

## Equation of state and metallization of neon

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The linear combination of Gaussian-type orbitals technique is used to study the bulk properties, equation of state, and metallization pressure of Ne using the Kohn-Sham-Gaspar local-density approximation to density-functional theory. Unlike previous non-muffin-tin calculations for Ne, the present results are obtained for enough values of the lattice parameter to allow a careful determination of the equilibrium lattice constant, binding energy, and bulk modulus. Although the properties of Ne for pressures up to about 3 Mbar are in qualitative agreement with prior results, there are quantitative differences. In particular, as has been found in Li and Fe, the non-muffin-tin lattice constant is contracted relative to the muffin-tin result. The metallization pressure of Ne is determined to be 1.34 Gbar at a lattice constant of 2.32 a.u. as opposed to an earlier augmented plane wave prediction of 1.58 Gbar at 2.256 a.u. An explanation is given for what has been referred to as the "anomalously" large metallization pressure of Ne.

### I. INTRODUCTION

In recent years, a new variant of the linear combination of Gaussian-type orbitals (LCGTO) technique, based on the one-electron LCGTO formalism of Wang and Callaway<sup>1</sup> (WC), has been shown to be useful in studying the equation of state (EOS) and crystallographic phase stability of elemental solids,<sup>2-6</sup> within the local density approximation (LDA) to density-functional theory.<sup>7,8</sup> LCGTO results are especially useful due to the absence of the muffin-tin approximation employed by some other techniques. Thus it has been possible to study systematic errors introduced into calculations by the muffin-tin approximation.<sup>4</sup>

Neon provides an appealing subject for a precise non-muffin-tin investigation. Recently, Hama<sup>9</sup> predicted, on the basis of muffin-tin augmented-plane-wave (APW) calculations, that fcc Ne would metallize at a pressure of 1.58 Gbar. That pressure is by far the largest metallization pressure reported to date and is characterized by Hama as anomalous. Hama speculates that although the muffin-tin approximation should have little impact on the EOS, it may significantly shift the energy bands near the edge of the Brillouin zone, thereby altering the transition pressure.

A non-muffin-tin calculation of the equilibrium properties of Ne would also be useful. To date, there has been only one non-muffin-tin investigation of the EOS of Ne.<sup>5</sup> That study, using the APW-LCGTO technique,<sup>10</sup> only obtained results at four widely spaced volumes corresponding to pressures ranging from about 0 to 2.8 Mbar. Thus, Ref. 5 was unable to produce predictions for the equilibrium lattice constant and bulk modulus.

In this investigation, the LCGTO technique was used to compute the total energy and virial pressure of Ne within the Kohn-Sham-Gaspar<sup>8</sup> (KSG) LDA model for volumes ranging from the experimental zero-pressure volume to less than 2% of that volume. These calculations were carried out at a sufficiently large number of volumes near the

equilibrium that it is possible for the first time to obtain precise non-muffin-tin values for the equilibrium lattice constant, cohesive energy, and bulk modulus of Ne. For the largest compressions considered here, Ne changes from an insulator to a metal. The calculated metallization pressure is 15% smaller than the earlier APW prediction.<sup>9</sup> The source of the disagreement is discussed and an explanation is given for the exceptionally large metallization pressure of Ne.

The basic LCGTO technique used here has been described elsewhere.<sup>4,5,11</sup> The input parameters used here were chosen to ensure consistency with Ref. 5, other than the choice of the initial electron density. The basis sets used for the lattice constants 8.4323, 7.7, 6.1, and 5.1 a.u. are given in Ref. 5. For other lattice constants, the basis sets were scaled using the  $1/a^2$  scaling rule described in Ref. 4. To permit a calculation of the binding energy, the energy of a Ne atom was computed using the same  $15s\ 8p\ 3d$  basis as was used for  $a = 8.4323$  a.u. That energy ( $-254.980\ 337$  Ry) differs slightly from the value given in Ref. 5 due to the use here of a more precise atomic code.

In Sec. II, results for Ne, including the zero-pressure bulk properties, EOS, and metallization pressure are presented and discussed. The anomalous metallization pressure of Ne is discussed in Sec. III.

