containers used after the measurements were completed, and hence were not present in the specific-heat samples.

Because the samples were large (approximately two g moles), the measurement of mass by the conventional method (measurements of its pressure and volume at known temperature) would have been awkward. Hence, the mass was determined by direct weighing to well within 0.1% accuracy in a pressure vessel, which was also made part of the gas handling and retrieval system.[36] The numbers of g moles were 2.1385 for the argon sample (assuming a molecular weight 39.944) and 1.6055 g moles for the krypton sample (molecular weight 83.80).

The cool-down procedure, after the argon or krypton sample had been well frozen, was briefly as follows: The liquid refrigerant was removed from the Dewar, and a flow of cool helium gas to the Dewar commenced. The temperature of the sample did not increase appreciably during this time. Liquid helium-4 was then transferred; care was taken that there was no exchange gas surrounding the calorimeter. When the calorimeter was at 4.2°K, the pressure above the liquid helium-4 was reduced until the temperature was about 1.2°K. Helium-3 was then allowed to condense into its chamber: When it had condensed, its vapor pressure was reduced until a temperature below 0.3°K was attained.

### Specific-Heat Measurements

The well-known heat-pulse method of measuring specific heats[37] was used. The thermometer resistance was measured by the usual four-probe method, using a six-dial potentiometer[38] and a chopper amplifier with a few nanovolts resolution.[39] The output of the amplifier was fed to a variable-speed chart recorder. Temperature increments were from $T/20$ to $T/10$: There was no observable dependence of the results on heater power. The quantity of heat applied to the sample was measured to within 0.1%. Measurements could not be made reliably below about 0.4°K, because of electrical and vibrational noise (even though the cryostat was on antivibration supports).

The specific heat of the empty calorimeter was measured in a later run, and in the argon measurements accounted for 23% of the measured heat capacity at 0.5°K and 7% at 1°K. For the krypton measurements, the corresponding figures are 16 and 5%. The measured heat capacities are given for argon in Table I and for krypton in Table II.

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[34] Obtained from the Linde Division of Union Carbide, Inc., New York, N. Y.

[35] The analysis was carried out by Dr. Amos S. Newton, Lawrence Radiation Laboratory, Berkeley, Calif.

[36] L. Finegold, J. Sci. Instr. **44**, 789 (1967).

[37] For an excellent description of this method, and a comparison with a continuous heating method, see J. F. Cochran, C. A. Shiffman, and J. E. Neighbor, Rev. Sci. Instr. **37**, 499 (1966).

[38] Leeds and Northrup, Inc., Philadelphia, Pa; Model No. 7556.

[39] Keithley, Inc., Cleveland, Ohio; Model No. 149.

TABLE I. Measured heat capacities of argon.

