Comments and Addenda

Augmented plane wave calculation of the zero-temperature isotherm of solid xenon

J. P. Worth and S. B. Trickey*

Quantum Theory Project, Department of Physics and Astronomy, University of Florida, Gainesville, Florida 32611

(Received 6 November 1978)

A high-precision recalculation (augmented plane wave, $X\alpha$) of the $T = 0$ K isotherm of fcc xenon is reported and compared with Syassen's x-ray measurements. The calculated isotherm can be put in very good agreement with the measured values by a small overall pressure shift.

Some time ago it was discovered[1] that the very simple local-density energy-band model known as the $X\alpha$ method[2,3] gave a surprisingly useful description of the bulk properties of rare-gas crystals. The "muffin-tin" augmented plane wave (APW) technique was used and, among other results, a calculated zero-temperature isotherm of fcc Xe was presented.[1] Except at the highest pressures, that calculation was in surprisingly good agreement with experiment. For example, the calculated static-lattice constant was only 0.091 a.u. larger than the experimental value (11.677 vs 11.586 a.u., respectively).

Subsequently, Syassen[4] did a very careful set of x-ray measurements from which he determined the zero-temperature isotherm of fcc xenon up to 110 kbar. On the basis of the APW-$X\alpha$ results published to that time, he concluded that there was very good agreement between the experimentally determined and calculated zero-temperature static-lattice isotherms. In a preliminary report[5] of the data presented in this note, we also suggested in passing that the agreement seemed quite good. Upon careful analysis, we find reason to temper, though not abandon, that claim.

The calculations reported here were improved over those of Ref. 1 in several ways: (i) a Brillouin-zone scan of 256 evenly-spaced points in the first zone was used (as opposed to 32 in Ref. 1); (ii) very stringent (one part in 10^9) iteration-to-iteration convergence constraints on the $X\alpha$ one-electron eigenvalues were used;

(iii) some minor program anomalies were removed. In other respects, the procedures used were as reported previously.

Twelve calculations were done, at molar volumes of about 20–36 cm^3/mole. The iteration-to-iteration convergence limits of the potential energy, total energy, and pressure were 10^{-5} Ry, 10^{-6} Ry, and 1 bar, respectively. All calculations used a statistical exchange-correlation parameter $\alpha = 0.69962$. The calculated results are displayed in Table I. In that table, the calculated binding energies were obtained by subtracting the $X\alpha$ atomic total energy (-14464.17415 Ry) from the APW-$X\alpha$ total energy. We estimate the numerical uncertainty in those binding energies conservatively as ± 0.0005 Ry, judging from the differences between this calculation and the earlier work. Judged on that same basis, the uncertainty in the pressures appears to be about ± 0.1 kbar. [Note that the pressures are computed from the $X\alpha$ kinetic and potential energies via the virial theorem; see Eq. (2.12) of Ref. 1.]

We fitted our results by the Keane equation of state,[6] just as Syassen treated his experimental data. That form involves the isothermal bulk modulus B_0, its pressure derivative at zero pressure B_0', its pressure derivative at arbitrarily large pressure B_∞', and the equilibrium molar volume V_0. The relationship is

$$P(V) = (B_0 B_0'/B_\infty'^2)[(V_0/V)^{B_\infty'} - 1]$$
$$- [B_0(B_0' - B_\infty')/B_\infty']\ln(V_0/V). \tag{1}$$

TABLE I. Results as calculated (fcc Xe, $\alpha = 0.699\,62$); Ry a.u. unless otherwise indicated.

a (a.u.)	V (cm³/mole)	Binding energy (Ry/particle)	Calculated pressure (kbar)
9.6421	19.9991	+0.0314	128.084
9.8001	20.9985	+0.0224	100.989
9.9534	21.9994	+0.0155	79.946
10.2463	23.9992	+0.0057	49.908
10.3865	24.9979	+0.0021	39.120
10.5233	25.9987	−0.0006	30.431
10.7864	27.9979	−0.0043	18.136
11.0373	29.9975	−0.0065	10.071
11.2773	31.9972	−0.0072	5.023
11.5077	33.9986	−0.0077	1.617
11.6194	34.9983	−0.0081	0.319
11.7290	35.9980	−0.0081	−0.629

TABLE II. Comparison of measured and unshifted APW-$X\alpha$ $T = 0$ K static-lattice isotherms for various volume ratios.

$\dfrac{V_{0,\text{APW}}}{V}$	$P_{\text{expt}}\left(\dfrac{V_{0,\text{APW}}}{V}\right)$ (kbar)	$P_{\text{APW},X\alpha}\left(\dfrac{V_{0,\text{APW}}}{V}\right)$ (kbar)
1.769 023	155.6056 [a]	128.0840
1.684 833	119.5455	100.9890
1.608 178	92.3270	79.9460
1.474 169	55.6367	49.9080
1.415 275	43.2443	39.1200
1.360 795	33.5156	30.4310
1.263 627	19.7692	18.1360
1.179 397	11.0320	10.0710
1.105 689	5.3980	5.0230
1.040 598	1.7395	1.6170
1.010 875	0.4281	0.3190
0.982 801	−0.6233	−0.6290

[a] These values are calculated from the Keane equation [Eq. (1)] using Syassen's $T = 0$ K static-lattice Keane equation parameters.

