Calculation of high-pressure phases of Al

Pui K. Lam and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

Possible high-pressure phases of Al are examined by comparing the total energies for three structures: fcc, bcc, and hcp. The energies are calculated using the density-functional formalism and the *ab initio* self-consistent pseudopotential approach. At zero pressure, the most stable structure is the fcc structure in agreement with experiment. At about 2 Mbar, the hcp structure is predicted to be the most stable, while at about 4 Mbar, the bcc structure is the most stable. The stability of the bcc phase at compressed volume is found to be caused by the lowering of the d states. This conclusion is based on an analysis of the occupancy of s, p, and d states at normal and compressed volumes.

I. INTRODUCTION

The behavior of materials under high pressure is of great current interest because high-pressure experiments are becoming more refined. An accurate first-principles method of calculating, and hence predicting, the structural properties of solids under high pressure is therefore very valuable. More importantly, such calculations can reveal the mechanisms of pressure-induced phase transitions. Recently, accurate calculations of structural properties have been obtained using the density-functional formalism and the *ab initio* pseudopotential approach. A wide range of materials have been investigated with this method, including insulators[1] (C), homopolar semiconductors[2,3] (Si and Ge), heteropolar semiconductors[4] (GaAs and AlAs), cubic metals[5] (Al), and noncubic semimetals[6] (Be). The success of this approach can be attributed to three reasons:

(1) The electronic screening is treated self-consistently in the density-functional formalism.

(2) The quality of the pseudopotentials is improved by using angular-momentum-dependent pseudopotentials (i.e., nonlocal pseudopotentials). The energy dependence of the pseudopotentials is taken into account by using different potentials for different angular momenta. The behavior of the valence electrons is correctly simulated over a wide range of excitation energy [about 1 Ry (Ref. 7)].

(3) The crystal potential at the interstitial site (bonding region) is accurately represented using a plane-wave expansion as compared to using a spherical (muffin-tin) approximation. This accurate representation may be important when two similar structures are compared.

The approach outlined above is employed here to determine the stable phase of Al under high pressure and to analyze the driving mechanisms for the phase transitions. Al is chosen as a prototype simple close-packed metal. There have been previous investigations by Friedli and Ashcroft[8] using a local (angular-momentum-independent) pseudopotential and a nearly-free-electron perturbation expansion technique, and more recently by Moriarty and McMahan[9] using generalized pseudopotential theory (GPT) and linear-muffin-tin orbital (LMTO) methods. Comparison between our results and those of the previous investigators will be discussed below. Our findings indicate that Al undergoes the following transformation sequence: fcc-hcp-bcc. However, the transition pressures are quite high, ~ 2 and ~ 4 Mbar, respectively; hence these transitions have not yet been observed experimentally. We also investigate in detail the importance of the d states for the stability of the high-pressure phase. The amount of s, p, and d character of the wave functions is analyzed as a function of volume. The role of the d states is also addressed by Moriarty and McMahan.[9]

This paper is organized as follows. In Sec. II, the procedures for the total-energy calculation and the s-p-d decomposition of the wave functions are described. In Sec. III the results are presented and discussed. A brief summary is given in Sec. IV.

II. CALCULATIONAL PROCEDURE

The total energy of a solid consists of two parts: a static lattice contribution and a contribution due

to the vibrations of the lattice. The static lattice part includes the electron kinetic energy, the electron-electron interactions, the electron-ion interactions, and the static Coulomb interactions between the ions. The vibrational part includes all the occupied phonon modes and the zero-point motion of the lattice. The separation of the total energy into these two parts is a consequence of the adiabatic approximation. The applicability of the adiabatic approximation in Al is shown in detail by Friedli and Ashcroft.[8] The static lattice part can be calculated using the zero-temperature formulation because at room temperature $k_B T$ is much less than the Fermi energy. The Debye temperature, on the other hand, is of the order of the room temperature (at normal volume, $T_d = 430$ K). The vibrational part is extremely difficult to calculate from first-principles because the phonon spectra for the various structures must be known. However, its contribution can be estimated using the Debye model. The vibrational energy is of the order of $k_B T_D$. At normal volume, $k_B T_D \sim 3$ mRy. The Debye temperature is not expected to differ much among the various close-packed structures. Even for a 10% difference in T_D, the energy difference is only 0.3 mRy. The vibrational part is probably not important in determining the stable phase of Al and is not included in our total-energy calculation.