| $T$(°K) | $C$(mJ/mole °K) | $T$(°K) | $C$(mJ/mole °K) | $T$(°K) | $C$(mJ/mole °K) | $T$(°K) | $C$(mJ/mole °K) |
|---|---|---|---|---|---|---|---|
| Run I | | | | Run II | | | |
| 4.8913 | 354.0 | 1.8332 | 15.71 | 0.4367 | 0.2130 | 10.0900 | 3341.0 |
| 5.4764 | 510.9 | 1.9575 | 19.11 | 0.4840 | 0.2818 | 11.2269 | 4376.0 |
| 6.0978 | 731.8 | 2.1398 | 25.11 | 0.5332 | 0.3765 | 4.5362 | 275.1 |
| 6.6429 | 971.6 | 2.3312 | 32.73 | 0.5833 | 0.4976 | 4.9792 | 372.3 |
| 7.1685 | 1235.0 | 2.5233 | 41.68 | 0.6374 | 0.6486 | 5.4175 | 495.7 |
| 8.0024 | 1735.0 | 2.7478 | 54.33 | 0.6645 | 0.7397 | 5.9462 | 672.1 |
| 8.7131 | 2216.0 | 2.9965 | 71.17 | 0.7100 | 0.8876 | 6.5000 | 906.8 |
| 4.4551 | 255.5 | 3.2243 | 89.91 | 0.7669 | 1.122 | 1.2380 | 4.785 |
| 0.4978 | 0.3083 | 3.4492 | 111.1 | 0.8464 | 1.540 | 1.3722 | 6.523 |
| 0.5334 | 0.3741 | 3.7407 | 143.8 | 0.8934 | 1.793 | 1.5863 | 10.13 |
| 0.5693 | 0.4690 | 4.0687 | 189.9 | 0.9205 | 1.949 | 1.6516 | 11.42 |
| 0.5960 | 0.5364 | 4.4499 | 255.7 | 1.0026 | 2.555 | 1.7380 | 13.42 |
| 0.6292 | 0.6176 | 4.8235 | 331.1 | 1.1060 | 3.418 | 1.8316 | 15.75 |
| 0.6587 | 0.7065 | 1.4206 | 7.212 | 1.2146 | 4.513 | 1.9309 | 18.43 |
| 0.6896 | 0.8131 | 1.5774 | 9.906 | 1.2511 | 4.930 | 2.0162 | 21.19 |
| 0.8283 | 1.423 | 1.6606 | 11.56 | 1.3693 | 6.455 | 2.1260 | 24.72 |
| 0.8817 | 1.725 | 1.7543 | 13.71 | 1.4809 | 8.167 | 2.2769 | 30.53 |
| 0.9578 | 2.237 | 1.8423 | 15.89 | 0.3960 | 0.1553 | 2.4627 | 38.88 |
| 1.0376 | 2.826 | 1.9193 | 17.85 | 0.5527 | 0.4374 | 2.6562 | 49.03 |
| 1.1253 | 3.584 | 1.9920 | 20.21 | 0.6546 | 0.7025 | 2.8708 | 62.44 |
| 1.1735 | 4.020 | 2.0690 | 22.71 | 0.7183 | 0.9353 | 3.0846 | 78.30 |
| 1.2253 | 4.603 | 0.5104 | 0.3368 | 0.7722 | 1.153 | 3.3288 | 99.79 |
| 1.2844 | 5.288 | 0.5576 | 0.4270 | 0.8648 | 1.642 | 3.5949 | 127.9 |
| 1.3414 | 6.050 | 0.6003 | 0.5313 | 0.9569 | 2.187 | 3.9063 | 167.0 |
| 1.4059 | 6.973 | 0.6052 | 0.5487 | 1.0338 | 2.761 | 4.2602 | 222.1 |
| 1.4735 | 7.958 | 0.6613 | 0.7315 | 1.1024 | 3.313 | 4.6114 | 289.6 |
| 1.5289 | 9.035 | 0.7147 | 0.9246 | 1.1528 | 3.840 | 4.9798 | 375.1 |
| 2.0727 | 22.85 | 0.7621 | 1.130 | 1.2036 | 4.395 | 1.2428 | 4.838 |
| 2.1614 | 25.94 | 0.8100 | 1.317 | 1.3098 | 5.669 | 1.3559 | 6.299 |
| 2.1183 | 24.42 | 0.8617 | 1.616 | 1.3968 | 6.889 | 1.4604 | 7.863 |
| 2.2907 | 31.12 | 0.9265 | 2.007 | 1.4903 | 8.342 | 1.5269 | 9.020 |
| 2.3979 | 35.85 | 0.9896 | 2.439 | 0.4969 | 0.3041 | 1.6035 | 10.49 |
| 2.5257 | 41.72 | 0.9508 | 2.173 | 0.5910 | 0.5338 | 1.9228 | 18.24 |
| 2.6255 | 47.21 | 1.0195 | 2.648 | 0.6450 | 0.6813 | 2.0508 | 22.20 |
| 2.7569 | 55.02 | 1.0927 | 3.293 | 0.7042 | 0.8869 | 2.2399 | 29.21 |
| 2.9071 | 64.64 | 1.2683 | 5.144 | 0.7693 | 1.162 | 2.4571 | 38.78 |
| 3.0710 | 76.88 | 1.3650 | 6.403 | 0.8449 | 1.543 | 2.6673 | 49.92 |
| 3.2732 | 94.38 | 4.3091 | 231.2 | 4.1810 | 210.1 | 2.9187 | 66.09 |
| 3.5483 | 121.5 | 4.8241 | 334.1 | 4.6041 | 287.6 | 3.1743 | 86.27 |
| 3.8604 | 160.2 | 5.3373 | 466.8 | 5.1224 | 408.3 | 3.4365 | 111.5 |
| 4.2258 | 216.1 | 5.8326 | 630.2 | 5.6733 | 574.4 | 3.7313 | 144.6 |
| 1.2105 | 4.507 | 6.3069 | 816.2 | 6.2357 | 784.6 | 4.6987 | 310.2 |
| 1.2989 | 5.480 | 6.9139 | 1103.0 | 7.5256 | 1456.0 | 5.1263 | 417.5 |
| 1.3832 | 6.630 | 8.2931 | 1948.0 | 8.3630 | 1995.0 | 1.4946 | 8.44 |
| 1.4828 | 8.167 | 9.0860 | 2480.0 | 9.1864 | 2598.0 | | |
| 1.5852 | 10.07 | 11.2261 | 4366.0 | | | | |
| 1.7119 | 12.77 | | | | | | |

