PHYSICAL REVIEW B VOLUME 52, NUMBER 21 1 DECEMBER 1995-I

First-principles study of solid Ar and Kr under high compression

I. Kwon, L. A. Collins, and J. D. Kress
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

N. Troullier
Minnesota Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455

(Received 19 July 1995)

We have performed first-principles total energy calculations for solid Ar and Kr to study phase transitions under high pressure. We used relativistic, nonlocal, norm-conserving pseudopotentials with a plane wave basis in solving the Kohn-Sham equations within the local density approximation for fcc, hcp, and bcc structures of Ar and Kr. Within the volume range we have studied ($V/V_0 = 1.0$ to 0.1, where V_0 is the observed volume at 1 atm and 0 K), both Ar and Kr undergo a phase transition from the fcc to the hcp structure at pressures of about 220 and 130 GPa, respectively, and the insulator-metal transition should occur around 510 GPa (Ar) and 310 GPa (Kr) in the hcp phase.

Due to recent advances in high-pressure technologies such as diamond-anvil cell (DAC) techniques, experimentally attainable pressures have reached to multimegabars (1 Mbar=100 GPa). Rare-gas solids are excellent candidates to study phase transitions under such high compression. Rare gases form the simplest crystals. The electron distribution is very close to that of the free atoms. The crystal structures are all fcc, except He at room pressure (1 atm).[1] Up to 100 GPa, the fcc structure is stable for Ne, Ar, and Kr. However, Xe transforms from the fcc structure to an intermediate, close-packed structure at a pressure around 20 GPa and then to the hcp structure around 80 GPa.[2,3] No further structural transition is seen up to 170 GPa. Therefore, it is of great interest to know whether or not Ar or Kr would have a structural phase transition at a pressure higher than 100 GPa. Ar has been compressed in the DAC at room temperature to 80 GPa with no change in structure.[4,5] DAC measurements of solid Kr at room temperature to 55 GPa indicate no change of phase.[6,7] Also, the feasibility of the pressure-induced metallization of the rare-gas solids is an attractive subject. There are experimental indications for the metallization of solid Xe in the range 130–150 GPa.[2,8]

Linear muffin-tin orbital (LMTO) calculations predict that the compression of Ar leads to the sequence of structures fcc → hcp → bcc → fcc.[9] With the augmented-plane-wave (APW) method, the metallization pressure of the fcc Kr is predicted to 316 GPa.[10] In this paper, we report the study of pressure effects on Ar and Kr using the local-density-functional total energy calculations in the plane wave basis with pseudopotentials. We predict a phase transition from the fcc structure to the hcp structure for both Ar and Kr at pressures of about 220 GPa and 130 GPa, respectively. The hcp structure is stable up to 2 TPa for Ar and up to 3 TPa for Kr. The metallization of the hcp structure occurs around 510 GPa (Ar) and 310 GPa (Kr).

Plane wave, pseudopotential total energy calculations with the local-density approximation (LDA) have been applied for a wide range of materials with success to study pressure-induced phase transitions.[11] In this work, we investigate rare-gas solids with this method. In total energy calculations within the density-functional formalism, we consider contributions from a static lattice only, which include the electron kinetic energy, the electron-electron interactions, the electron-ion interactions, and the static Coulomb interactions between the ions. With the local-density approximation, the electron-electron interactions can be divided into the Hartree term and the exchange-correlation term. We separate again the exchange-correlation term into exchange and correlation contributions and for the exchange part, we take a form proportional to the cube root of the density. For the correlation part, we employ the Ceperley-Alder correlation[12] parametrized by Perdew and Zunger.[13] We use pseudopotentials for the electron-ion interactions.