TABLE III. Comparison of measured and shifted APW-$X\alpha$ $T = 0$ K static-lattice isotherms for various volume ratios ($V_{0,\text{expt}} = V_{0,\text{APW}}$ gives the pressure shift, corresponding to 1.150 941-kbar lowering of the APW values).

$\dfrac{V_0}{V}$	$P_{\text{expt}}\left(\dfrac{V_0}{V}\right)$ (kbar)	$P_{\text{APW},X\alpha}\left(\dfrac{V_0}{V}\right)$ (kbar)	$\dfrac{V_0}{V}$	$P_{\text{expt}}\left(\dfrac{V_0}{V}\right)$ (kbar)	$P_{\text{APW},X\alpha}\left(\dfrac{V_0}{V}\right)$ (kbar)
1.714 076	131.2962 [a]	126.9330	1.224 378	15.3654	16.9850
1.632 501	100.4267	99.8380	1.142 764	8.0180	8.9200
1.553 226	77.1485	78.7950	1.071 345	3.3265	3.8720
1.428 380	45.3260	48.7570	1.008 276	0.3234	0.4660
1.371 315	35.2729	37.9690	0.979 476	−0.7363	−0.8320
1.318 527	27.0048	29.2800	0.952 274	−1.5746	−1.7800

[a]These values are calculated from the Keane equation [Eq. (1)] using Syassen's $T = 0$ K static-lattice Keane equation parameters.

A fit of this equation to the pressures shown in Table I yields $B_0 = 31.7827$ kbar (38.14 kbar, experimental); $B_0' = 8.9906$ (6.88 kbar, experimental); $B_\infty' = 3.7914$ (4.81 kbar, experimental); $V_0 = 35.3789$ cm^3/mole (34.28 cm^3/mole, experimental); $a = 11.6614$ a.u. (11.5394 a.u., experimental). The experimental values listed parenthetically are those obtained by Syassen for the $T = 0$ K static-lattice isotherm. See Table II for the full comparison.

It is clear from examination of these results that, just as in the earlier calculations, there is a significant difference between the calculated and measured equilibrium molar volumes. If we do a rigid pressure shift of the APW data so as to make the equilibrium molar volumes coincide while changing nothing else, we get the results shown in Table III. The required shift is a 1.150 941-kbar reduction of each of the APW-$X\alpha$ calculated values. The Keane equation which results from fitting to the shifted values is $B_0 = 41.3483$ kbar (38.14 kbar experimental); $B_0' = 7.7863$ (6.88 kbar experimental); $B_\infty' = 3.7914$ (4.81 kbar experimental); $V_0 = 34.28$ cm^3/mole (same as experimental, by construction). Both of these values and the comparison of $P(V)$ given in Table III show clearly that the shape of the calculated PV curve is quite satisfactory. It is the insufficient binding predicted by the APW-$X\alpha$ method and the associated larger-than-measured equilibrium molar volume that are the major deficiencies in the calculation.

In consequence of these considerations we may derive the following conclusions: (i) The primary failure of the APW-$X\alpha$ treatment of crystalline Xe is in the prediction of the cohesive energy (-0.0081 Ry/particle calculated vs $-0.012 59$ Ry/particle experimental); (ii) because of the calcu-

lated underbinding, the calculated equilibrium molar volume is too large by 3.2%; (iii) though the molar volume discrepancy is rather small, it is sufficient to conceal the fact that the *shape* of the calculated $E(V)$ (binding energy as a function of volume) curve is quite realistic. The comparisons made earlier by both Syassen[4] and us[5] were ambiguous regarding this point; (iv) none of these results varies dramatically in comparison with the original, much-less-refined calculation,[1] in marked contrast to the Brillouin-zone scan sensitivities uncovered by McMahan[7] in Cs. It is easy to understand why this is so, since the Cs problem involves sensitive shifts of electronic population near the Fermi surface, a problem which is irrelevant to the present work.

ACKNOWLEDGMENT

APPENDIX

The conversion factors used in considering rare-gas crystals in high-precision energy-band calculations are a matter of some importance, particularly because of the weak binding. We have used values published by the Particle Data Group (S. J. Brodsay)[8] to find

1 (a.u.)$^3 = 8.923 924 6 \times 10^{-2}$ cm^3/mole;

1 Ry/particle $= 1.578 935 6 \times 10^5$ K/particle;

1 Ry/(a.u.)$^3 = 1.471 080 7 \times 10^5$ kbar.

*Present address: Dept. of Physics, Texas Tech Univ., Lubbock, Tex. 79409.

[1] S. B. Trickey, F. R. Green, Jr., and F. W. Averill, Phys. Rev. B 8, 4822 (1973).

[2] J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 4 (McGraw-Hill, New York, 1974), and references therein.

[3] J. W. D. Connolly, in *Modern Theoretical Chemistry*, Vol. 7, edited by G. Segal (Plenum, New York, 1976),

pp. 105–132, and references therein.

[4] K. Syassen, Thesis (Stuttgart, 1974) (unpublished); K. Syassen and W. B. Holzapfel, Phys. Rev. B 18, 5826 (1978).

[5] S. B. Trickey and J. P. Worth, Internat. J. Quantum Chem. S 11, 529 (1977).

[6] A. Keane, Austr. J. Phys. 7, 323 (1954).

[7] A. K. McMahan, Phys. Rev. B 17, 1521 (1978).

[8] Rev. Mod. Phys. 45 (2), S29 (1973).