### Possible Existence of Two Phases

Meyer, Barrett, and Haasen[40] discovered the existence of an hcp phase in solid argon in addition to the more usual fcc structure. This discovery was encouraging, because theories based on central two-body forces of the Mie–Lennard-Jones type had predicted that the hcp structure would be slightly more stable than the fcc.[41] However, of the noble-gas solids only helium had previously been shown to exhibit polymorphism. Hence, many authors have postulated noncentral many-body forces, but there is still discussion about the necessity of this postulate.[42] Feldman[43] has calculated the difference between $\Theta_0$ for the hcp and fcc phases based on a Mie–Lennard-Jones all-neighbor model in the quasi-harmonic approximation, and found that $[\Theta_0(\text{hcp})-\Theta_0(\text{fcc})]/\Theta_0(\text{fcc})$ is of the order of 2% for argon. Present specific-heat techniques are therefore sufficient to detect the difference between a completely hcp sample of solid argon and a completely fcc sample. Should a sample be of mixed hcp and fcc phases—as is indeed more probable than hcp alone—then it is of course necessary to know, by independent means, the proportion of each phase present. (An analogous situation is well discussed in Martin's analysis of the marten-

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[40] L. Meyer, C. S. Barrett, and P. Haasen, J. Chem. Phys. **40**, 2744 (1964); C. S. Barrett and L. Meyer, J. Chem. Phys. **41**, 1078 (1964).

[41] T. H. K. Barron and C. Domb, Proc. Roy. Soc. (London) **A227**, 447 (1955).

[42] See Ref. 32. A list of references is given by D. L. Losee and R. O. Simmons, Phys. Rev. Letters **18**, 451 (1967).

[43] C. Feldman, Proc. Phys. Soc. (London) **86**, 865 (1965).

TABLE II. Measured heat capacities of krypton.

| $T$(°K) | $C$(mJ/mole °K) | $T$(°K) | $C$(mJ/mole °K) |
|---|---|---|---|
| 4.6496 | 688.7 | 0.8480 | 3.219 |
| 5.1110 | 942.5 | 0.9368 | 4.325 |
| 5.5990 | 1263.0 | 1.0076 | 5.412 |
| 5.9839 | 1552.0 | 1.1048 | 7.091 |
| 6.2566 | 1775.0 | 1.1996 | 9.140 |
| 6.5436 | 2017.0 | 1.2906 | 11.31 |
| 6.8930 | 2361.0 | 1.4011 | 14.58 |
| 7.2669 | 2726.0 | 1.5133 | 18.40 |
| 7.6586 | 3143.0 | 1.6322 | 23.33 |
| 8.1047 | 3648.0 | 0.5089 | 0.6796 |
| 8.6887 | 4334.0 | 0.5602 | 0.9173 |
| 9.3577 | 5105.0 | 0.6133 | 1.206 |
| 10.1437 | 6088.0 | 0.6721 | 1.576 |
| 12.2790 | 8738.0 | 0.3600 | 0.2390 |
| 11.0851 | 7270.0 | 0.3872 | 0.2970 |
| 1.2404 | 10.11 | 0.4198 | 0.3826 |
| 1.3379 | 12.67 | 0.4817 | 0.5904 |
| 1.4466 | 16.14 | 0.5269 | 0.7796 |
| 1.5450 | 19.69 | 0.5803 | 1.047 |
| 1.6552 | 24.39 | 0.6417 | 1.416 |
| 1.7768 | 30.39 | 0.6910 | 1.757 |
| 1.8961 | 36.79 | 0.7565 | 2.295 |
| 2.0212 | 45.13 | 0.8350 | 3.115 |
| 2.1616 | 55.42 | 0.9155 | 4.047 |
| 2.3144 | 68.84 | 1.0066 | 5.441 |
| 2.4920 | 86.53 | 1.1086 | 7.240 |
| 2.7118 | 113.5 | 1.2068 | 9.316 |
| 2.9379 | 147.1 | 1.3168 | 12.09 |
| 3.1875 | 193.2 | 1.4260 | 15.44 |
| 3.4782 | 258.5 | 1.5257 | 18.97 |
| 3.8040 | 348.5 | 1.6066 | 22.31 |
| 4.1726 | 479.3 | 1.7651 | 29.79 |
| 4.5926 | 658.3 | 1.9367 | 39.64 |
| 5.0652 | 913.0 | 2.1092 | 51.81 |
| 0.3684 | 0.2540 | 2.3038 | 68.21 |
| 0.4114 | 0.3683 | 2.5354 | 92.28 |
| 0.4581 | 0.5175 | 2.8180 | 129.2 |
| 0.4994 | 0.6347 | 3.1263 | 182.5 |
| 0.5452 | 0.8265 | 3.4622 | 256.5 |
| 0.5949 | 1.100 | 3.8311 | 357.9 |
| 0.6566 | 1.480 | 4.2416 | 505.7 |
| 0.7106 | 1.883 | 4.7103 | 723.5 |
| 0.7716 | 2.414 | | |

