PHYSICAL REVIEW B VOLUME 1, NUMBER 8 15 APRIL 1970

# Band Structure of Cubic and Hexagonal Argon

RICARDO RAMIREZ* AND L. M. FALICOV
*Department of Physics,† University of California, Berkeley, California 94720*

(Received 10 November, 1969)

A pseudopotential calculation of the band structure of both cubic-close-packed and hexagonal-close-packed solid argon is presented. The pseudopotential form factor is obtained by fitting energy gaps to Mattheiss's augmented-plane-wave calculation. The direct gaps obtained are 1.03 Ry in the cubic phase and 0.84 Ry in the hexagonal plane, i.e., a sizable reduction is found in the hexagonal structure. The hexagonal valence band splits into two subbands of $p_z$ and $p_x - p_y$ character with an energy gap clearly appearing between them; the $p_z$-like band lies higher in energy and constitutes the top of the valence band. Several other features of the structures are discussed. Convergence of both calculations is checked to be about 0.01 Ry. Sensitivity of the results to changes in the form factors is also discussed.

## I. INTRODUCTION

In recent years many investigators have been interested in the electronic structure of rare-gas solids.[1] The optical spectra, whose structure is mainly due to excitons, has been studied in several experimental as well as theoretical works.[2–5] The phase transitions in two-component systems involving rare-gas solids have been the subject of a series of papers by Barrett *et al.*[6–9] Finally, there have been many attempts[10–16] to explain the higher stability of the face-centered-cubic (fcc) structure, in which these gases crystallize, compared to the hexagonal-close-packed (hcp) configuration.

The commonly known, well-determined phase of solid argon is the fcc structure, with nearest-neighbor distance[1] at 4°K of $a_0 = 3.7477$ Å. Some years ago a metastable hcp phase of the solid argon was found[17] at temperatures below its melting point of 84°K. The axial ratio of this structure was found to be that of the close-packed spheres, 1.633, and the lattice constant $a = 3.748$ Å, i.e., the same nearest-neighbor distance of the cubic phase within experimental error.[1]

From the point of view of its electronic properties, the band structure of the fcc phase has been calculated by Knox and Bassani[18] and Mattheiss.[19] In the former calculation a combination of tight-binding and orthogonalized plane waves was used, while Mattheiss used in his calculation the augmented-plane-wave method. As far as we are aware, no calculation of the electronic properties of the hcp structure has been performed.

Of those methods suitable for band-structure calculations, the pseudopotential[20] has the appealing feature of allowing to transfer in a fairly straightforward way information concerning a given element from one crystal structure to another; this procedure has been applied successfully in several cases.[20–25] On the other hand, it is well known that the pseudopotential method converges rather slowly in those cases which depart substantially from free-electron-like structures.[20]

In order to test the usefulness of the pseudopotential approach in the case of van der Waals solids like argon and to use once again the "transferring" properties of the method, we performed in the present work a pseudopotential calculation of argon in both its fcc and hcp phases. An empirical local pseudopotential form factor for argon was obtained by reproducing within a few percent the band structure of the cubic phase as calculated by Mattheiss; this form factor was then used to obtain the band structure in the hcp phase. Although the convergence of the method was rather slow and a fairly large secular equation had to be solved, the approach proved to be successful and sensible and reliable band structures were obtained.

The calculation and results are presented in Sec. II and a discussion and conclusions constitute Sec. III.

## II. CALCULATION AND RESULTS

### A. Method

In order to obtain the band structure, we have to solve Schrödinger's equation

$$(-(\hbar^2/2m)\nabla^2 + V(\mathbf{r}))\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}), \quad (2.1)$$

---

[*] Chile-California Cooperative Program Fellow (supported by the Ford Foundation).

[†] Work supported in part by the National Science Foundation through Grant No. GP 13889.

[1] For a complete review of the subject, see L. Meyer, Advan. Chem. Phys. **16**, 343 (1969).

[2] G. Baldini, Phys. Rev. **128**, 1562 (1962).

[3] O. Bostanjoglo and L. Schmidt, Phys. Letters **22**, 130 (1966).

[4] J. Hermanson, Phys. Rev. **150**, 660 (1966).

[5] K. Moorjani, Phys. Letters **23**, 652 (1966).

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

[7] C. S. Barrett and L. Meyer, J. Chem. Phys. **43**, 3502 (1965).

[8] C. S. Barrett and L. Meyer, J. Chem. Phys. **45**, 834 (1966).

[9] C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys. **44**, 998 (1966); **47**, 740 (1967).

[10] B. M. Axilrod, J. Chem. Phys. **17**, 1349 (1949).

[11] B. M. Axilrod, J. Chem. Phys. **19**, 719 (1951).

[12] J. Linderberg and F. W. Bystrand, Arkiv Fysik **26**, 383 (1964).

[13] L. Jansen, Phys. Letters **4**, 91 (1963).

[14] L. Jansen, Phys. Rev. **135**, A1292 (1964).

[15] L. Jansen and S. Zimring, Phys. Letters **4**, 95 (1963).

[16] A. Lucas, Physica **35**, 353 (1967).

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

[18] R. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

[19] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

[20] L. M. Falicov, in *Energy Band in Metals and Alloys* (Gordon and Breach Science Publishers, Inc., New York, 1968), p. 73.

[21] P. J. Lin and L. M. Falicov, Phys. Rev. **142**, 441 (1966).

[22] L. M. Falicov and P. J. Lin, Phys. Rev. **141**, 562 (1966).

[23] M. Y. Au-Yang and M. L. Cohen, Solid State Commun. **6**, 855 (1968).

[24] M. Y. Au-Yang and M. L. Cohen, Phys. Rev. **178**, 1279 (1969).