### II. RESULTS

The binding energy and virial pressure of fcc Ne has been calculated for 15 lattice constants ranging from the experimental equilibrium lattice constant (8.4323 a.u.) (Ref. 12) to the lattice constant at which Hama<sup>9</sup> found metallization in Ne (2.256 a.u.). The results are given in Table I. For comparison, Table I also lists binding energies and virial pressures for fcc Ne obtained using the APW and APW-LCGTO methods.<sup>5</sup>

For the experimental equilibrium lattice constant (8.4323 a.u.), the APW-LCGTO and LCGTO results for

TABLE I. The calculated binding energy  $E_b$  and pressure  $P$  as a function of lattice constant  $a$  for the present LCGTO ( $L$ ) calculations compared with those obtained with the APW-LCGTO ( $AL$ ) and APW ( $A$ ) methods in Ref. 5.

$a$ (a.u.)	$E_b$ (Ry)			$P$ (Mbar)		
	$L$	$AL$	$A$	$L$	$AL$	$A$
8.4323	-0.002 20	-0.002 22	-0.002 84	-0.0096	-0.0037	-0.0046
7.7	-0.004 02	-0.003 73	-0.003 70	-0.0070	0.0019	-0.0002
7.6	-0.004 14			-0.0053		
7.5	-0.004 20			-0.0029		
7.4	-0.004 17			0.0003		
7.3	-0.004 04			0.0045		
6.8	-0.000 71			0.0521		
6.1	0.021 85	0.023 90	0.025 80	0.3213	0.3430	0.3442
5.6	0.073 15			0.9706		
5.1	0.197 25	0.202 18	0.206 84	2.7763	2.8410	2.8467
4.4	0.684 88			11.780		
3.5	3.041 57			79.279		
2.4	18.624 97			1080.7		
2.3	22.110 47			1414.6		
2.256	23.886 15			1598.3		

$E_b$  are virtually identical and both lie above the APW result due to truncation errors in the needed Fourier sums.<sup>5</sup> For the remaining lattice constants, the LCGTO results are more bound than are the APW-LCGTO results, which in turn are more bound than the APW results. The difference between the energies obtained with the APW-LCGTO technique and the LCGTO technique is probably due to the inherent inconsistency between the APW starting density and the LCGTO basis used in the former technique.<sup>13</sup>

#### A. Bulk properties and equation of state

To obtain the zero-pressure lattice constant, cohesive energy, and bulk modulus, the  $E$  vs  $V$  curve near the equilibrium ( $a = 7.7, 7.6, 7.5, 7.4,$  and  $7.3$  a.u.) was fitted to the Murnaghan equation.<sup>14</sup> For the five lattice constants nearest equilibrium, the fitted pressures differ from the virial pressures in Table I by a nearly uniform shift of about  $-2.2$  kbar, indicating the precision of the virial pressure calculation. In Table II, the present theoretical zero-pressure bulk properties of Ne are compared with those obtained using the APW method<sup>15</sup> (also using the KSG model) and with experimental values.<sup>12</sup> The theoretical binding energies are too large by roughly a factor of 2 and the lattice constants are about 10% too small. (This

TABLE II. The lattice constant  $a_0$ , static lattice-binding energy  $E_b$ , and bulk modulus  $B$  of Ne found in this study using the LCGTO method and KSG model compared to APW results obtained using the same model in Ref. 15 and the experimental values in Ref. 12.

	$a_0$ (a.u.)	$E_b$ (mRy)	$B$ (kbar)
LCGTO	7.48	-4.20	74.7
APW	7.7	-3.69	
Expt.	8.4323	-1.92	10.0

overbinding will be discussed further below.) The non-muffin-tin results are more overbound than are the APW results and the lattice constant is smaller. This lattice contraction upon removal of the muffin-tin constraint has been observed in both Li (Ref. 4) and Fe (Ref. 16). However, in those studies, the lattice constants only contracted by about 0.05 a.u. while for Ne the contraction amounts to about 0.2 a.u. This larger contraction may be due to the flatness of the minimum in the Ne  $E$  vs  $V$  curve.

The present value of the bulk modulus (74.7 kbar) is more than seven times as large as the experimental value (10 kbar).<sup>12</sup> This discrepancy is due to the underestimate of the equilibrium lattice constant. For the Murnaghan equation, the bulk modulus scales as  $V^{-\gamma}$ , where in this case  $\gamma = 7.209 695$ . Thus the present equation of state gives a bulk modulus of 5.6 kbar at the experimental lattice constant. For such a small value, this agreement with experiment is quite good.