sitic change in sodium and lithium.[44]) An attempt was made in this work to detect a difference of the above type. In run I (Table I), an argon sample was cooled as rapidly as possible from 80 to 4°K, in the hope that the rapid cooling would induce as much stress, and hence as much hcp phase, as possible.[40] After the specific-heat measurements had been made, the same sample was annealed at 77°K for half a day, and then cooled slowly to 4°K, in the expectation that the sample would be mainly, if not all, fcc. The measurements of run II (Table I) were then made. Care was taken that there were no changes in the apparatus, or in the sample mass, between runs I and II. A comparison of the results of runs I and II shows that the low-temperature $\Theta$ was unchanged, within the precision of the measurements. However, it is estimated, on the basis of the predicted 2% difference in $\Theta_0$ and a precision of 1% in $C$, that as much as 17% of the hcp phase could have been present.

In the work of Barrett and Meyer,[40,45] the x rays do not penetrate deeply into the solid, and so it is possible that the hcp phase existed only near the surface. In electron-diffraction experiments on thin films of solidified noble gases, Curzon and Pawlowicz[46] found that when observed in transmission, argon, neon, krypton, and xenon crystallized in the fcc structure. However, when observed in reflection, krypton showed an hcp form. The possibility of a phase transformation occurring at a solid argon surface has been discussed by Burton and Jura.[47]

## ANALYSIS OF RESULTS

In Figs. 2 and 3, the heat capacities are plotted as $C/T^3$ versus $T$ and compared with the measurements of Morrison and co-workers.[17,18] Smoothed values of $C/T^3$, corresponding to the curves of Figs. 2 and 3, are given in Table III, which also includes equivalent values of the effective Debye temperatures. As Fig. 2 shows, the results obtained in the two argon runs do not differ significantly. They have therefore been considered together in the following analysis, and no distinction between them is made in subsequent figures. For both argon and krypton our results differ from the earlier work by an amount which is, over most the common temperature range, qualitatively similar in temperature dependence and only slightly greater than the combined

TABLE III. Smoothed values of $C/T^3$ and $\Theta/\Theta_0$ for argon and krypton. ($\Theta_0$ was taken as 91.953 and 71.896°K for argon and krypton, respectively.)