[25] T. K. Bergstresser and M. L. Cohen, Phys. Rev. **164**, 1069 (1967).

where $V(\mathbf{r})$ is the self-consistent periodic potential. Expanding the eigenfunctions in terms of orthogonalized plane waves, this equation becomes the usual pseudopotential equation[20]

$$\mathcal{H}(\mathbf{k})\varphi_{\mathbf{k}}(\mathbf{r}) = (-(\hbar^2/2m)\nabla^2 + U(\mathbf{r},\mathbf{k}))\varphi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\varphi_{\mathbf{k}}(\mathbf{r}), \quad (2.2)$$

where

$$U(\mathbf{r},\mathbf{k}) = V(\mathbf{r}) + \sum_c [E(\mathbf{k}) - E_c] |\varphi_c\rangle\langle\varphi_c| \quad (2.3)$$

is the nonlocal pseudopotential, and the functions $\varphi_c(\mathbf{r})$ correspond to core states.

If we expand the pseudo-wave-functions $\varphi_{\mathbf{k}}(\mathbf{r})$ as a linear combination of plane waves, i.e.,

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}}(\mathbf{k}) \exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}] \quad (2.4)$$

(**G** denotes reciprocal lattice vectors), and then approximate $U(\mathbf{r},\mathbf{k})$ to a local pseudopotential

$$U(\mathbf{r},\mathbf{k}) = \sum_{\mathbf{G}} U(\mathbf{G})S(\mathbf{G}) \exp[i\mathbf{G}\cdot\mathbf{r}], \quad (2.5)$$

Eq. (2.2) becomes

$$\sum_{\mathbf{G}'} [\mathcal{H}_{\mathbf{GG}'}(\mathbf{k}) - E(\mathbf{k})\delta_{\mathbf{GG}'}] f_{\mathbf{G}'}(\mathbf{k}) = 0, \quad (2.6)$$

where

$$\mathcal{H}_{\mathbf{GG}'}(\mathbf{k}) = (\hbar^2/2m)(\mathbf{k}+\mathbf{G})^2\delta_{\mathbf{GG}'} + S(\mathbf{G}-\mathbf{G}')U(\mathbf{G}-\mathbf{G}').$$

In our cases, the structure factor takes the values

$$\begin{aligned} S(\mathbf{G}) &= 1 && \text{for the fcc structure} \\ &= \cos[\tfrac{1}{6}\pi(3h+8k+4l)] && \text{for the hcp structure,} \end{aligned}$$

where, for the hcp structure, in the system of coordinates of Fig. 1

$$\mathbf{G} = h\mathbf{G}_1 + k\mathbf{G}_2 + l\mathbf{G}_3,$$

and in the four-index notation

$$\mathbf{G} \equiv (k, l, -k-l, h).$$

The Fourier coefficients $U(\mathbf{G})$ are determined in our case from the known fcc band structure of argon.[19]

In order to solve the secular equation

$$|\mathcal{H}_{\mathbf{GG}'}(\mathbf{k}) - E(\mathbf{k})\delta_{\mathbf{GG}'}| = 0, \quad (2.7)$$

we first truncate the matrix $\mathcal{H}_{\mathbf{GG}'}(\mathbf{k})$ at a certain value of $|\mathbf{G}| = K_1$, then we apply the perturbation method due to Löwdin,[26] in the form described by Brust,[27] i.e., we solve the equation

$$|\bar{\mathcal{H}}_{\mathbf{GG}'}(\mathbf{k}) - E(\mathbf{k})\delta_{\mathbf{GG}'}| = 0, \quad |\mathbf{G}|, |\mathbf{G}'| \leqq K_1 \quad (2.8)$$

where

$$\bar{\mathcal{H}}_{\mathbf{GG}'}(\mathbf{k}) = \mathcal{H}_{\mathbf{GG}'}(\mathbf{k}) + \sum_{|\mathbf{K}|>K_1, |\mathbf{K}|\leq K_2} \frac{\mathcal{H}_{\mathbf{GK}}(\mathbf{k})\mathcal{H}_{\mathbf{KG}'}(\mathbf{k})}{A_{\mathbf{GG}'} - \mathcal{H}_{\mathbf{KK}}(\mathbf{k})}. \quad (2.9)$$

Here $A_{\mathbf{GG}'}$ is chosen as[27]

$$\begin{aligned} A_{\mathbf{GG}'} &= \text{average of the energy levels for } \mathbf{G}=\mathbf{G}' \\ &= \mathcal{H}_{\mathbf{GG}'} \qquad \text{for } \mathbf{G}\neq\mathbf{G}'. \end{aligned}$$

$K_2$ is the maximum absolute value of the reciprocal-lattice vectors **G** of the matrix elements to be considered in the perturbation.

TABLE I. Energy gaps and pseudopotential form factors for fcc argon.

| Symmetry point | Gaps to be fitted (Ry) | Best values obtained (Ry) | Reciprocal-lattice vector | Form factors (Ry) |
|---|---|---|---|---|
| Γ | 0.979 | 1.027 | (1, 1, 1) | −0.35 |
| $X$ | 1.183 | 1.180 | (2, 0, 0) | −0.27 |
| $W$ | 1.241 | 1.255 | (2, 2, 0) | −0.03 |
| $L$ | 1.181 | 1.165 | (3, 1, 1) | 0.09 |
| $K$ | 1.227 | 1.211 | (2, 2, 2) | −0.01 |

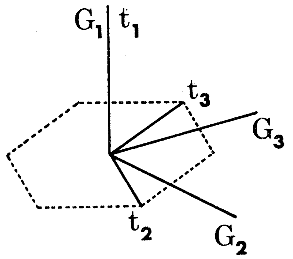

FIG. 1. System of coordinates for the hcp structure.

In our case the value of $K_1$ was taken to be approximately 6.0 a.u.; this corresponds to a matrix of order ~60 for the fcc case and ~125 for the hcp case. For the perturbation calculation those matrix elements with $|\mathbf{G}|$ from 6.0 a.u. up to $K_2 \cong 16$ a.u. were taken into account.