In generating pseudopotentials, we used the method developed by Troullier and Martins.[14] For both Ar and Kr, we generated relativistic, nonlocal, norm-conserving pseudopotentials, although relativistic effects for Ar are small. We used the Kleinman-Bylander form[15] of the separable nonlocal pseudopotentials. $1s$, $2s$, and $2p$ electrons are treated as

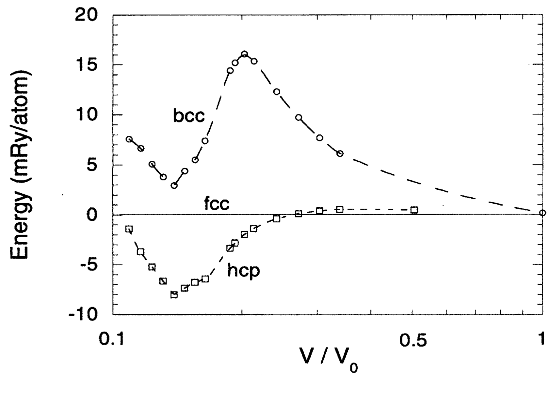

FIG. 1. Total energies of the solid Ar of the hcp and bcc structures relative to the fcc structure as a function of volume ratio V/V_0: fcc (solid line), hcp (open square), and bcc (open circle). $V_0 = 37.45$ Å^3/atom.

0163-1829/95/52(21)/15165(5)/$06.00 52 15 165

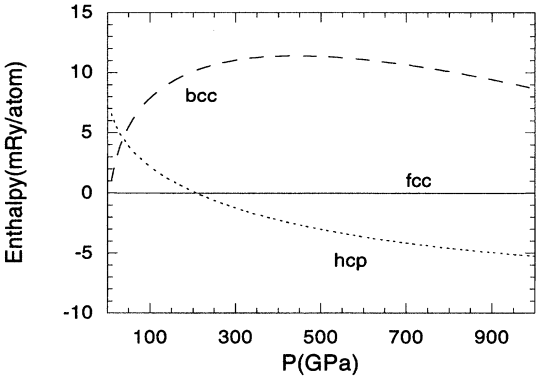

FIG. 2. Enthalpies of the solid Ar of the hcp and bcc structures relative to the fcc structure as a function of pressure: fcc (solid line), hcp (dotted line), and bcc (dashed line).

core electrons while $3s$ and $3p$ electrons as valence electrons for Ar. For Kr, $4s$ and $4p$ electrons are valence electrons. We emphasize that in the study of phase transitions under very high compression, it is essential to include high angular momentum components in the pseudopotential. We have to consider the possibility of the valence electron occupations in high angular momentum states at high pressure. The overlap with high angular momentum states with valence electrons, for example between $3p$ and $3d$ states for Ar, could occur at high pressure. Therefore, we include up to g components for both Ar and Kr pseudopotentials. Also, it is important to make sure that the cores do not overlap. We use 1.58 and 1.70 bohrs for Ar and Kr, respectively, as the core radius of the pseudopotential.

In Fig. 1, we compare the total energy of the hcp and bcc structure with that of the fcc structure of Ar at the volume V range from $1.0V_0$ to $0.1V_0$. Here, $V_0=37.45$ Å^3/atom is the observed volume at 1 atm and 0 K.[16] The convergence of the total energy versus the plane wave cutoff enengy E_{cut} and the number of k points sampled in the irreducible Brillouin zone has been tested and $E_{\text{cut}}=64$ Ry has been used. The difference in the total energy with larger $E_{\text{cut}}=76$ Ry is 0.7 mRy/atom at $V/V_0=0.109$ and smaller at larger volumes. In the k-point samplings, 145, 270, and 145 points were sampled for the fcc, hcp, and bcc structures, respectively. The difference in the total energy with more k points (408 points) never exceeds 1 mRy/atom, which occurs at $V/V_0=0.109$ of the fcc structure. For the hcp structure, only

