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Cohesive properties of bcc and fcc rubidium from *ab initio* pseudopotentials

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Total-energy calculations have been performed for Rb at zero temperature using a self-consistent *ab initio* pseudopotential approach within a local-density-functional scheme. The energy difference between fcc and bcc Rb, and the energy barrier between these structures, are found to be extremely small near the equilibrium volume. Agreement of the calculated cohesive properties of bcc Rb with experimental values is good in view of the softness of the material. A transition from bcc to fcc has been calculated to occur at a pressure of about 52 kbar for $T=0$ K, which compares favorably with the observed value of 70 kbar for this transition at room temperature.

I. INTRODUCTION

Since the early days of solid-state physics, the alkali metals have been popular materials for theoretical studies. Their reputation, however, has changed remarkably from being prototypes of simple metals (with the landmark calculation of the cohesive properties of Na by Wigner and Seitz[1] in 1933, and many calculations involving nearly-free-electron-gas models or empirical pseudopotentials) to that of a group of elements with an unforeseen manifold of structural transitions. At ambient conditions all alkali metals are found in the bcc structure, but cooling to low temperatures or the application of pressure reveals numerous phase transitions[2] with some structures still undetermined. The most recent development in this field is a suggestion for the structure of Li at low temperature and zero pressure to be a relatively complicated one with possible implications for superconductivity.[3] The stable phase at low temperature and zero pressure for Na is hcp, whereas K and Cs appear to stay bcc.[2] The case of Rb is unclear in this regime since the de Haas—van Alphen effect measurements by Templeton[4] indicated a shock-induced (martensitic?) transformation at 4.2 K and below. At room temperature and lower pressures all alkali metals except Na show a transition from bcc to fcc.[5] Additional transitions to more open and more complicated structures have been observed for the heavy alkali metals K, Rb, and Cs.[5,6]

Understanding the structural transitions of the alkali metals is therefore a challenge for the theorist. Band-structure calculations[7] have shown that with decreasing volume the originally unoccupied d bands come closer to the occupied s band. Some transitions are expected to take place at certain critical d-band occupation numbers (correlated with the fraction of the atomic volume occupied by the ion core), which should be similar for corresponding transitions in the heavy alkali metals.[5,6] At high pressures the s-d transfer of the valence electrons is complete and core-core interactions appear to play an important role in the structural stability.[8] Quantitative predictions of the transitions, however, are still a difficult matter.

The goal of this paper is a modest one in view of the complexity of the situation: We confine ourselves to the study of the cohesive properties of the heavy alkali metal Rb and consider the bcc and fcc structures only. Rb is an extreme case in some sense, because it has the smallest bcc shear moduli among all alkali metals (Cs has the smallest bulk modulus). It is also of particular interest because of the low-temperature transition mentioned above.

In contrast to the majority of previous calculations, which are based on empirical pseudopotentials and will not be reviewed in detail here, we use a self-consistent *ab initio* pseudopotential approach within a local-density-functional scheme. This method has proven successful, not only for a wide variety of semiconductors and insulators,[9] but also for a number of metals, such as Na,[10] Be,[11] and Al.[12] The results for Rb reported below indicate that this method is capable of reproducing the cohesive properties with the expected accuracy and also the bcc-fcc transition under pressure. The energy differences between the two structures at zero pressure and zero temperature are, however, extremely small, and the question of the stable structure in this regime remains open.

II. METHOD

The pseudopotentials for Rb have been generated using the scheme of Hamann, Schlüter, and Chiang[13] with cutoff radii of 2.4, 2.8, and 1.5 a.u. for the s, p, and d component of the potentials, respectively. In the calculation for the crystal, we choose the s component for the local potential and we refer to the differences between the p (d) component and the local potential as the nonlocal p (d) part of the potential. Because of the strong overlap of the $5s$ valence electron with the outer-core electrons, the partial core correction introduced (e.g., for Na) by Louie, Froyen, and Cohen[10] has been applied in order to improve the transferability of the pseudopotential. The parameter r_0 involved was chosen to be the radius where core and valence charges are equal. To elucidate the role of the $4d$ levels, two ionic pseudopotentials were generated: potential I, which has no nonlocal d part was generated from the configuration $5s^{0.9}5p^{0.1}$, and potential II (with nonlocal p and d parts) was generated from the configuration $5s^{0.8}5p^{0.1}4d^{0.1}$. The transferability of the potentials was tested with several other configurations, including Rb^+ (excitation energy 0.3144 Ry), and we found that the excitation energies of all-electron and pseudopotential calculations agree within 0.7 mRy or better.