### B. Form Factors and Band Structure

The form factors $U(\mathbf{G})$ were obtained by reproducing the energy gaps between the conduction band and the valence band in the fcc phase at the symmetry points[28] Γ, $X$, $W$, $L$, and $K$. The gaps were taken from the band structure calculated by Mattheiss.[19] These gaps as well as the obtained gaps and the corresponding form factors are given in Table I. The form factor $U(\mathbf{G})$ as a function $|\mathbf{G}|^2$ is shown in Fig. 2. The values of $U$ at the reciprocal lattice vectors **G** of the cubic structure were obtained by the above mentioned fitting. The value of $U(0)$, obtained from

$$U(0) = -\tfrac{2}{3}E_F = -(\hbar^2/3m)(3\pi^2N/V)^{2/3}, \quad (3.1)$$

is −0.65147 Ry and the slope

$$dU(\mathbf{G})/d|\mathbf{G}|^2|_{\mathbf{G}=0} = |U(0)|^2V/(4\pi e^2N) \quad (3.2)$$

is 0.1080 Ry/$|G|^2$, with $|G|^2$ in units of $(2\pi/a)^2 = 0.3933$

---

[26] P. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

[27] D. Brust, Phys. Rev. **134**, A1337 (1964).

[28] L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

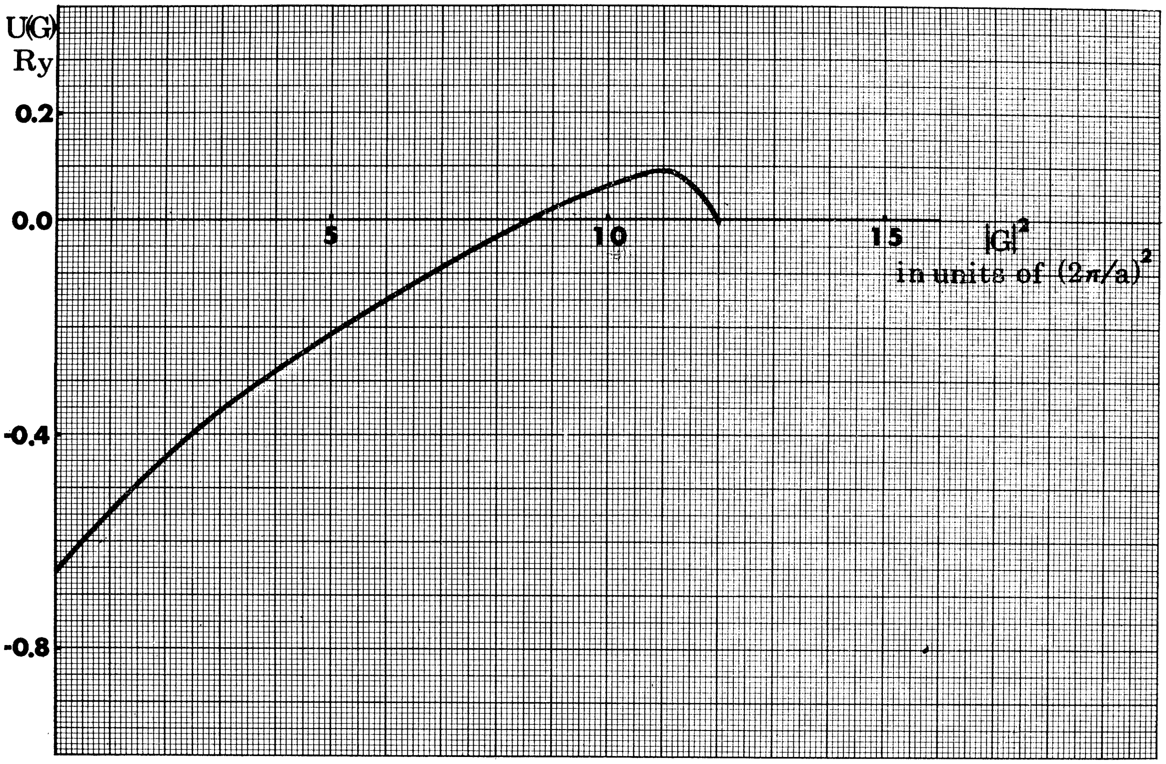

FIG. 2. Pseudopotential form factor $U$ as a function of $|\mathbf{G}|^2$.

a.u. A smooth curve was interpolated through the points thus determined (Fig. 2).

The values of $U(\mathbf{G})$ used in the calculation of the hcp phase are given in the Table II. The energy levels at some symmetry points of the fcc and the hcp Brillouin zone are given in Tables III and IV. The energy bands for both the fcc and the hcp phases are shown in Figs. 3 and 4. Standard notation for symmetry points and lines is used for both structures.[28,29]

### C. Convergence

The convergence of the calculations is illustrated in Fig. 5 where a typical case, i.e., the symmetry point $\Gamma$ of the hcp structure is shown. We notice that with the value of the cutoff $K_1$ which was used, the accuracy of the energy levels is within 0.01 Ry.

### D. Density of States

The density of states of the valence bands of both structures was obtained by means of a tight-binding fitting of the bands.

The fitting of the fcc valence band was made by means of three parameters $p_0$, $(pp\sigma)$, and $(pp\pi)$, using the notation of Slater and Koster[30] for the two-center integrals. The values obtained for these parameters are $p_0=-0.29824$ Ry, $(pp\sigma)=0.020506$ Ry, $(pp\pi)=-0.0028611$ Ry. They give, with no appreciable error, the bands of Fig. 3 and Table III. The density

TABLE II. Form factors for hcp argon.

| Reciprocal-lattice vector | Form factors (Ry) |
|---|---|
| $(1, 0, \bar{1}, 0)$ | $-0.38$ |
| $(0, 0, 0, 2)$ | $-0.35$ |
| $(1, 0, \bar{1}, 1)$ | $-0.33$ |
| $(1, 0, \bar{1}, 2)$ | $-0.17$ |
| $(1, 1, \bar{2}, 0)$ | $-0.03$ |
| $(1, 0, \bar{1}, 3)$ | $0.04$ |
| $(2, 0, \bar{2}, 0)$ | $0.09$ |
| $(1, 1, \bar{2}, 2)$ | $0.09$ |
| $(2, 0, \bar{2}, 1)$ | $0.08$ |
| $(0, 0, 0, 4)$ | $-0.01$ |

