PHYSICAL REVIEW B **80**, 094112 (2009)

Lattice distortion of hcp solid helium under pressure

Yu. A. Freiman,[1,*] S. M. Tretyak,[1] A. Grechnev,[1] Alexander F. Goncharov,[2] John S. Tse,[3] D. Errandonea,[4]
Ho-kwang Mao,[2] and Russell J. Hemley[2]
[1]*B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine,
47 Lenin Avenue, Kharkov 61103, Ukraine*
[2]*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, USA*
[3]*Department of Physics and Engineering Physics, University of Saskatchewan, 116 Science Place, Saskatoon,
Saskatchewan, Canada S7N 5E2*
[4]*Departamento de Fisica Aplicada-ICMUV, Universitàt de València, c/Dr Moliner 50, E-46100 Burjassot, Spain*

(Received 16 April 2009; revised manuscript received 12 August 2009; published 25 September 2009)

The lattice distortion of hcp solid He under pressure is calculated using semiempirical and first-principle approaches. While three-body forces tend to flatten the lattice at all compressions, the effect of pair forces changes from the flattening at small compression to elongation at large one. At large compressions, the lattice distortion due to the triple forces is more than twice as large as those due to pair forces and the lattice is slightly flattened. First-principles results show that over approximately fivefold compressions higher-order, many-body forces become important.

DOI: 10.1103/PhysRevB.80.094112 PACS number(s): 62.50.−p, 67.25.−k, 67.30.−n

In line with the close-packing principle, rare gases He, Ne, Ar, Kr, and Xe crystallize into structures having the largest packing coefficient for spherical entities—the hexagonal close-packed (hcp) and face-centered cubic (fcc) structures. At low pressures and temperatures ^{4}He crystallizes into the hcp structure. High-pressure (HP) x-ray diffraction measurements[1,2] have shown that in a wide temperature (up to 300 K) and pressure (up to 57 GPa) range hcp ^{4}He is stable. The heavier or classical rare-gas solids (RGS)—Ne, Ar, Kr, and Xe—crystallize into the fcc structure. HP diamond-cell studies[3–6] have shown that the hcp phase can be stabilized at high compression in Xe,[3,4,6] Kr,[4] and Ar,[5] with the fcc and hcp phases coexisting over a broad range of pressures. Contrary to expectations, a HP x-ray diffraction study of solid Ne at the pressure range up to 208 GPa (Ref. 7) found that the crystal structure of neon remains fcc.

One of the fingerprints of hcp RGS is their lattice-dynamic properties. Unlike fcc, the hcp structure has optical branches in the phonon spectrum. The doubly degenerate Raman-active E_{2g} mode corresponds to a shear out-of-phase motion of the layers of atoms in the *ab* plane. There are low-pressure neutron data up to 0.5 GPa (Ref. 8) and Raman data up to 1 GPa (Ref. 9) on the E_{2g} phonons in solid He. The first-principle and semiempirical theoretical data on the HP behavior of the E_{2g} phonons in solid He (Ref. 10) were compared with data obtained using the experimental elastic constant C_{44} data from Ref. 2. Recently Raman data were obtained for Ar up to 58 GPa,[10] Kr up to 75 GPa,[11] and Xe up to 41 and 135 GPa in Refs. 10 and 12, respectively.

Another distinctive feature of the hcp structure is an additional degree of freedom associated with the c/a ratio. A lattice of closed-packed hard spheres has $c/a=\sqrt{8/3}\approx 1.633$ (the ideal hcp structure). The quantity $\delta = c/a - \sqrt{8/3}$, the lattice distortion parameter, describes the deviation of the axial ratio from the ideal value. In the case of $\delta < 0$, this distortion involves extension within close-packed planes, and contraction along the *c*-axis direction, and vice versa, for $\delta > 0$ the lattice is expanded along the *c* axis and contracted within close-packed planes. For all hcp elemental solids except helium, hydrogen, and heavy rare gases (Ar, Kr, and Xe) under pressure the behavior of δ with pressure and temperature is well established. Typical values are on the order of 10^{-2}. For solid helium δ is an order of magnitude less.[13,14] In this paper we present results of the first theoretical determination of the pressure dependence of the lattice distortion parameter δ for hcp ^{4}He and ^{3}He. The calculations were performed using semiempirical and first-principle approaches which complement each other: the former works better for low pressures, the latter for high pressures. The semiempirical calculations were done for the interatomic potential composed of a two-body and a three-body part and for the two-body potential.