The EOS for Ne obtained here is in excellent agreement with the APW-LCGTO and APW results in Table I (all using the KSG model) with the LCGTO EOS being slightly softer due to the complete removal of the muffin-tin constraint. (The LCGTO pressure is only 70 kbar below the APW result at about 2.8 Mbar.) The present EOS is also in qualitative agreement with the APW result obtained by Hama<sup>9</sup> using the Hedin-Lundqvist<sup>17</sup> (HL) LDA model. For all volumes, the present KSG pressures are larger than the HL pressures for Ne. Thus, the HL lattice constant would be even more contracted than is the KSG value. At very large pressures, the fractional difference between the KSG and HL pressures becomes negligible. (At  $a = 2.256$  a.u., Hama reports 1.58 Gbar as opposed to the present value of 1.598 Gbar.) These results show that the ultrahigh pressure EOS is not significantly altered by the muffin-tin approximation or the choice of the LDA model.

All of the theoretical EOS's lie well below the low-pressure EOS measured by Finger *et al.*<sup>18</sup> (see Fig. 1 of

Ref. 9). Hama attributed the underestimate of the pressure to muffin-tin effects. However, the present results are non-muffin-tin and utilize an LDA model which produces less binding (and higher pressures) than the model used by Hama, yet the pressures are still too small. This underestimate is actually an intrinsic feature of all LDA calculations for Ne.<sup>9,15,19</sup> It has been suggested<sup>20</sup> that this failure of LDA band theory to adequately describe the low-pressure EOS of Ne is due to the large zero-point motion of the nuclei. Clearly, this problem warrants further study.

### B. One-electron properties and the metallization of neon

The electronic band structure for Ne at the non-muffin-tin KSG equilibrium lattice constant (7.5 a.u.) is shown in Fig. 1. This band structure is in good agreement with previous results obtained using both the KSG (Ref. 21) and HL (Ref. 9) LDA models. The band structure of Ne for a lattice constant of 2.3 a.u. ( $P=1.41$  Gbar) is shown in Fig. 2. At this large compression, Ne has just become a metal with the  $3d$ -like  $X_3$  state lying slightly below the  $2p$ -like  $\Gamma_{15}$  state, in qualitative agreement with previous results.<sup>9</sup> Comparison of Figs. 1 and 2 also reveals other rather drastic modifications to the Ne band structure at high pressures, including a 10-fold increase in the separation between the  $2s$ -like  $\Gamma_1$  state and the  $2p$ -like  $\Gamma_{15}$  state. In addition, the pure  $3s$ -like  $\Gamma_1$  conduction state has been raised through both the  $3d$  bands and the  $3p$  bands. This is similar to the band crossings under pressure found for Li (Ref. 9) and Ni (Ref. 22).

Table III shows the position of the  $X_3$  state relative to the  $\Gamma_{15}$  state for the three most compressed lattice constants considered in this investigation together with the corresponding virial pressures. Based on these results, the metallization pressure of Ne is 1.34 Gbar at  $a=2.32$  a.u. (It has been noted<sup>19</sup> that the LDA estimate of a metalliza-

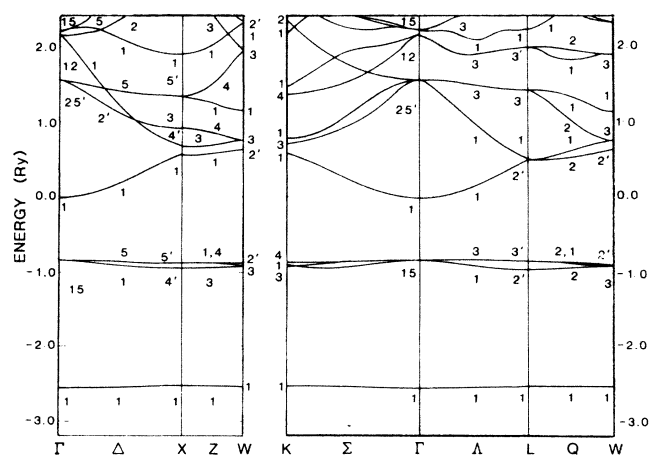


FIG. 1. The band structure of fcc Ne for  $P=0.0$  Mbar ( $a=7.5$  a.u.) using the KSG model.