TABLE III. Energy-band levels in fcc argon.[a]

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_{25}'$ | 0.908 | $X_4'$ | 1.096 | $W_1$ | 1.091 | $L_2'$ | 1.094 | $K_4$ | 1.025 |
| $\Gamma_1$ | 0.788 | $X_3$ | 0.957 | $W_3$ | 1.008 | $L_1$ | 0.915 | $K_3$ | 0.999 |
| | | $X_1$ | 0.914 | $W_2'$ | 0.990 | | | $K_1$ | 0.956 |
| | | | | | | | | $K_1$ | 0.916 |
| $\Gamma_{15}$ | $-0.239$ | $X_5'$ | $-0.279$ | $W_2'$ | $-0.278$ | $L_3'$ | $-0.245$ | $K_4$ | $-0.271$ |
| | | $X_4'$ | $-0.373$ | $W_3$ | $-0.326$ | $L_2'$ | $-0.384$ | $K_1$ | $-0.305$ |
| | | | | | | | | $K_3$ | $-0.351$ |
| $\Gamma_1$ | $-1.466$ | $X_1$ | $-1.444$ | $W_1$ | $-1.463$ | $L_1$ | $-1.456$ | $K_1$ | $-1.459$ |

[a] All energies in Ry.

---

[29] C. Herring, J. Franklin. Inst. **233**, 525 (1942).

[30] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

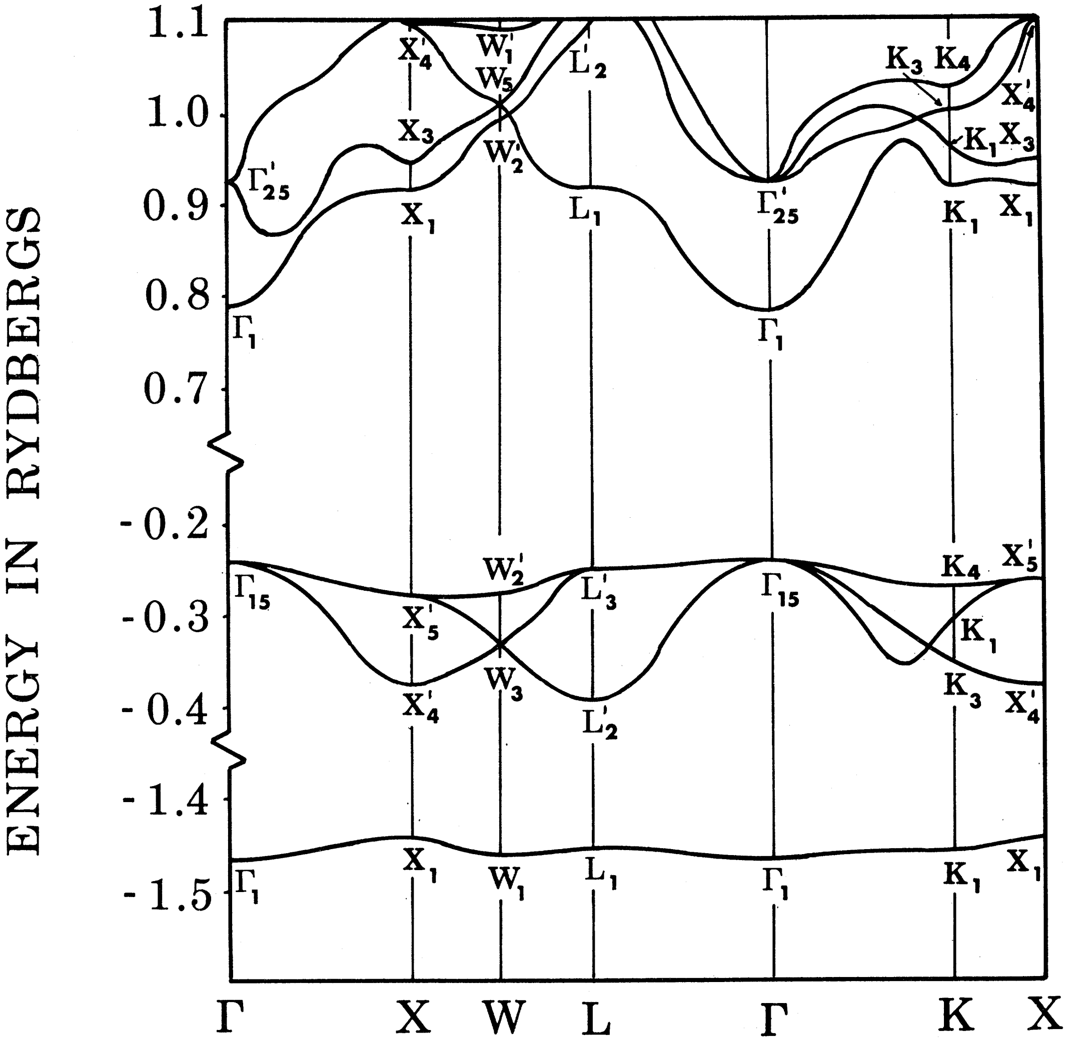

FIG. 3. Energy bands of fcc argon [with $U(0)=0$].

of states of this band was thus calculated in the two-center nearest-neighbor approximation.