Experimentally, various measurements of the axial ratio in solid He were performed. Low-pressure experimental data are summarized in Table I. The sole attempt to undertake a systematic study of the pressure dependence of the axial ratio in solid He was made by Vos *et al.*[13,14] by using an optical method based on the presence of birefringence in the hcp phase. They found a small deviation of the c/a ratio from the ideal value at small pressures and low temperatures. In these experiments δ was about -10^{-3} at the lowest density (20.6 cm^3/mol) and decreased in magnitude (about -6×10^{-4}) at higher densities at $\sim$1 kbar (12.5 cm^3/mol). Though uncertainties in neutron-diffraction and x-ray studies were too large to reveal unambiguously changes in c/a with pressure, experimental data show systematically that c/a is slightly lower than the ideal value 1.633. X-ray studies of He at HP gave the value 1.630 ± 0.005.[1,2] It is interesting to note that not counting RGS all hcp elemental crystals except Zn and Cd have negative δ.[23]

From the theoretical side, only one attempt was made to analyze the behavior of the lattice distortion parameter in solid He,[24] however the precision of calculations was insufficient to reach trustworthy results. Additionally, Howard[25] calculated the static energy of the hcp (6–12) Lennard-Jones (LJ) lattice at equilibrium lattice spacing as a function of δ

TABLE I. The axial ratio c/a for ^{4}He.

V ($\mathrm{cm}^3/\mathrm{mol}$)	c/a	δ	Ref.
		Birefringence	
20.6	1.6320	-0.001 ± 0.0005	13
18.8	1.6323	-0.0007 ± 0.0005	14
17.0	1.6324	-0.0006 ± 0.0005	14
12.5	1.6324	-0.0006 ± 0.0005	14
		Neutron diffraction	
21.1	1.638	$+0.005 \pm 0.016$	15
20.32	1.6290	-0.0040 ± 0.0061	16
18.51	1.612	-0.021 ± 0.004	17
17.41	1.6294	-0.0036 ± 0.016	16
16.02	1.6292	-0.004 ± 0.002	18
15.13	1.6310	-0.0020 ± 0.0035	16
11.61	1.630	-0.003 ± 0.002	8
9.41	1.632	-0.001 ± 0.002	8
		X ray	
21.3(1)	1.638	$+0.005 \pm 0.005$	19
20.66	1.628	-0.005 ± 0.008	20
17.4	1.627	-0.006	21
12.1	1.6310[a]	-0.002 ± 0.0005	22

[a] An average value for eight samples of ^{3}He with V in the range 11.6–12.8 $\mathrm{cm}^3/\mathrm{mol}$ and two samples of ^{4}He with $V = 12.1$ $\mathrm{cm}^3/\mathrm{mol}$.

and found that energy minimum occurs for $\delta = -2.286 \times 10^{-4}$. (Close results were founds for various pair potentials.[26]) Stillinger[27] extended these calculations to compressed hcp LJ lattices and found that δ decreases in magnitude with rising compression and changes the sign at the compression of about 1.86.

The deviation of the axial ratio from the ideal value in the hcp solids can be attributed ultimately to a lowering of the band-structure energy through lattice distortion. In the molecular hcp solids we can explicitly ascribe this effect to the reduction in the ground-state energy due to lattice distortion. In the case of solid helium the effect of lattice distortion both on the static energy and zero-point energy is essential.