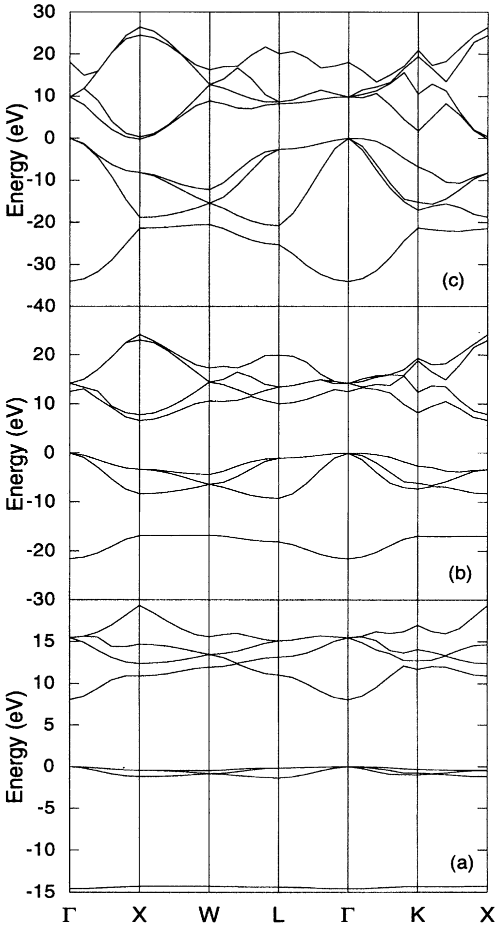

FIG. 3. Electronic band structures for the fcc structure of Ar at different volumes: (a) $1.0V_0$; (b) $0.339V_0$; and (c) $0.188V_0$.

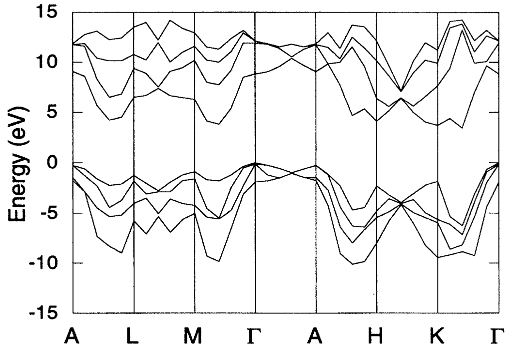

FIG. 4. Electronic band structure for the hcp structure of Ar at $V=0.241V_0$.

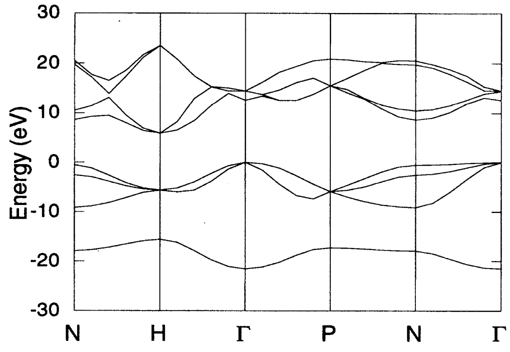

FIG. 5. Electronic band structure for the bcc structure of Ar at $V=0.339V_0$.

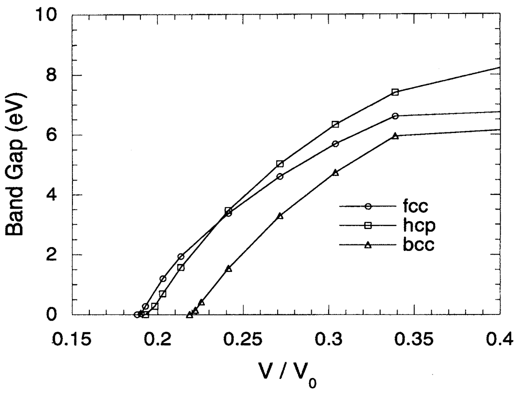

FIG. 6. Band-gap energies of the fcc, hcp, bcc structures of solid Ar as a function of volume ratio V/V_0.

the ideal c/a ratio (1.633) is considered. The energy change associated with the variation of the c/a ratio is at most 1 mRy/atom at $V/V_0=0.109$.