In the case of the hcp valence band it was not possible to use only three adjustable parameters in the form given by Miasek.[31] It was necessary, because of the splitting of the $p_z$ and $p_x-p_y$ subbands, to make the

TABLE IV. Energy-band levels in hcp argon.[a]

| | | | | | |
|---|---|---|---|---|---|
| $\Gamma_5^+$ 0.879 | $K_1$ 0.876 | $M_3^+$ 0.848 | $A_3$ 0.863 | $H_1$ 0.861 | $L_1$ 0.826 |
| $\Gamma_1^+$ 0.869 | $K_5$ 0.854 | $M_2^-$ 0.773 | $A_1$ 0.773 | $H_2$ 0.834 | $L_1$ 0.762 |
| $\Gamma_6^-$ 0.857 | $K_2$ 0.822 | $M_1^+$ 0.741 | | | |
| $\Gamma_4^-$ 0.764 | | | | | |
| $\Gamma_1^+$ 0.690 | | | | | |
| $\Gamma_2^-$ $-0.149$ | $K_6$ $-0.192$ | $M_4^-$ $-0.179$ | $A_1$ $-0.206$ | $H_3$ $-0.191$ | $L_1$ $-0.191$ |
| $\Gamma_3^+$ $-0.255$ | $K_3$ $-0.336$ | $M_3^+$ $-0.210$ | $A_3$ $-0.301$ | $H_1$ $-0.350$ | $L_2$ $-0.136$ |
| $\Gamma_6^-$ $-0.293$ | $K_5$ $-0.345$ | $M_4^+$ $-0.307$ | | $H_3$ $-0.352$ | $L_1$ $-0.367$ |
| $\Gamma_5^+$ $-0.313$ | $K_1$ $-0.358$ | $M_3^-$ $-0.328$ | | | |
| | | $M_2^-$ $-0.358$ | | | |
| | | $M_1^+$ $-0.373$ | | | |
| $\Gamma_4^-$ $-1.476$ | $K_5$ $-1.473$ | $M_1^+$ $-1.471$ | $A_1$ $-1.481$ | $H_2$ $-1.473$ | $L_1$ $-1.474$ |
| $\Gamma_1^+$ $-1.486$ | | $M_2^-$ $-1.475$ | | | |

[a] All energies in Ry.

---

[31] M. Miasek, Phys. Rev. **107**, 92 (1957).

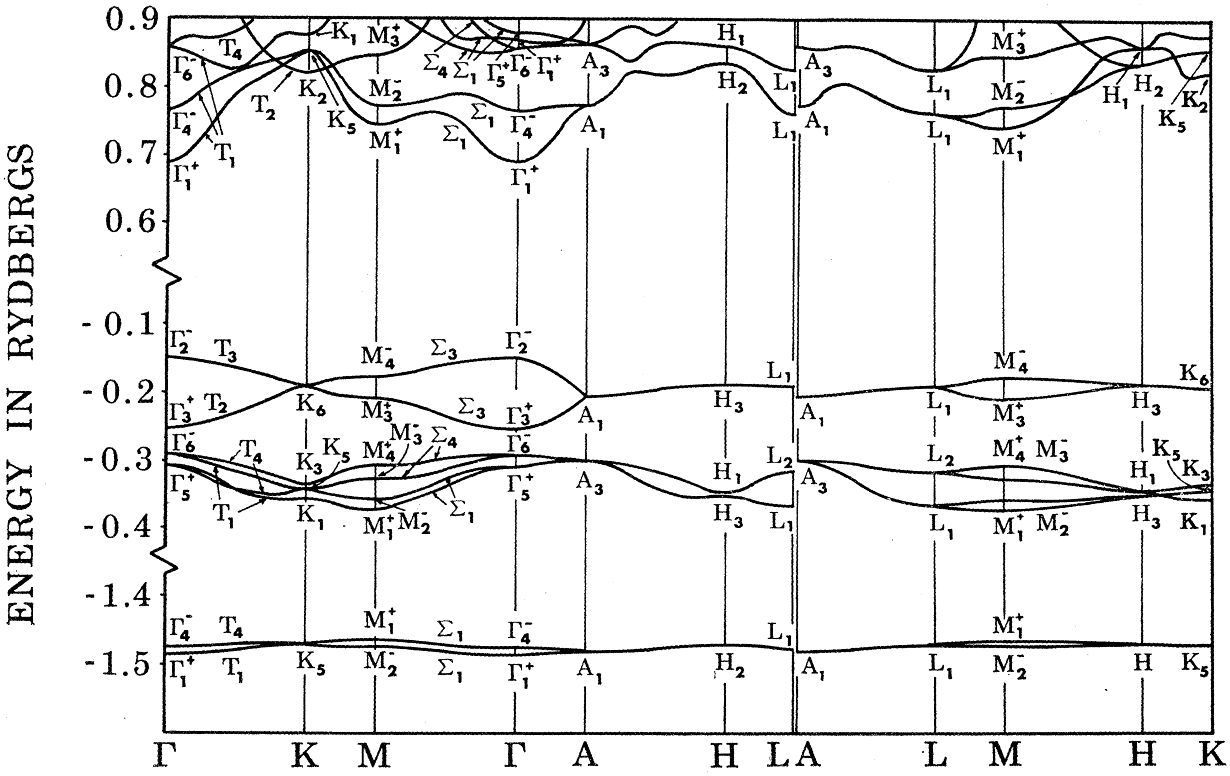

FIG. 4. Energy bands of hcp argon [with $U(0)=0$].