Let us use the fact that $|\delta| \ll 1$ and expand the ground-state energy of the system in powers of δ restricting ourselves to the terms of the second order in δ

$$E_{gs}(\delta) = E_{gs}^0 + b_1 \delta + b_2 \delta^2, \tag{1}$$

where E_{gs}^0 is the ground-state energy of the ideal hcp lattice, b_i $(i=1,2)$ are the coefficients depending on the parameters of the interatomic potential and molar volume. Minimizing $E_{gs}(\delta)$ over δ, we obtain

$$\delta = -b_1/(2b_2). \tag{2}$$

Thus, to find the $\delta(V)$ dependence one has to calculate the quantities $b_1(V)$ and $b_2(V)$. In spite of the short-range character of the interparticle interaction to calculate b_1 unambiguously one has to take into account contributions from a large number of shells of neighbors. The reason is that the contributions of the first two shells to b_1 are exactly equal to zero while the contributions from more distant shells decrease rather slowly and tend to alternate in signs. These are the reasons why δ is small. The alternation of the sign of the effect ceases after taking into account rather long-distance contributions. To get a reliable result we took into account contributions from 50 shells of neighbors.

In these calculations we use an interatomic potential U_{tot}, accounting for pair (U_p), and triple (U_{tr}) interatomic forces $(U_{\mathrm{tot}} = U_p + U_{\mathrm{tr}})$. For the two-body interaction, we have taken the HFDHE2 Aziz *et al.*[28] potential which was used previously in our equation of state and Raman calculations.[10,29] We also performed calculations using the HFD-B3-FCI1 Aziz[30] potential and found that the results for these two pair potentials practically coincide. The three-body potential includes the long-range Axilrod-Teller dispersive interaction and a short-range three-body exchange interaction.[29,31–37] The latter was used in a Slater-Kirkwood form (Bruch-McGee potential[38]). The parameters employed for the three-body terms are given in Ref. 29. We restrict ourselves to $T=0$ K with the zero-point energy taken into account using the Einstein approximation. A small pressure range ($\sim$0.1 GPa) where quantum-crystal effects play a decisive role was excluded from consideration. The equation of state, Raman frequencies, and elastic shear modulus calculated previously[10,29] within this model are in excellent agreement with experiment.

The hcp lattice distortion parameter δ for ^{3}He and ^{4}He as a function of molar volume is shown in Fig. 1. The calculations were performed for the many-body potential U_{tot} and for the pair potential U_p. For both potentials calculations were performed with and without the zero-point contribution. The resulting $\delta(V)$ dependencies are qualitatively different: for the total potential, δ is negative in the whole range of molar volumes studied and increases in magnitude monotonically with decreasing V. At 2.5 $\mathrm{cm}^3/\mathrm{mole}$ ($\sim$ tenfold compression, $P \sim 60$ GPa) $\delta \approx -0.001$. For the pair potential the $\delta(V)$ dependence is nonmonotonic in qualitative agreement with results of Stillinger[27] for the LJ potential. For large molar volumes where the triple forces are negligible, the resulting δ is very close to that obtained using the total potential. But under increasing compression, the curves diverge. The curve for the pair potential after passing through a minimum changes sign at $V \approx 5$ $\mathrm{cm}^3/\mathrm{mol}$ and increases monotonically with decreasing V.

A comparison of the two curves shows that at large compressions, pair and triple forces exert opposing effects on the lattice distortion. The former acts to elongate the lattice while the latter flattens it. The lattice distortion is determined by the competition of three-body and two-body forces, and we see that the action of the former dominates at high compressions. The difference between the two curves gives an estimate of the net contribution of the three-body forces to the lattice distortion. At high compressions, the lattice distortions due to the triple forces are more than twice as large as those due to pair forces and have the opposite sign. A simple qualitative explanation of the obtained curves probably does