The static lattice part of total energy is computed using the density-functional formalism,[10] with Wigner's formula for the correlation energy.[11] The interaction between the core and the valence electrons is represented by nonlocal pseudopotentials, which are generated using only the atomic number as input.[7] The potentials are the same as those used in our previous calculations of the structural properties[5] and phonon frequencies[12] of Al. The crystal wave functions are calculated by solving the Schrödinger equation in a plane-waves basis set. The procedure is iterated until the input and output potentials differ by less than 10^{-5} Ry. The self-consistent pseudopotential approach is described elsewhere.[13] With the wave functions expanded in a plane-waves basis, the total energy can be evaluated very easily in a momentum-space representation.[14]

In addition to comparing the total energies of the three structures, we also analyze the structures in terms of the number of s, p, and d electrons present inside the Wigner-Seitz sphere around the atom. The s, p, and d occupations are defined as follows: The crystal wave function $\psi_{\vec{k}}$ is given in the plane-wave basis by

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} . \qquad (1)$$

Using the identity,

$$e^{i\vec{k}\cdot\vec{r}} = \sum_l i^l 4\pi j_l(kr) \sum_{m=-l}^{l} Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r}) , \qquad (2)$$

where j_l is the spherical Bessel function and Y_{lm} is the spherical harmonic function, $\psi_{\vec{k}}$ can easily be projected into spherical harmonics centered at each atom,

$$C_{lm}(\vec{k},r) = \langle \psi_{\vec{k}} | Y_{lm} \rangle \langle Y_{lm} | \psi_{\vec{k}} \rangle . \qquad (3)$$

The projections are then integrated over the Wigner-Seitz sphere to get the s, p, and d occupation of $\psi_{\vec{k}}$,

$$n_{lm}(\vec{k}) = \int_0^R C_{lm}(\vec{k},r) 4\pi r^2 dr , \qquad (4)$$

where R is the Wigner-Seitz radius. Finally, n_{lm} is summed over all the k-points which are below the Fermi level ϵ_F to obtain the total s, p, and d occupations, N_{lm}:

$$N_{lm} = \int n_{lm}(\vec{k}) \Theta(\epsilon_F - \epsilon(\vec{k})) d^3k . \qquad (5)$$

The Brillouin-zone integration is performed with the tetrahedron method.[15]

III. RESULTS AND DISCUSSION

The total energies of Al for the three structures are calculated at four different volumes, $1.0V_0$, $0.8V_0$, $0.6V_0$, and $0.4V_0$, where V_0 is the equilibrium volume at zero pressure. The value of V_0 is obtained from our previous calculation[5] and is equal to 109.14 in atomic units. For the hcp structure, only the ideal c/a ratio structure is considered because the energy change associated with the variation in c/a ratio is only a few tenths of a mRy while the structural energy difference between hcp and fcc is ~ 3 mRy. Taking the ideal c/a ratio is convenient and is not crucial to the conclusion of this paper.
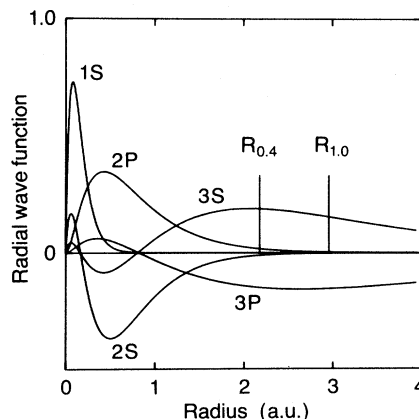