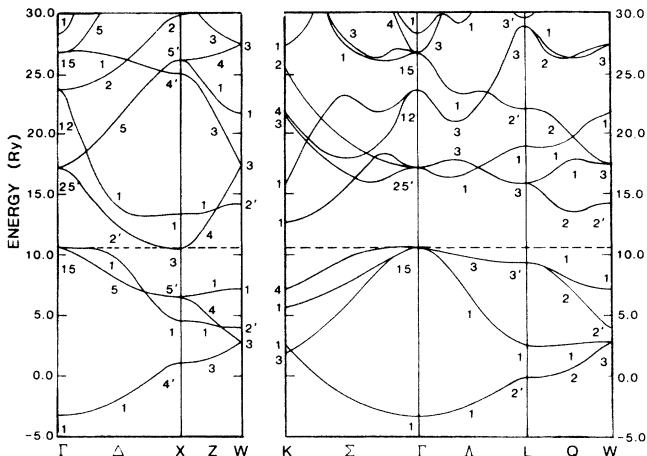


FIG. 2. The band structure of fcc Ne for  $P=1.41$  Gbar ( $a=2.3$  a.u.) using the KSG model. The dashed line indicates the Fermi energy.

tion pressure should provide a lower bound to the true metallization pressure since the LDA band gap underestimates the true gap.) Given the rapid shifts in the band gap and the pressure as a function of lattice constant, the present prediction is in reasonable agreement with Hama's. Nevertheless, the quantitative difference is significant (about 15%) and warrants further analysis.

Given the good agreement between the present EOS and Hama's EOS at high pressure, it is clear that the discrepancy between the two metallization pressures must be due to differences between the one-electron results. To determine if those differences are from the use of different LDA models (KSG vs HL), the LCGTO calculation at  $a=2.256$  a.u. was repeated using the HL model. This change in model only shifted the separation between the  $X_3$  state and the  $\Gamma_{15}$  state by 0.1 eV, a negligible amount. This suggests that the discrepancy between the two metallization pressures might be due to muffin-tin effects on the APW band structure, which Hama felt might be significant. To test this possibility, Bennett<sup>23</sup> has performed KKR calculations on Ne near the metallization point (using both the KSG and HL models) obtaining nearly perfect agreement with the present LCGTO results. Since the KKR and APW methods both use the muffin-tin approximation, they should produce identical results. This seems to indicate that there is some flaw in the one-electron part of Hama's calculation.

TABLE III. The energy separation between the  $X_3$  state and the  $\Gamma_{15}$  state ( $\Delta E$ ) and the virial pressure for the three smallest lattice constants considered in this investigation.

$a$ (a.u.)	$\Delta E$ (eV)	$P$ (Gbar)
2.4	4.0	1.080
2.3	-1.0	1.415
2.256	-3.5	1.598

### III. DISCUSSION

As has been pointed out,<sup>9</sup> the rare-gas crystals (He, Ne, Ar, Kr, and Xe) may be separated into two classes with respect to metallization under pressure. The heavy rare-gas crystals (Ar, Kr, and Xe) all become metallic when the  $(n, l + 1)$ -like conduction band overlaps with the  $(n, l)$ -like valence band, where the shell number  $n = 3, 4, 5$ , respectively and the angular momentum type  $l = 1$ . For the light rare-gas crystals (He and Ne) metallization is produced by having the  $(n + 1, l + 1)$ -like conduction band overlap the  $(n, l)$  valence band, where  $(n, l)$  is  $(1, 0)$  for He and is  $(2, 1)$  for Ne. Thus the metallization of the heavy rare gases is due to intrashell band overlap, whereas the metallization of the light rare gases is due to intershell band overlap.

Based on the analysis given above, one might anticipate that the metallization pressures for He and Ne would be similar and would be much larger than those for the other rare gases. The latter conclusion is true but the former is not. The theoretical metallization pressure of He (112 Mbar) (Ref. 24) is an order of magnitude smaller than that of Ne. Hence, Hama's assertion of an anomalously large metallization pressure for Ne.

Although the metallization pressure of Ne is much larger than that of He, it is not, in fact, anomalous. The metallization of a crystal is directly related to intersite

overlap, which in turn is related to the volume of the primitive unit cell. From Table II of Ref. 24, the cell volume of He at metallization is about 3.3 a.u.<sup>3</sup> compared to a theoretical zero-pressure volume of about 141.2 a.u.<sup>3</sup> (see Fig. 2 of Ref. 24), i.e., metallization occurs in He at roughly a 43-fold compression. In this investigation, metallization of Ne occurs for a cell volume of about 3.1 a.u.<sup>3</sup>, which corresponds to a 34-fold compression relative to the theoretical zero-pressure volume. It is clear that in terms of volume and compression at metallization He and Ne are similar, just as would be expected based on the analysis given earlier. The much higher metallization pressure in Ne is due to the repulsive effect of the core electrons (He has no core) which results in a much larger pressure in Ne compared to He for a given volume compression.

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