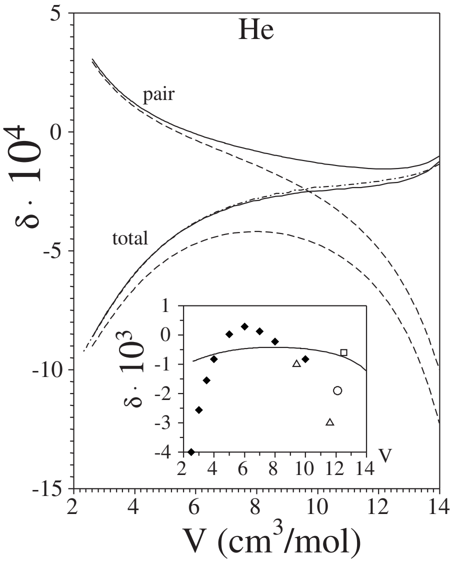

FIG. 1. Lattice distortion parameter δ for hcp He as a function of volume calculated for the semiempirical total and pair potentials with (solid curves—^{4}He, dot dash—^{3}He) and without (dashed curves), respectively, zero-point oscillations. The inset shows the comparison between the first-principles results (diamonds) and semiempirical results (solid curve). Experiment: birefringence data [open square (Ref. 14)]; neutron data [open triangles (Ref. 8)]; x-ray data [open circle (Ref. 22)].

not exist: even for the pair potential it is impossible to attribute a certain sign of δ to the repulsive or attractive part of the interatomic interaction since the sign of the effect varies for the contributions from different shells.

The effect of zero-point vibrations decreases with rising compression (Fig. 1). But at low compressions the lattice becomes unstable with respect to flattening both for the many-body and pair potentials if the zero-point energy is disregarded. The isotope effect in the lattice distortion parameter is due to the difference in contributions of the zero-point energy for the two isotopes. The calculated effect is small (Fig. 1) which is in agreement with experiments.[17,22,39]

To investigate the contribution of higher-order many-body forces to the lattice distortion we also carried out density-functional theory (DFT) calculations. Our calculations have been done using the full-potential linear muffin-tin orbital method[40] within the generalized gradient approximation (GGA) for $T=0$ K, disregarding zero-point oscillations. Although the GGA is not optimal for handling van der Waals interactions,[41] it is accurate for high compressions, where the repulsive forces dominate. The first-principles results (Fig. 1, inset) are in good agreement with our semiempirical many-body potential calculations without zero-point oscillations up to approximately fivefold compressions ($\sim$4 cm^3/mol). At higher compressions the magnitude of δ obtained in DFT calculations increases far more rapidly than that following from the semiempirical calculations. Comparing the results of these two approaches, we conclude that at higher compressions higher-order, many-body forces become important. It should be noted that many-body interactions are important for many physical properties of molecular solids: the observed stability of the fcc RGS, stacking-fault energy, elastic constants,[42] equation of state,[29,31,34,36,37] and vacancy-formation energy.[43,44] However, these properties can be modeled with effective two-body potentials. On the other hand, for the hcp lattice distortion the role of the many-body terms is crucial at high compressions. The pressure behavior of the hcp lattice distortion parameter is qualitatively different for the many-body and pair potentials, and thus cannot be described by the effective pair potentials. This sensitivity of the lattice distortion parameter to the many-body component of the intermolecular potential makes it a unique thermodynamic characteristic which thus can be used as a probe of many-body forces.[45]

Finally we address the issue of feasibility of experimental studies of the lattice distortion of solid He under pressure. The experimental data from Table I which fall in the range of molar volumes corresponding to the outlined theoretical approach are shown in Fig. 1. Though the large scatter of the experimental points does not permit to reveal a certain pressure dependence, experimental and theoretical data for the many-body potential have the same order of magnitude and the same sign. The method of an internal standard developed by Krupskii *et al.*[46] which made it possible to significantly increase the precision of their x-ray measurements[47] of the c/a ratio for solid parahydrogen at zero pressure could be use in x-ray and neutron-diffraction measurements under pressure.