matrix elements $(z/z)_{11}$ and $(z/z)_{12}$ depend on three new parameters $p_0'$, $(pp\sigma)_1'$, $(pp\pi)_1'$. The values obtained for the parameters corresponding to the $p_x-p_y$ subbands are

$$p_0=-0.35848, \quad (pp\sigma)_1=0.00872331,$$

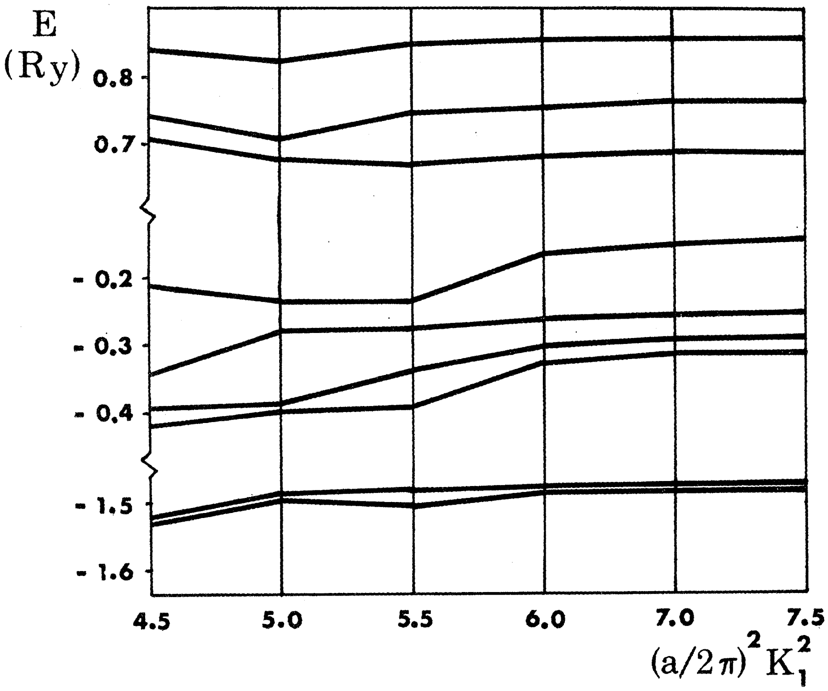

FIG. 5. Convergence of the energy levels at Γ(hcp).

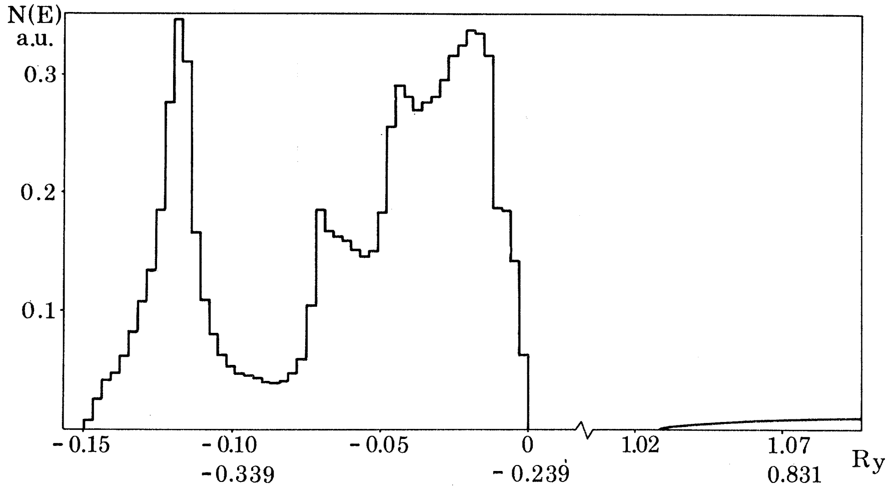

FIG. 6. Density of states of the valence and the conduction bands of fcc argon. Energy values are referred to the top of the valence band (upper scale) and to the ordinary scale used in Fig. 3 (lower scale).

and

$$(pp\pi)_1 = 0.000899335\,,$$

while those corresponding to the $p_z$ subbands are

$$p_0' = -0.17621\,, \quad (pp\sigma)_1' = -0.0109504\,,$$

and

$$(pp\pi)_1' = -0.00436301\,.$$

All these quantities are given in Ry. They reproduce the values of Fig. 4 and Table IV with no appreciable error.

For the conduction bands, the density of states was found by fitting a parabola near Γ in the fcc phase and near Γ and $M$ in the hcp case. The resulting density of states are

$$N(E) = 0.0703(E-E_\Gamma)^{1/2} \text{ a.u.}, \quad \text{for the fcc case}$$

where $E_\Gamma = 0.788$ Ry, and

$$N(E) = 0.0676(E-E_\Gamma)^{1/2} \text{ a.u.} + 1.0741(E-E_M)^{1/2}\theta(E-E_M) \text{ a.u.}, \quad \text{for the hcp case}$$

where $E_\Gamma = 0.690$ Ry is the bottom of the conduction band and $E_M = 0.741$ Ry is the energy of the $M_1^+$ level. In these equations $E$ is given in Ry and $\theta(x)$ is the ordinary step function

$$\theta(x) = 1\,, \quad x > 0$$
$$= 0\,, \quad x < 0\,.$$

The corresponding effective masses are 0.622 for the fcc and 0.606 and 1.84 for the Γ and each of the three $M$ points of the hcp structure, respectively.

For comparison, the density-of-state effective masses at the top of the valence band are 10.182 for each of the three $p$ bands of the fcc structure and 11.467 for the $p_z$-like antibonding band of the hcp structure.

Figures 6 and 7 are diagrams of the calculated densities of state for the fcc and hcp phases, respectively.

### E. Sensitivity of the Energy Levels to the Form Factors

It is interesting to determine how sensitive are the energy levels to small changes of the form factors from the values given in Table II. For this purpose we considered the point Γ of the hcp structure and made several calculations,[32] in which various form factors $U(\mathbf{G})$ were varied from their best values. The results are shown in Table V. We notice that the order of the levels is not affected even when the absolute value of the energy levels varies considerably from one set of form factors to another. The energy-gap changes in the most drastic case by about 14%; the $p_z$ levels are always higher in energy than the $p_x - p_y$ ones and a gap always appears between the subbands. The conduction band is fairly insensitive to form-factor changes.

## III. DISCUSSION AND CONCLUSIONS

From the calculation described in Sec. II, the following conclusions can be drawn:

(a) The direct gaps of the fcc structure at the points $X$, $W$, $L$, $K$, and Γ, as determined by Mattheiss,[19] were chosen to determine the pseudopotential form factors. The gap at Γ, however, could not be fitted accurately,[33] and disagreement between our best value and Mattheiss's is about 5%. This gap is important since it represents the actual energy gap in the solid. Our value is 1.027 Ry compared with 0.979 Ry reported by Mattheiss. Baldini[2] quoted an experimental value of 1.05 Ry. It is evident that our value is much closer to experiment than the one obtained by the augmented-plane-wave calculation.