| | Argon | | Krypton | |
|---|---|---|---|---|
| $T$ (°K) | $C/T^3$ (mJ/mole °K$^4$) | $\Theta/\Theta_0$ | $C/T^3$ (mJ/mole °K$^4$) | $\Theta/\Theta_0$ |
| 0.5 | 2.502 | 0.9997 | 5.237 | 0.9996 |
| 1.0 | 2.510 | 0.9987 | 5.265 | 0.9978 |
| 1.5 | 2.527 | 0.9964 | 5.331 | 0.9937 |
| 2.0 | 2.557 | 0.9925 | 5.447 | 0.9866 |
| 2.5 | 2.602 | 0.9868 | 5.622 | 0.9762 |
| 3.0 | 2.662 | 0.9793 | 5.868 | 0.9624 |
| 3.5 | 2.737 | 0.9703 | 6.170 | 0.9464 |
| 4.0 | 2.827 | 0.9599 | 6.488 | 0.9307 |
| 4.5 | 2.927 | 0.9488 | 6.784 | 0.9166 |
| 5.0 | 3.029 | 0.9380 | 7.013 | 0.9058 |
| 5.5 | 3.126 | 0.9282 | 7.158 | 0.8981 |
| 6.0 | 3.214 | 0.9192 | 7.227 | 0.8927 |
| 6.5 | 3.290 | 0.9114 | 7.225 | 0.8888 |
| 7.0 | 3.350 | 0.9048 | 7.159 | 0.8861 |
| 7.5 | 3.390 | 0.8993 | 7.039 | 0.8843 |
| 8.0 | 3.406 | 0.8953 | 6.867 | 0.8830 |
| 8.5 | 3.398 | 0.8925 | 6.657 | 0.8829 |
| 9.0 | 3.368 | 0.8908 | 6.421 | 0.8828 |
| 9.5 | 3.322 | 0.8897 | 6.169 | 0.8827 |
| 10.0 | 3.263 | 0.8888 | .910 | 0.8825 |
| 10.5 | 3.197 | 0.8881 | 5.648 | 0.8821 |
| 11.0 | 3.123 | 0.8871 | 5.386 | 0.8815 |
| 11.5 | 3.045 | 0.8860 | 5.124 | 0.8811 |
| 12.0 | 2.964 | 0.8845 | 4.862 | 0.8810 |
| 12.5 | 2.880 | 0.8828 | 4.600 | 0.8817 |

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[44] D. L. Martin, Proc. Roy. Soc. (London) **A254**, 433, (1960); **A254**, 444 (1960); Phys. Rev. **139**, A150 (1965).

[45] C. S. Barrett and L. Meyer, J. Chem. Phys. **42**, 107 (1965).

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

[47] J. J. Burton and G. Jura, Phys. Rev. Letters **18**, 740 (1967).

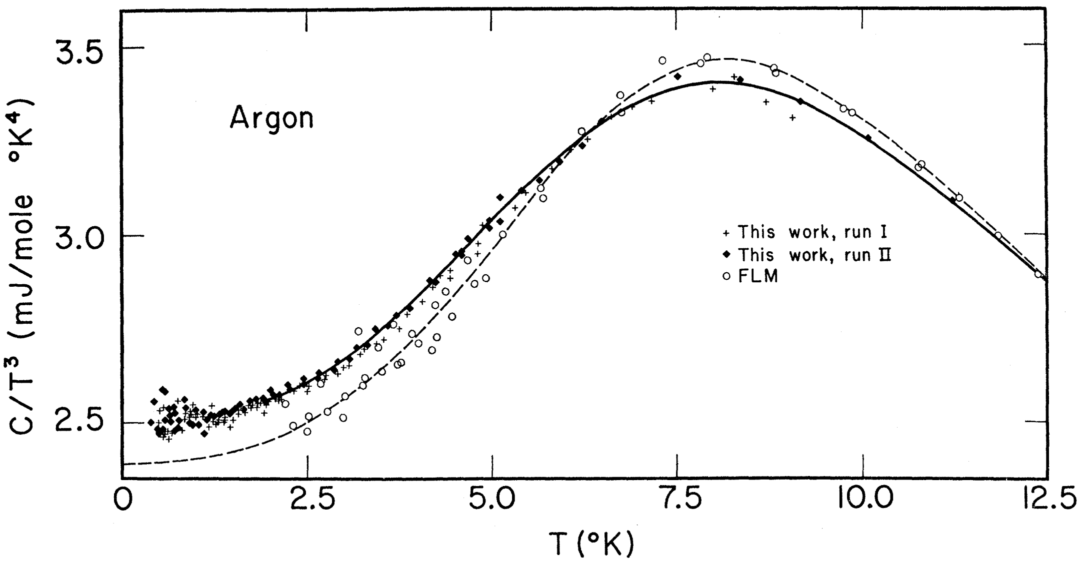

FIG. 2. Heat capacity of argon between 0.4 and 12°K. FLM refers to Flubacher, Leadbetter, and Morrison (Ref. 17), and the dashed curve represents their smoothed values and extrapolation to 0°K. The solid curve corresponds to the smoothed values given in Table I.

scatter of the points. [The largest differences between the two sets of measurements occur in the regions just above and just below 6°K, where the slope of the deviation plot for the carbon thermometer used in the earlier measurements is large (see Fig. 3 of Ref. 17) and therefore most likely to introduce errors in the heat capacity.] However, the extension of the new results to 0.5°K and their greater precision at temperatures below 5°K define the extrapolation of 0°K more precisely, and, as will be shown, this leads to significant differences in the dependence of $\Theta/\Theta_0$ on $T/\Theta_0$.