In conclusion, we present results of theoretical calculations of the lattice distortion parameter δ for solid He. The $\delta(V)$ dependencies calculated for the total (two plus three-body) and for pair intermolecular potentials are qualitatively different. Three-body forces flatten the lattice while pair forces at large compressions tend to elongate it with the action of the former being more than twice as large. So, the resulting lattice distortion parameter δ in accordance with all the set of experimental data is negative and the lattice is slightly flattened. Up to approximately fivefold compressions, the results based on the many-body potential agree well with the first-principles results. At larger compressions higher-order many-body forces become important. Thus, we have shown that the lattice distortion parameter is a unique characteristic which is very sensitive to the many-body component of the intermolecular potential and can therefore be used as a probe of the many-body forces.

We thank Ralph Simmons for a very useful correspondence and Anatolii Prokhvatilov and Nikolai Galtsov for valuable discussions.

*freiman@ilt.kharkov.ua

[1] P. Loubeyre, R. LeToullec, J. P. Pinceaux, H. K. Mao, J. Hu, and R. J. Hemley, Phys. Rev. Lett. **71**, 2272 (1993).

[2] C. S. Zha, H. K. Mao, and R. J. Hemley, Phys. Rev. B **70**, 174107 (2004).

[3] A. P. Jephcoat, H.-k. Mao, L. W. Finger, D. E. Cox, R. J. Hemley, and C.-s. Zha, Phys. Rev. Lett. **59**, 2670 (1987).

[4] D. Errandonea, B. Schwager, R. Boehler, and M. Ross, Phys. Rev. B **65**, 214110 (2002).

[5] D. Errandonea, R. Boehler, S. Japel, M. Mezouar, and L. R. Benedetti, Phys. Rev. B **73**, 092106 (2006).

[6] H. Cynn, C. S. Yoo, B. Baer, V. Iota-Herbei, A. K. McMahan, M. Nicol, and S. Carlson, Phys. Rev. Lett. **86**, 4552 (2001).

[7] A. Dewaele, F. Datchi, P. Loubeyre, and M. Mezouar, Phys. Rev. B **77**, 094106 (2008).

[8] J. Eckert, W. Thomlinson, and G. Shirane, Phys. Rev. B **18**, 3074 (1978).

[9] G. H. Watson and W. B. Daniels, Phys. Rev. B **31**, 4705 (1985).

[10] Yu. A. Freiman, A. F. Goncharov, S. M. Tretyak, A. Grechnev, J. S. Tse, D. Errandonea, H.-K. Mao, and R. J. Hemley, Phys. Rev. B **78**, 014301 (2008).

[11] H. Shimizu, M. Kawajiri, T. Kume, S. Sasaki, Yu. A. Freiman, and S. M. Tretyak, Phys. Rev. B **79**, 132101 (2009).

[12] H. Shimizu, N. Wada, T. Kume, S. Sasaki, Y. Yao, and J. S. Tse, Phys. Rev. B **77**, 052101 (2008).

[13] J. E. Vos, B. S. Blaisse, D. A. E. Boon, W. J. Scherpenzeel, and R. V. Kingma, Physica (Utrecht) **37**, 51 (1967).

[14] J. E. Vos, R. V. Kingma, F. J. van der Gaag, and B. S. Blaisse, Phys. Lett. **24A**, 738 (1967).

[15] V. J. Minkiewicz, T. A. Kitchens, F. P. Lipshultz, R. Natchans, and G. Shirane, Phys. Rev. **174**, 267 (1968).

[16] R. O. Simmons and R. Blasdell, see also Proceedings of the 2007 APS March Meeting (unpublished).

[17] J. Donohue, Phys. Rev. **114**, 1009 (1959).

[18] R. A. Reese, S. K. Sinha, T. O. Brun, and C. R. Tilford, Phys. Rev. A **3**, 1688 (1971).