FIG. 1. Al atomic radial functions $r\psi$ and the Wigner-Seitz radius for $0.4V_0(R_{0.4})$ and $1.0V_0(R_{1.0})$.
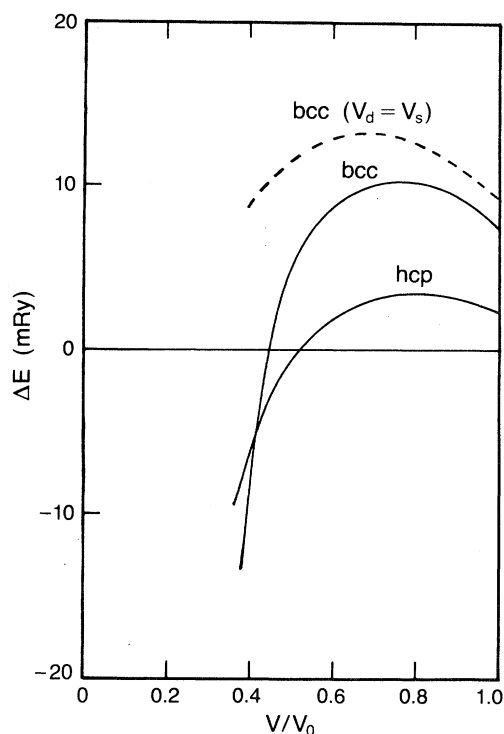
FIG. 2. Energy difference, bcc-fcc (bcc) and hcp-fcc (hcp), as a function of volume (solid curves). The dashed curve is the bcc-fcc [bcc $(V_d = V_s)$] with the d potential V_d set equal to the s potential V_s.

FIG. 3. Enthalpy difference, bcc-fcc (bcc-fcc) and hcp-fcc (hcp-fcc), as a function of pressure.

In pseudopotential or frozen-core calculations, it is important to make sure that the cores do not overlap. The atomic orbitals and the positions of the Wigner-Seitz radius for $0.4V_0$ and $1.0V_0$ are shown in Fig. 1. Even at $0.4V_0$, the outermost core orbitals $(2p)$ are quite well separated.

The energy difference between bcc and fcc and between hcp and fcc are plotted in Fig. 2 as a function of volume. At normal volume $1.0V_0$, the fcc structure is the most stable one in agreement with experiment.[16] In order to determine the most stable structure at finite pressure, the enthalpy, $H = E + PV$, must be considered; the structure with the lowest enthalpy is the most stable. Since the total energy is calculated only at four volumes, the pressure cannot be obtained directly. Murnaghan's equation of state[17] is therefore used to fit our calculated energies, and pressure is obtained by differentiation, $-dE/dV$. The enthalpy differences between bcc and fcc and between hcp and fcc are plotted in Fig. 3 as functions of pressure. It has been reported that Al remains in the fcc structure at least up to a pressure of 200 kbar, which corresponds[18] to $0.85V_0$. Our calculation indicates that the fcc structure persists even up to about 2 Mbar, where the fcc-hcp
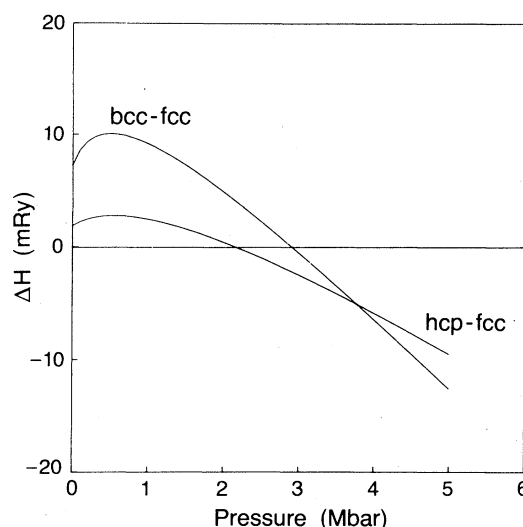
transition occurs. The corresponding atomic volumes at this transition are about $0.5V_0$ for both fcc and hcp. The volume change is less than $0.01V_0$. At about 4 Mbar, the bcc structure begins to have the lowest enthalpy, and a hcp-bcc transition occurs. The corresponding atomic volumes at this transition are about $0.4V_0$ for both hcp and bcc. The volume change is again less than $0.01V_0$. Notice that the volume changes are very small at both transitions. Therefore, the stable phase can be determined by comparing the total energies without the PV term, as in Ref. 9. Our estimates of the transition pressure should only be accurate to within a few tenths of a Mbar because we only fit to within a few calculated values.