The data have been analyzed on the usual assumption that the heat capacity can be expressed by a series of odd powers of $T$ starting with $T^3$,

$$C=\sum_{i=1}^{n} A_{2i+1}T^{2i+1}. \tag{1}$$

The coefficients of the $T^3$ terms, and the values of $\Theta_0$, were obtained by the extrapolation of plots of $C/T^3$ versus $T^2$ to $T^2=0$, as shown in Figs. 4 and 5. Since the extrapolations are short, the $\Theta_0$ values, 92.0°K for

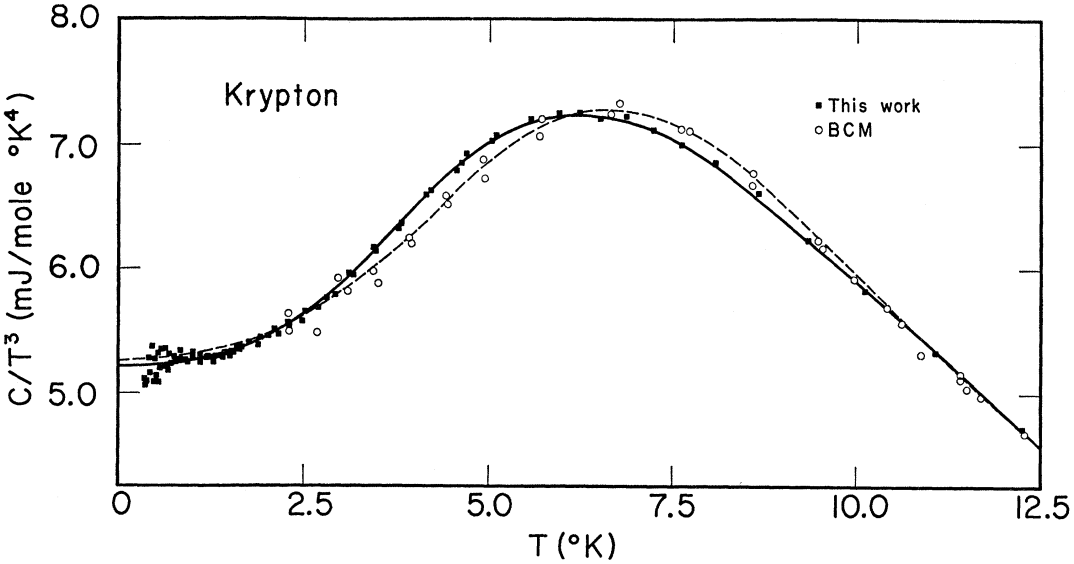

FIG. 3. Heat capacity of krypton between 0.4 and 12°K. BCM refers to Beaumont, Chihara, and Morrison (Ref. 18) and the dashed curve represents their smoothed values and extrapolation to 0°K. The solid curve corresponds to the smoothed values given in Table I.

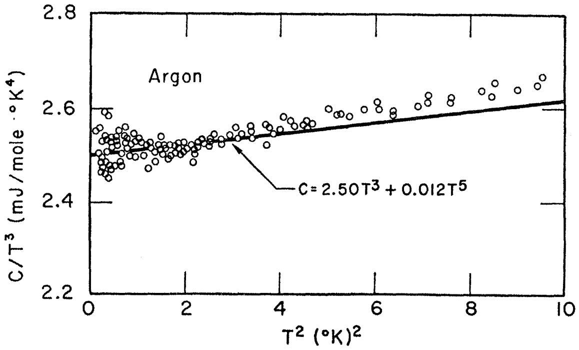

FIG. 4. Heat capacity of argon below ~3°K.