[19] E. Blackburn, J. M. Goodkind, S. K. Sinha, J. Hudis, C. Broholm, J. van Duijn, C. D. Frost, O. Kirichek, and R. B. E. Down, Phys. Rev. B **76**, 024523 (2007).

[20] R. L. Mills and A. F. Schuch, Proceedings of the VIIIth International Conference on Low Temperature Physics, London, 1962 (unpublished), p. 423.

[21] A. F. Schuch and R. L. Mills, Proceedings of the Sixth Congress of the International Union of Crystallography, Rome (unpublished), p. A21.

[22] D. A. Arms, R. S. Shah, and R. O. Simmons, Phys. Rev. B **67**, 094303 (2003).

[23] T. Kenichi, Phys. Rev. B **60**, 6171 (1999); **56**, 5170 (1997).

[24] S. M. Tretyak, T. N. Antsygina, and Yu. A. Freiman, Low Temp. Phys. **32**, 1072 (2006).

[25] R. Howard, Phys. Lett. **32A**, 37 (1970).

[26] P. Schwerdtfeger, N. Gaston, R. P. Krawczyk, Ralf Tonner, and G. E. Moyano, Phys. Rev. B **73**, 064112 (2006).

[27] F. H. Stillinger, J. Chem. Phys. **115**, 5208 (2001).

[28] R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, J. Chem. Phys. **70**, 4330 (1979).

[29] Yu. A. Freiman and S. M. Tretyak, Low Temp. Phys. **33**, 545 (2007).

[30] R. A. Aziz, A. R. Janzen, and M. R. Moldover, Phys. Rev. Lett. **74**, 1586 (1995).

[31] P. Loubeyre, Phys. Rev. Lett. **58**, 1857 (1987); Phys. Rev. B **37**, 5432 (1988).

[32] M. J. Cohen and J. N. Murrell, Chem. Phys. Lett. **260**, 371 (1996).

[33] U. Kleinekathöfer, T. I. Sachse, K. T. Tang, J. P. Toennies, and C. L. Yiu, J. Chem. Phys. **113**, 948 (2000).

[34] S.-Y. Chang and M. Boninsegni, J. Chem. Phys. **115**, 2629 (2001).

[35] W. Cencek, M. Jeziorska, O. Akin-Ojo, and K. Szalewicz, J. Phys. Chem. A **111**, 11311 (2007).

[36] C. P. Herrero, J. Phys.: Condens. Matter **18**, 3469 (2006).

[37] C. Cazorla and J. Boronat, J. Phys.: Condens. Matter **20**, 015223 (2008).

[38] L. W. Bruch and I. J. McGee, J. Chem. Phys. **59**, 409 (1973).

[39] A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. **110**, 775 (1958).

[40] J. M. Wills *et al.*, in *Electronic Structure and Physical Properties of Solids: The Uses of the LMTO Method*, edited by H. Dreysse (Springer, New York, 1998).

[41] J. M. Pérez-Jordá and A. D. Becke, Chem. Phys. Lett. **233**, 134 (1995).

[42] *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, London, 1976).

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

[44] R. O. Simmons, J. Phys. Chem. Solids **55**, 895 (1994).

[45] As a test, we repeated the calculations using the Cohen-Murrell three-body potential (Ref. 32) and found that it gives rise to a nonphysical minimum point at molar volume ~4 $\mathrm{cm}^3/\mathrm{mol}$.

[46] I. N. Krupskii, A. I. Prokhvatilov, and G. N. Shcherbakov, Sov. J. Low Temp Phys. **9**, 42 (1983).

[47] As a standard substance Krupskii *et al.*(Ref. 46) used solid Kr. Hydrogen was condensed in the pores of the snow-shaped Kr deposited on a precooled copper substrate. The angular location of the triplet of reflections (100), (002), and (101) corresponding to hcp p-H_2 was determined relative to the nearby (111) line of the fcc Kr lattice with the lattice parameter known within ±0.0001 Å.