Moriarty and McMahan calculated the energy vs volume using two different methods, generalized pseudopotential theory (GPT) and LMTO.[9] Our E vs V curve (Fig. 2) agrees well with their GPT result at normal volume, and with their LMTO result at smaller volume.[9] As pointed out by the authors of Ref. 9, the GPT approach gives better result at normal volume while the LMTO is more appropriate for smaller volume. Moriarty and McMahan did not include the PV term in determining the most stable structure. As pointed out earlier, the PV term is not important because the volume change is small. They obtained a value for the fcc-hcp transition pressure equal to 1.3 Mbar and the transition volume equal to $0.58V_0$ from their LMTO calculation[9] but a much higher pressure (about 3.6 Mbar) and a smaller volume $(0.44V_0)$ from their GPT calculation.[19] Our result falls in between. The apparent large deviation between their transition pressure and ours is caused by the rapid increase in pres-

TABLE I. The s, p, and d (d_Σ and d_γ) occupations in the fcc and bcc structures for $V/V_0 = 1.0$ and $V/V_0 = 0.4$

		s	p	d_Σ	d_γ
$V/V_0 = 1.0$	fcc	1.067	1.514	0.305	0.113
	bcc	1.031	1.524	0.289	0.157
$V/V_0 = 0.4$	fcc	0.827	1.546	0.393	0.235
	bcc	0.789	1.490	0.346	0.375

sure as the volume decreases. If the energy of one structure is systematically shifted up or down by a small constant amount, the transition volume will change by a small amount but the transition pressure can change by a large amount. Since the energies involved are so small, their prediction and ours should be considered in good agreement.

Friedli and Ashcroft predicted no transition up to 3 Mbar.[8] They employed a local pseudopotential[20] which is fitted to give the correct normal density. The effect of electron-ion interaction is treated by perturbation on a free electron gas to second order. Their pressure vs lattice constant curve agrees very well with ours at low pressure, up to about 1 Mbar, but deviates somewhat at higher pressure. We suspect that their calculation does not show a transition because of the use of a local potential. This conclusion is supported by our analysis of the wave function at compressed volume, which will be discussed next.

Moriarty and McMahan found that the energy difference between structures is well correlated with the difference in the sum of eigenvalues.[9] They examined the eigenvalue sum for the various structures and found that for Al the bcc structure has the lowest eigenvalue sum at compressed volume. They also suggested that the stability of the bcc structure for Al at the compressed volume is caused by the lowering of the d states. They found that the lowering of the d states causes a dip in the fcc density of states at two electron occupation. From this they concluded that the fcc structure is unfavorable for atoms with three valence electrons, and that the bcc structure is more favorable.[9] Based on our decomposition of the wave functions, we find that the stability of the bcc phase at compressed volume is a direct consequence of the bcc structure having more bonding d states than the other structures. By examining the s, p, and d occupations at $1.0V_0$ and $0.4V_0$ (Table I) one sees that the effect of compression is to decrease the s character of the wave functions and to increase the d character. In particular, at $0.4V_0$ the wave functions have substantially more d character in the bcc structure than in the fcc structure.
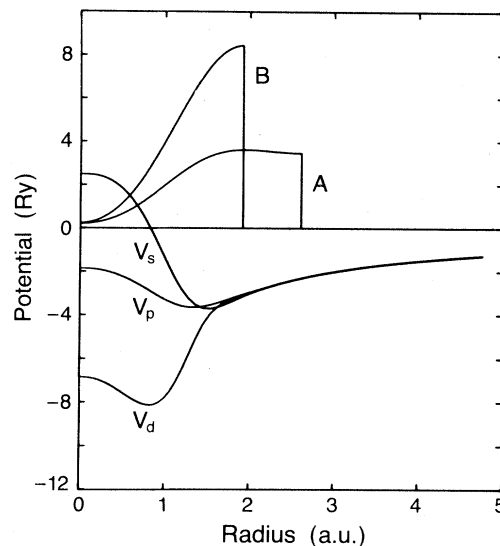
The fact that the structure with the most d char-