From $V/V_0=1$ to about 0.271, the total energy of the hcp phase is slightly higher than that of the fcc structure and then lower at higher compression. Therefore, we expect a phase transition from the fcc to the hcp structure of Ar around at the volume $V \simeq 0.256V_0$ and pressure $P \sim$ 220 GPa. The pressure was obtained from the stress theorem.[17] However, for the bcc structure, the total energy is always higher than those of the fcc and hcp structures for the entire volume range investigated. This is contradictory to the earlier study by McMahan.[9] Using LMTO total energy calculations, McMahan predicted a phase transition from the fcc to the hcp structure at the volume $V > 0.25V_0$ and pressure $P <$ 230 GPa. And then, the hcp phase transforms to the bcc structure at $V/V_0=0.148$ and $P=970$ GPa, and back to the fcc phase at further compression ($V/V_0=0.103$, $P=2.2$ TPa). We believe that the difference in the bcc structure may arise from the atomic-sphere approximation of the charge density in the LMTO method, which is best for the close-packed fcc and hcp structures, but less adequate for the more open-packed bcc structure. Also, the LMTO calculations[9] use the force theorem[18] in which only the differences in the one-electron eigenvalue sums obtained with the use of the same self-consistent fcc potential for the bcc and hcp structures are considered in the total energy differences.

TABLE I. Metallization volumes and pressures of solid Ar. $V_0=37.45$ Å^3/atom.

Structure	V/V_0	P (GPa)
fcc	0.188	561
hcp	0.193	514
bcc	0.219	369

In zero-temperature, isothermal phase transitions, we have to consider enthalpy $H=E+PV$, although it is common to compare total energy differences rather than enthalpy differences when the volumn change in passing from one phase to another is very small. Figure 2 shows the enthalpy of the hcp and the bcc structure of Ar relative to that of the fcc structure. We fit numerically the enthalpy of each structure with the pressure obtained by the stress theorem[17] which is less than 6% different from the pressure obtained by the differentiation of E versus V curve. From the enthalpy differences, we expect a phase transition from the fcc structure to the hcp at pressure 210 GPa, which is very close to the transition pressure 220 GPa obtained from the total energy differences. The corresponding volume for the fcc structure at this transition pressure is $0.263V_0$ and the estimated volume change is 0.09%. As observed from the total energy differences, a phase transition to the bcc structure is not expected to occur in the entire range of the pressure we have considered. We note that up to 40 GPa, the bcc structure is stable against the hcp. However, the fcc structure is the most stable in this range of the pressure. Therefore, the sequence of the structures for solid Ar under compression is fcc $\rightarrow$ hcp up to 2 TPa.

By studying electronic band structures as a function of volume, we estimate metallization pressures. Figure 3 shows the band structures of the fcc structure at different volumes. The band gaps are direct ($\Gamma \rightarrow \Gamma$) at large volumes, as shown in Fig. 3(a) as an example. As the compression increased, the gaps are indirect, where the bottom of the conduction bands is at the X point and the top of the valence bands is at the

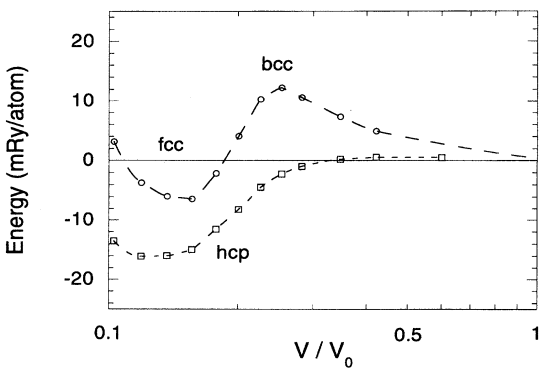

FIG. 7. Same as Fig. 1 except for Kr. $V_0=44.95$ Å^3/atom.