(b) Several other differences can be noted between our bands (Fig. 4) and those of Ref. 19. In the conduction band, for instance, the energy difference between the $\Gamma_1$ and the $\Gamma_{25}'$ levels is in our calculation about one quarter of the value reported by Mattheiss. The total

---

[32] A smaller secular equation was used for this test; this does not alter the variation of the levels considerably, although convergence is by no means achieved.

[33] As seen in Table I, our best least-squares fit to the five energy gaps gave accurate values for all energy gaps except the one at Γ. Any attempt to improve the gap at Γ gave a much worse agreement for the other gaps.

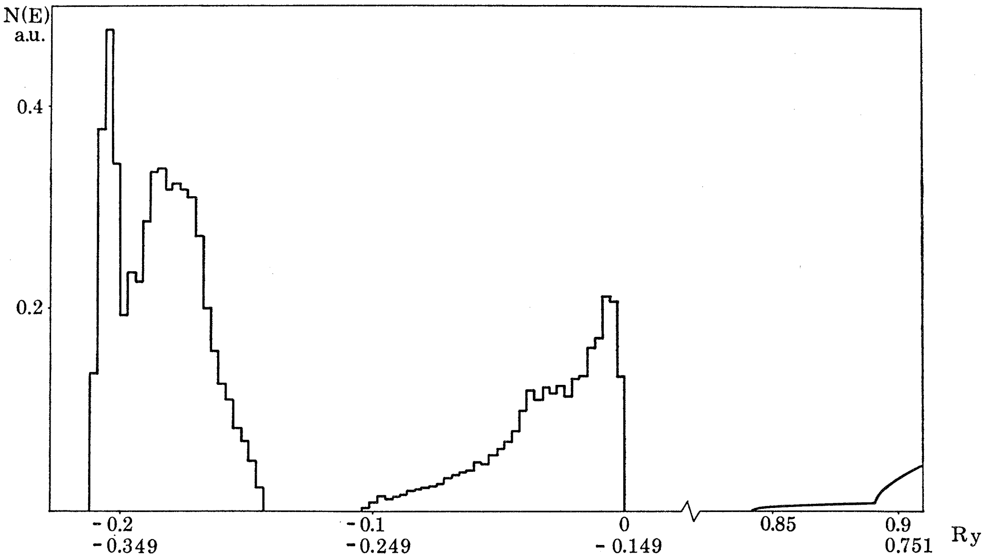

FIG. 7. Density of states of the valence and the conduction bands of hcp argon. Energy values are referred to the top of the valence band (upper scale) and to the ordinary scale used in Fig. 4 (lower scale).

width of the valence $p$ band is, on the other hand, three times larger in our calculation.[34]

(c) An inspection of the hcp band structure (Fig. 5) reveals that the energy gap is about 0.84 Ry, i.e., 25% smaller than the gap in the fcc structure.

(d) The valence $p$ band of the hcp structure splits into two subbands with a separation of 0.1 Ry between them and an actual gap of 0.04 Ry (see Fig. 7). The lower subband contains states of $p_x - p_y$ symmetry, both of bonding and antibonding character: a total amount of four electrons per atom. The higher subband contains the $p_z$-like bonding and antibonding states adding up to two electrons per atom.

(e) It is worth remarking that the splitting of the subbands in the hcp structure as discussed in the previous paragraph does not occur in the fcc phase, where it is forbidden by symmetry. The density of states, however, shows a tendency for the states to group into two distinct sets (see Fig. 6), a low-energy one with roughly two electrons per atom and a high-energy group with roughly four electrons per atom. This is just opposite to the splitting in the hcp phase. This inversion can be more clearly seen if one looks at equivalent directions in the structure, for example, the [111] direction in the fcc as compared to the [0001] direction of the hcp structure. In this case the points $\Gamma$(fcc) and $L$(fcc) correspond both to the point $\Gamma$(hcp). The point $A$(hcp) corresponds to the midpoint of the symmetry line $\Lambda$(fcc), which goes from $\Gamma$(fcc) to $L$(fcc). The energies at $A$(hcp) and its equivalent fcc point are

$$\text{hcp:}\quad -0.206\ \text{Ry (single level)};\qquad -0.301\ \text{Ry (double level)},$$

$$\text{fcc:}\quad -0.242\ \text{Ry (double level)};\qquad -0.277\ \text{Ry (single level)}.$$

The inversion is apparent. Reasonable changes in the form factors $U(G)$ do not alter this feature of the band.[35]

(f) The fact that the $p$ band of the hcp structure could not be fitted to a tight-binding band with two-center integrals and nearest-neighbor contributions only, points out the inadequacy of the commonly made assumptions that the electronic distribution in the rare-gas solids can be considered as a superposition of spherically symmetric tightly bound atomic-like orbitals centered about the nuclear sites. Our results make clear the facts that departure from spherical distribution should be sizable, and that second (and probably third and higher also) nearest-neighbor interaction are not negligible.

(g) The binding energy of cubic argon is extremely small[36] (0.006 Ry/atom). The difference in binding energies between the fcc and the hcp phases, as calculated with the Lennard-Jones potential,[37] gives the staggeringly small value of $8\times10^{-7}$ Ry/atom, with the hcp structure being the stable one. The experimental evidence[1] is, of course, the opposite. The fcc structure is more stable than the hcp, with the difference in free energies of the order of 0.1% of the binding energy, i.e., of the order of $10^{-5}-10^{-6}$ Ry/atom. Under these

---

[34] L. F. Mattheiss, Ref. 19, reports a band width for the $3p$ states of 0.044 Ry, while our calculation gives a band width of 0.145 Ry. The discrepancy is about 0.1 Ry, which we believe is real and ten times larger than our estimated error of 0.01 Ry. Since we try to compare the band structures in a range of about 2.5 Ry, the over-all discrepancy is still very small, of the order of 4%, and about 10% of the values of the gap chosen for the parameter fitting.