FIG. 4. Nonlocal pseudopotentials for Al. V_s is the s potential, etc. Curve A and B show the charge density along the first-nearest-neighbor direction in the bcc structure for $1.0V_0$ and $0.4V_0$, respectively. The charge density is in arbitrary units. The absolute units of the charge density are shown in Fig. 6.

acter is also the most stable structure at compressed volume can be understood in terms of the pseudopotentials, Fig. 4. At $0.4V_0$ the wave functions start to penetrate into the core region where the d potential is more attractive than the s potential. In fact, if the d potential is set equal to the s potential in our calculations, then the total energy of the bcc structure remains above the fcc energy for the entire range of volumes that we have considered (see dashed curve in Fig. 2). The enthalpy of the bcc structure also
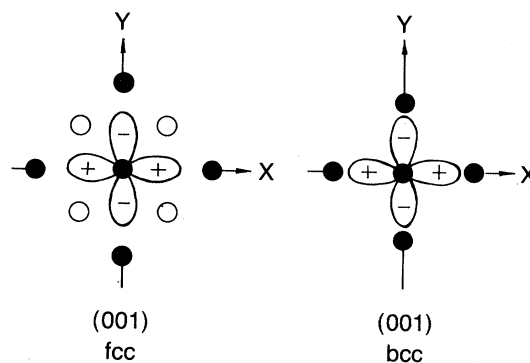

FIG. 5. d_γ interaction in the fcc and bcc structures; the x^2-y^2 orbital is shown. The first-nearest neighbors are denoted by open circles; the central atom and second-nearest neighbors are denoted by filled circles. The plane shown is the (001) plane.
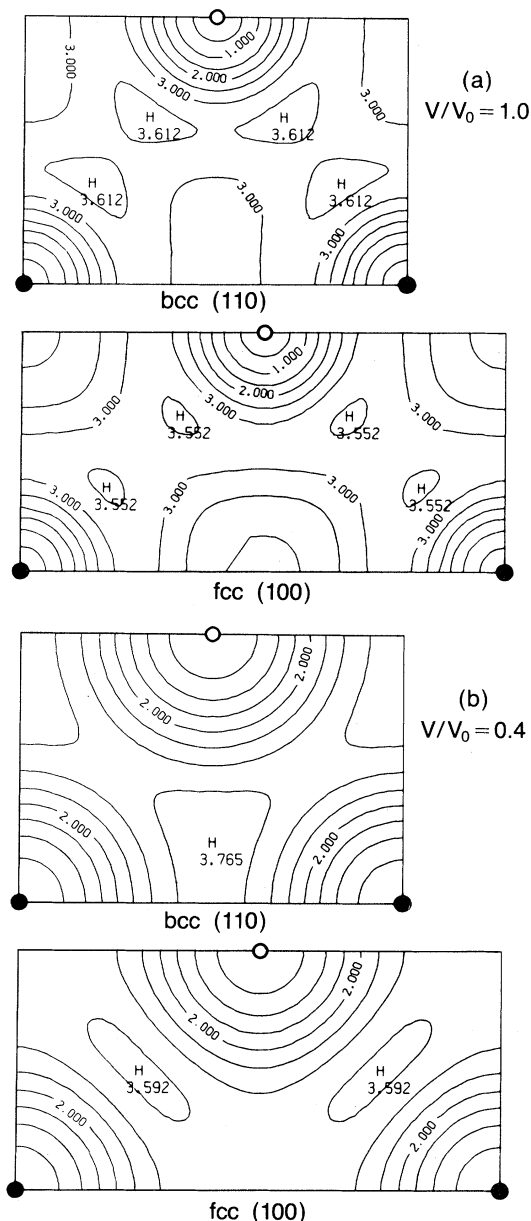
FIG. 6. Charge density in the bcc and fcc structures for (a) $1.0V_0$ and (b) $0.4V_0$. The units are in electrons per unit cell, hence 3.0 is the average density. The contour step size is 0.5 electrons per unit cell. The first-nearest neighbors are denoted by open circles; the central atom and second-nearest neighbors are denoted by filled circles.