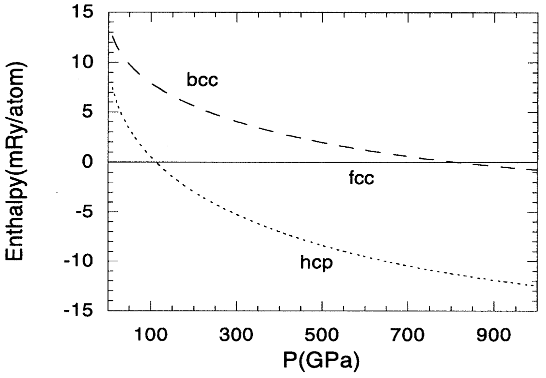

FIG. 8. Same as Fig. 2 except for Kr.

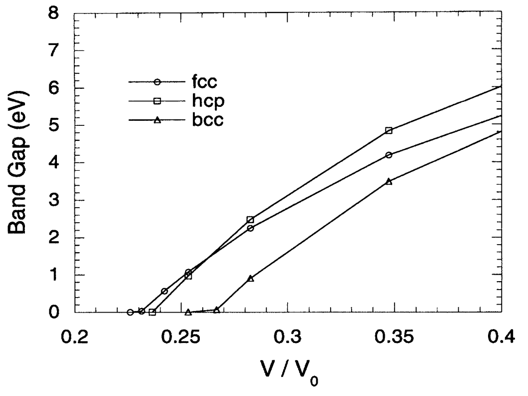

FIG. 9. Same as Fig. 6 except for Kr.

TABLE II. Metallization volumes and pressures of solid Kr. $V_0=44.95$ Å^3/atom.

Structure	V/V_0	P (GPa)
fcc	0.226	356
hcp	0.236	306
bcc	0.253	251

Γ point [Fig. 3(b)]. Finally, the metallization occurs at further compression due to the overlap of the bands at these points [Fig. 3(c)]. The band structures of the hcp and bcc structures show the similar behaviors except that the bottom of the conduction bands is at near K for the hcp (Fig. 4) and at H for the bcc (Fig. 5). The closure of the band gaps occurs due to the overlap between the valence p bands at the Γ point and the hybrid conduction bands which include d and even f components together with s and p components. Figure 6 shows the band-gap energies of the fcc, hcp, and bcc structures of Ar as a function of volume ratio. The closure of the band gap occurs at larger volume for the bcc than that of the fcc or hcp structure. This is due to the fact that at fixed atomic volume, the nearest neighbor distance is shorter for bcc than for fcc or hcp, and hence the band width for bcc becomes wider. The calculated insulator-metal transition volumes and the corresponding pressures are listed in Table I. These values are in excellent agreement with the LMTO results.[9]

Figure 7 shows the total energy differences of solid Kr. $E_{\text{cut}}=64$ Ry has been used and the c/a ratio for the hcp structure is fixed to the ideal value 1.633. The number of k points sampled in the irreducible Brillouin zone is the same as for the Ar case. A phase transition from the fcc structure of solid Kr to the hcp structure should occur at $V/V_0 \simeq 0.315$ and $P \sim 130$ GPa. Here, $V_0=44.95$ Å^3/atom has been used.[16] Unlike Ar, there is a structural phase transition of Kr from the fcc phase to the bcc at $V/V_0 \simeq 0.189$ and $P \sim 580$ GPa, and then back to the fcc structure at $V/V_0 \simeq 0.111$ and $P \sim 2.4$ TPa. However, we cannot expect to observe these phase transitions in experiments because the hcp structure is stable against the fcc and the bcc structures in this volume range. From the enthalpy differences (Fig. 8), we estimate a transition pressure from the fcc structure to the hcp of 110 GPa, and a volume change of 0.34%. The phase transition should occur at $V=0.327V_0$ for the fcc structure. These values are very close to the results from the total energy differences. We note that a transition pressure from the fcc structure to the bcc is 810 GPa, which is somewhat higher than 580 GPa obtained from the total energy differences. However, the sequence of the structures for solid Kr under compression is fcc → hcp up to 3 TPa. We note that Hama and Matsui predict a structural phase transition of solid Xe from the fcc phase to the bcc at $P=62$ GPa with the APW method.[19] However, Ray *et al.* predict the phase transition at higher pressure $P \geqslant 95$ GPa with the APW $X\alpha$ method.[20] Unfortunately, the hcp structure of solid Xe has not been considered in both calculations.