[35] The splitting of the subbands in the $3p$ band of hexagonal argon is larger than our estimated error of 0.01 Ry, and therefore, we believe, a real effect.

[36] See, for example, C. Kittel, *Introduction to Solid State Physics*, (J. Wiley and Sons, Inc., New York, 1966), 3rd ed., p. 81.

[37] J. A. Prins, J. M. Dumoré, and L. T. Tjoan, Physica **18**, 307 (1952).

TABLE V. Sensitivity of the $\Gamma$(hcp) levels to changes in form factors.[a]

Energy levels.

| | $\Gamma_1^+$ | $\Gamma_4^-$ | $\Gamma_6^-$ | $\Gamma_5^+$ | $\Gamma_3^+$ | $\Gamma_2^-$ | $\Gamma_1^+$ | $\Gamma_4^-$ |
|---|---|---|---|---|---|---|---|---|
| $U_1$ | −1.563 | −1.534 | −0.427 | −0.393 | −0.386 | −0.219 | 0.718 | 0.872 |
| $U_2$ | −1.777 | −1.736 | −0.578 | −0.543 | −0.527 | −0.359 | 0.711 | 0.850 |
| $U_3$ | −1.519 | −1.492 | −0.424 | −0.385 | −0.363 | −0.194 | 0.747 | 0.875 |
| $U_4$ | −1.518 | −1.494 | −0.458 | −0.418 | −0.373 | −0.206 | 0.754 | 0.860 |
| $U_5$ | −1.458 | −1.437 | −0.357 | −0.325 | −0.303 | −0.134 | 0.747 | 0.878 |

Form factors $U(\mathbf{G})$

| | $(10\bar{1}0)$ | $(0002)$ | $(10\bar{1}1)$ | $(10\bar{1}2)$ | $(11\bar{2}0)$ | $(10\bar{1}3)$ | $(20\bar{2}0)$ | $(11\bar{1}2)$ | $(20\bar{2}1)$ | $(0004)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $U_1$ | −0.38 | −0.35 | −0.33 | −0.17 | −0.03 | 0.04 | 0.09 | 0.09 | 0.08 | −0.01 |
| $U_2$ | −0.40 | −0.37 | −0.35 | −0.19 | −0.03 | 0.04 | 0.09 | 0.09 | 0.08 | −0.01 |
| $U_3$ | −0.38 | −0.35 | −0.32 | −0.16 | −0.02 | 0.04 | 0.09 | 0.09 | 0.08 | −0.01 |
| $U_4$ | −0.38 | −0.35 | −0.33 | −0.18 | −0.03 | 0.04 | 0.10 | 0.10 | 0.09 | −0.01 |
| $U_5$ | −0.37 | −0.35 | −0.31 | −0.18 | −0.03 | 0.05 | 0.09 | 0.09 | 0.08 | −0.01 |

[a] All energies in Ry. The first rows correspond to the values used throughout the paper.

circumstances any attempt to calculate stability of phases using pseudopotential theory would be foolish: Such tiny energies are outside the scope and the convergence range of the pseudopotential method. It is, however, interesting to notice that, if the band structures as described in this paper are taken at face value, the fcc structure is more stable than the hcp structure. This can be seen by comparing the average energies of the $s$ and $p$ bands of both structures. When exactly the same pseudopotential is used for both structures, as is the case in our calculation, the following numbers are obtained:

fcc:

| | |
|---|---|
| average energy of the $3s$ electrons | −1.458 Ry, |
| average energy of the $3p$ electrons | −0.299 Ry, |
| weighted average of $3s$ and $3p$ electrons | −0.589 Ry; |

hcp:

| | |
|---|---|
| average energy of the $3s$ electrons | −1.475 Ry, |
| average energy of the $3p_x$—$3p_y$ electrons | −0.335 Ry, |
| average energy of the $3p_z$ electrons | −0.174 Ry, |
| weighted average of the $3s$ and $3p$ electrons | −0.580 Ry. |

This clearly gives the fcc as the most stable structure, but by an amount of $9\times10^{-3}$ Ry, which is less than but of the order of our estimated convergence error.

(h) Our pseudopotential can also be tested against other calculations. If, to the energies quoted in the last paragraph, we add the value of $U(0)=-0.651$ Ry which for simplicity was not included in the band-structure calculations, we obtain the following results:

| | |
|---|---|
| average energy of $3s$ electrons | −2.109 Ry (fcc) |
| | −2.126 Ry (hcp); |
| average energy of $3p$ electrons | −0.950 Ry (fcc) |
| | −0.932 Ry (hcp). |

These are to be compared with the Hartree-Fock parameter for the argon atom, which are[38]

Hartree-Fock energy of the $3s$ electron −2.107 Ry,
Hartree-Fock energy of the $3p$ electron −1.065 Ry.

The agreement should be considered very good if we remember that the pseudopotential form factors were obtained from the augmented-plane-wave energy gaps of Mattheiss.[19]

It should be mentioned that from the present band-structure optical properties of cubic and hexagonal solid argon could in principle be calculated. Since the optical properties[2] are dominated by excitons,[4] such a calculation would be in fact a many-body one, with the one-electron effect playing only a secondary role. In any case, the band structures, as reported here, could be the starting point for unravelling the complicated spectra of these solids.

## ACKNOWLEDGMENTS

The authors would like to acknowledge several stimulating conversations with Professor Marvin L. Cohen and Professor C. Kittel. They are particularly grateful to Professor C. Y. Fong for his help and advice with the programming and many discussions on the best way of accomplishing their objectives.

---

[38] F. Herman and S. Skillman, *Atomic Structure Calculation* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965).