remains above that of the fcc structure. Setting the d potential equal to the s potential causes serious error at small volumes but very minor error near normal volumes (see Fig. 2), which indicates that the difference between the d potential and the s potential is very important at small volume but less essential

at normal volume. Therefore, a local potential which can give the correct behavior at normal volume may not be adequate for compressed volume. Moriarty and McMahan examined the importance of the d states by performing their LMTO calculation with and without d orbitals in the basis set.[9] They also concluded that there would be no transition if the d orbitals were not included.

The fact that the bcc structure possesses more d character can be understood geometrically. In a cubic system, the atomic d states are split into two groups, $d_\Sigma(xy,yz,zx)$ and $d_\gamma(x^2-y^2,3z^2-r^2)$. At $0.4V_0$ the bcc structure has more d_γ character than the fcc structure (Table I). The d_γ orbitals point toward the second-nearest neighbors in both the bcc and fcc structures (see Fig. 5). However, for a given volume, the second-nearest-neighbor distance in the bcc structure is about 20% shorter than that of the fcc structure. Since the interaction between neighbors is a very strong function of distance, the second-nearest-neighbor interaction becomes very important at compressed volume. The evidence of the strong second-nearest-neighbor interaction at compressed volume is revealed by the charge distribution. In Figs. 6(a) and 6(b), we plot the charge density for bcc and fcc at $1.0V_0$ and $0.4V_0$, respectively. At $1.0V_0$ the maximum charge density occurs along the direction to the first-nearest neighbor for both fcc and bcc structures, while at $0.4V_0$, the maximum charge density is along the first-nearest-neighbor direction for the fcc structure but is shifted toward the second-nearest-neighbor direction for the bcc direction.

IV. SUMMARY

We have determined the most stable structure of Al at normal volume correctly with an *ab initio* calculation. In addition, we predict a phase transition from the fcc to hcp structure at about 2 Mbar and from hcp to bcc at about 4 Mbar. At compressed volumes, the structure with the most d character is the most stable because of the attractiveness of the d potential in the core region, and the bcc structure possesses the most d character at compressed volume because of the strong second-nearest-neighbor interaction.

ACKNOWLEDGMENTS

[1]M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 6121 (1981).

[2]M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **45**, 1004 (1980).

[3]M. T. Yin and M. L. Cohen, Solid State Commun. **38**, 625 (1981).

[4]J. Ihm and J. D. Joannopoulos, Phys. Rev. B **24**, 4191 (1981).

[5]P. K. Lam and M. L. Cohen, Phys. Rev. B **24**, 4224 (1981).

[6]M. Y. Chou, P. K. Lam, and M. L. Cohen, Solid State Commun. **42**, 861 (1982).

[7]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[8]C. Friedli and N. W. Ashcroft, Phys. Rev. B **12**, 5552 (1975).

[9]J. A. Moriarty and A. K. McMahan, Phys. Rev. Lett. **48**, 809 (1982).

[10]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[11]E. Wigner, Phys. Rev. **46**, 1002 (1934).

[12]P. K. Lam and M. L. Cohen, Phys. Rev. B **25**, 6139 (1982).

[13]See M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975), and references therein.

[14]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[15]G. Lehmann and M. Taut, Phys. Status Solidi b **54**, 469 (1972).

[16]R. W. G. Wyckoff, *Crystal Structures,* 2nd ed. (Interscience, New York, 1963), Vol. I, p. 10.

[17]F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944); Orson L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).

[18]N. N. Roy and E. G. Steward, Nature (London) **224**, 905 (1969).

[19]A. K. McMahan and J. A. Moriarty, Phys. Rev. B **27**, 3235 (1983), and private communication with A. K. McMahan.

[20]M. L. Cohen and V. Heine, in *Solid State Physic,* edited by H. Ehrenreich, F. Seitz, and D. Turnball (Academic, New York, 1970), Vol. 24, p. 37.