argon and 71.9°K for krypton, are determined quite precisely. The temperature scale is believed to be the major source of systematic error, and comparison of the heat capacity of copper as determined on the same scale with values obtained in a number of other laboratories suggests that the error arising from this source is no more than 1% in heat capacity or $\frac{1}{3}$% in $\Theta$. The $\Theta_0$ value for krypton is close to that obtained by Beaumont, Chihara, and Morrison[18]—71.7°K—but there is a significant difference (corresponding to 4% in heat capacity) between our value for argon and the 93.3°K reported by Flubacher, Leadbetter, and Morrison.[17] The coefficients of the $T^5$ terms $A_5$, which correspond to the slopes of the lines in Figs. 4 and 5, are not so well established—their values are small, and depend strongly on the temperature interval over which the straight-line approximation is made. These conclusions were verified by making a number of least-squares fits of the data to Eq. (1) with different values of $n$ and different high-temperature cutoffs. With a sufficient number of terms this equation fits all the data with an rms deviation of 0.8% for argon and 0.9% for krypton. (The difference is apparently associated with a relatively large number of low-precision low-temperature points in the krypton data.) All fits which gave an rms deviation of 1.25% or less gave values of $A_3$ within 0.5% of those determined graphically, but the corresponding values of $A_5$ differed from each other by considerably larger amounts. The inclusion of even powers to $T$ in the expansion usually improved the fit obtained with a given number of terms, but the magnitude and sign of the coefficients of terms other than the $T^3$ term fluctuated erratically with changes in the number of terms. The $T^3$ coefficients, however, were still substantially the same as those obtained graphically except for some of the fits to the krypton data with a series containing a $T^4$ term. The downturn in $C/T^3$ for the lowest-temperature krypton points and the dip at $T \approx 1.4$°K (which also occurs in the argon data and presumably reflects an irregularity in the temperature scale) is probably responsible for this exception.

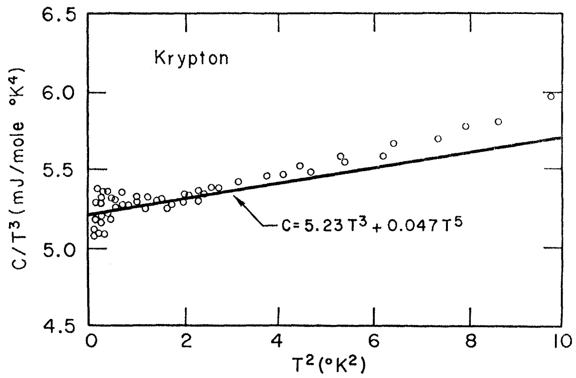

FIG. 5. Heat capacity of krypton below ~3°K.

## DISCUSSION

The effective Debye temperature has been calculated from the heat capacities in the usual way. (No correction for the difference between $C_P$ and $C_V$ or for thermal expansion is necessary at these temperatures.) As shown in Fig. 6, plots of $\Theta/\Theta_0$ versus $T/\Theta_0$ for argon and krypton in this temperature range are closely similar. Figure 6 also shows the results of calculations by Horton and Leech.[48] The approach of Horton and Leech, and of Grindlay and Howard in similar calculations,[49] was to consider a simplified model in which any mathematical approximations, necessary for the evaluation of the model, were well understood. They assumed a Mie–Lennard-Jones potential in the harmonic approximation, including zero-point energy only in the Boltzmann thermal-distribution terms. They then tested the sensitivity of their model to the exact form of the Mie–Lennard-Jones potential chosen and to the number of atomic neighbors whose interactions are considered important. Even though the effects of anharmonicity were specifically not included, this approach appears at present to be more useful than one in which an attempt is made to include all effects, but in which the mathematical assumptions may have more influence than the physical assumptions. Horton and Leech present calculations for nearest neighbors only (1N), nearest and next-nearest neighbors only (2N), and all neighbors (AN). For temperatures up to the minimum of the reduced $\Theta$-$T$ curves, they find a law of corresponding states for argon and krypton, for 1$N$, 2$N$, and AN models. Our experimental results agree with such a law, in contrast with the earlier results in this temperature range. Since the assumption of a Mie–Lennard-Jones potential would be expected to give a law of corresponding states, in the absence of zero-point energy, it appears that zero-point energy effects are indeed small here. Our experimental results fall midway between Horton and Leech's 1N and AN calculations for a 12-6 potential, and are in reasonable agreement

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

[49] J. Grindlay and R. Howard, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 129.