The electronic band gap energies of solid Kr as a function of volume are shown in Fig. 9 and the metallization pressures are listed in Table II. The band structures of Kr are very similar to those of Ar. As seen in Ar, the metallization pressure of the bcc structure is lowest and that of the fcc is highest. With the APW method, Hama and Suito predict the metallization of the fcc Kr at $V=6.5$ cm^3/mol ($V/V_0=0.241$) and $P=316$ GPa.[10]

In summary, with plane-wave pseudopotential total energy calculations, we predict a structural phase transition from the fcc structure to the hcp structure for both Ar and Kr at $P \sim 220$ GPa (Ar) and 130 GPa (Kr), respectively. The hcp structure is stable up to $P \sim 1.9$ TPa (Ar) and 2.9 TPa (Kr). Also, an insulator-metal transition should occur at $P \sim 510$ (Ar) and 310 (Kr) for the hcp structure of Ar and Kr, respectively. We note here that the one-electron theory in the density functional formalism underestimates the band gap energies of semiconductors and insulators by 30–50 % in general. However, we still believe that the metallization pressures of Ar and Kr are in an experimentally attainable range. Including gradient corrections to the LDA could improve the accuracy in the exchange-correlation interactions since the pressure range we have studied is very high.

The authors acknowledge useful conversations with Dr. R. Albers and Dr. A. McMahan. Los Alamos National Laboratory is operated under the auspices of the U.S. Department of Energy.

---

[1] D. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).

[2] R. Reichlin, K. E. Brister, A. K. McMahan, M. Ross, S. Martin, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. Lett. **62**, 669 (1989).

[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] L. W. Finger, R. M. Hazen, G. Zou, H. K. Mao, and P. M. Bell, Appl. Phys. Lett. **39**, 892 (1981).

[5] M. Ross, H. K. Mao, P. M. Bell, and J. A. Xu, J. Chem. Phys. **85**, 1028 (1986).

[6] I. V. Aleksandrov, A. N. Zisman, and S. M. Stishov, Zh. Éksp. Teor. Fiz. **92**, 657 (1987) [Sov. Phys. JETP **65**, 371 (1987)].

[7] A. Polian, J. M. Besson, M. Grimsditch, and W. A. Grosshans, Phys. Rev. B **39**, 1332 (1989).

[8] K. Goettel, J. H. Eggert, I. F. Silvera, and W. C. Moss, Phys. Rev. Lett. **62**, 665 (1989).

[9] A. K. McMahan, Phys. Rev. B **33**, 5344 (1986).

[10] J. Hama and K. Suito, Phys. Lett. A **140**, 117 (1989).

[11] See, for example, M. T. Yin and M. Cohen, Phys. Rev. Lett. **45**, 1004 (1980); P. K. Lam and M. Cohen, Phys. Rev. B **27**, 5986 (1983); S. Froyen and M. Cohen, *ibid.* **29**, 3770 (1984).

[12] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[13] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[15] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[16] J. Donohue, *The Structure of the Elements* (Wiley, New York, 1974), p. 27.

[17] O. H. Nielsen and R. M. Martin, Phys. Rev. Lett. **50**, 697 (1983); Phys. Rev. B **32**, 3780 (1985).

[18] A. R. Mackintosh and O. K. Andersen, in *Electrons at the Fermi Surface*, edited by M. Springford (Cambridge University Press, Cambridge, 1980).

[19] J. Hama and S. Matsui, Solid State Commun. **37**, 889 (1981).

[20] A. K. Ray, S. B. Trickey, and A. B. Kunz, Solid State Commun. **41**, 351 (1982).