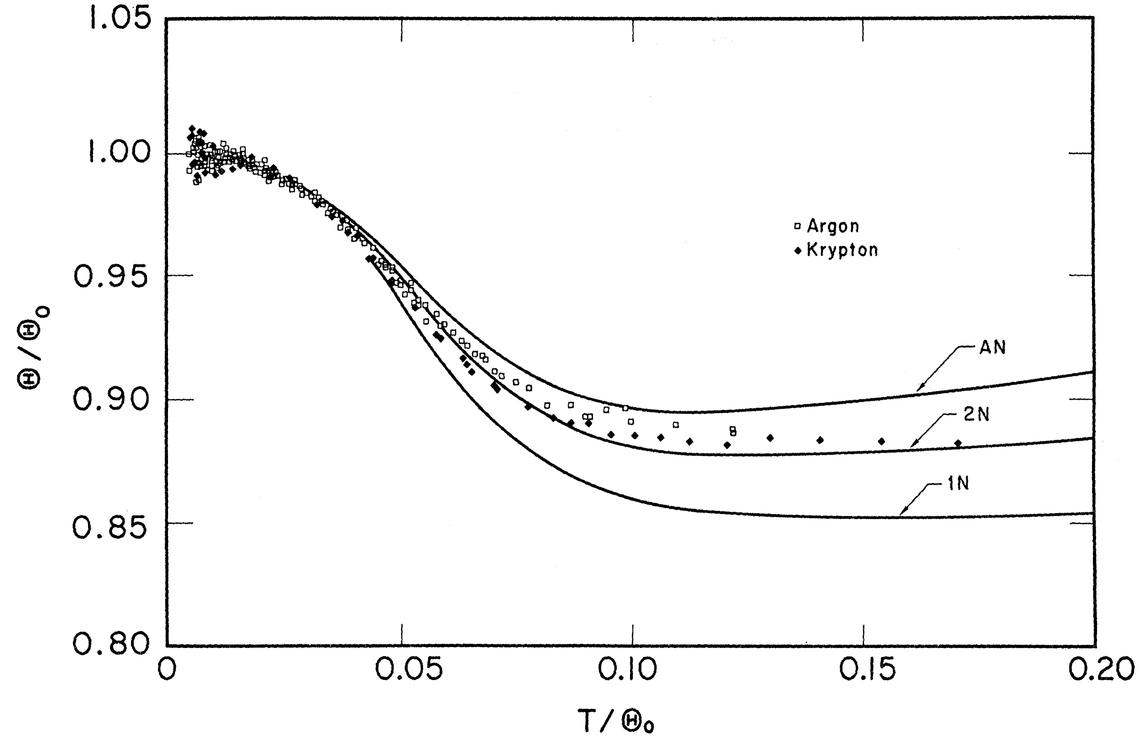

FIG. 6. Reduced Debye temperature plots for the argon and krypton data. The solid curves represent calculations by Horton and Leech (Ref. 48). 1N, 2N, and AN refer to first-, first- and second-, and all-neighbor calculations, respectively.

with, but a little higher than, their 2N calculations. Even though for short-range central forces the influence of temperature-dependent anharmonic effects would seem to be to raise the (harmonic) reduced Θ-$T$ curves, in the (low) temperature range of these measurements, such an influence would be rather small. The basic reason for the smallness of the effect is that, in our temperature range, the thermal energy is still small compared to any zero-point energy. Detailed estimates of anharmonic effects are difficult to make. One such estimate, due to Klein,[50] would expand the $T/\Theta_0$ axis of Fig. 6 by approximately 4% for argon and 2% for krypton. More recent calculations of Klein and Horton[51] combined the anharmonic calculation of Barron and Klein[52] into the quasiharmonic calculation of Horton and Leech[48] and show that a 13-6 (2N) potential gives good agreement with the experimental $\Theta_0$. A more sensitive test of the model is given by the predicted Θ-$T$ curves, and the 13-6 (2N) is the best of similar potentials. However, the fact that the AN calculation does not give the best agreement with experiment implies that corrections are needed to the potential, either in its shape or by the inclusion of three-body interactions. Also, Θ-$T$ plots show that different potentials are needed to fit different temperature regions,[51] confirming that the Mie-Lennard-Jones potential is still inadequate.

In summary, it would seem that these results are consistent with the present view of this field: That whereas some years ago the theories were more advanced than the experimental data available, now the need is for a better understanding of the interatomic forces as well as for improved anharmonic theories.

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We are grateful to W. B. Daniels, M. L. Klein, J. A. Morrison, R. O. Simmons, and C. A. Swenson for helpful conversations, and to A. S. Newton for analysis of the samples.

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[50] T. H. K. Barron, Ref. 49, p. 247, Sec. 4b.

[51] M. L. Klein (private communication). M. L. Klein and G. K. Horton, Proceedings of the Eleventh International Low-Temperature Conference, 1968, St. Andrews, Scotland (unpublished).

[52] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) 82, 523 (1965).