Density-functional theory is used in the local approximation with the formula of Hedin and Lundqvist[14] for exchange and correlation in the paramagnetic case and the modified formula of von Barth and Hedin in the spin-polarized case.[15–19] This choice facilitates the comparison with the calculations of Moruzzi, Janak, and Williams,[15] who used the same functionals. Thus, the spin-polarization energy of a Rb atom is -16.9 mRy.[19]

Plane waves in reciprocal-lattice vectors are used for the expansion of the one-electron wave function in the crystal, and the total energy is calculated using a momentum-space scheme.[20] The main numerical effort of this method consists of the diagonalization of the Hamiltonian matrix for a number of **k** points in the irreducible Brillouin zone (IBZ). The **k** points are generated in a uniform grid by subdividing each edge of the unit cell in reciprocal space n times, and each **k** point is associated with a weighting factor according to its phase-space volume. The number of plane waves which goes into the calculation of matrix elements is controlled by the parameter $G_{\max}$, the maximum length of allowed reciprocal-lattice vectors $\mathbf{G}_j$, and the size of the Hamiltonian matrix is determined by the kinetic-energy cutoff $E_{\max} \geq (\mathbf{G}_j + \mathbf{k}_i)^2$. (Rydberg units are used unless otherwise stated.) $G_{\max}$ can be varied between the lower limit $(E_{\max})^{1/2}$ (from the kinetic-energy cutoff) and $2(E_{\max})^{1/2}$ which is needed to allow for all off-diagonal elements of the Hamiltonian matrix to be determined properly. Often, $G_{\max} \approx 1.5(E_{\max})^{1/2}$ is sufficient for total-energy calculations with considerable savings in computing space and time.

III. RESULTS

The structural properties of Rb, such as the cohesive energy E_{coh}, equilibrium volume V_0, bulk modulus B_0, and its pressure derivative B_0', can be obtained via the *ab initio* pseudopotential approach with relatively little numerical effort. Column I of Table I is calculated with pseudopotential I (which contains no nonlocal d part), 27 **k** points in the IBZ, and cutoff parameters $E_{\max} = 4.6$ Ry and $G_{\max} = 3.2$ a.u., which yield matrix sizes around 100×100 and a **G** space of ≈ 300 plane waves near the minimum of the total-energy curve $E_{\mathrm{tot}}(V)$. With this cutoff, the total energy was found to be converged to about 1 mRy. Nine values of E_{tot} for volumes between 470 and 710 a.u. have been used for a fit to Murnaghan's equation of state.[21] Column II a shows the results of a similar calculation with the same cutoff parameters, but with potential II instead, which has an additional nonlocal d part. Obviously, the added admixture of d components to the electronic energy is able to increase the cohesive energy by about 7%. At the same time, the equilibrium volume decreases by 7%, while B_0 and B_0' are less affected. The rest of Table I will be discussed later.

Breaking down the individual contributions to the cohesive energy, as done before by Lam and Cohen[12] for Al, we come to the same conclusion, namely that the gain in Coulomb energy by forming the crystal is not sufficient to overcome the kinetic-energy increase, and that the exchange-correlation energy is the dominant cause of cohesion. However, the ratios between the individual contributions are different for Rb and Al. In percent of the cohesive energy, we have, for Rb (Al), Coulomb energy $+24\%$ ($+125\%$), kinetic energy -41% (-180%), exchange-correlation energy $+143\%$ ($+160\%$), and spin-polarization energy -26% (-5%), resulting in cohesive energies of 63 mRy (268 mRy). Whereas, in Al, the first three terms are of comparable magnitude, the exchange-correlation term is more than 3 times larger than the other contributions in Rb. This difference is attributable to the fact that Rb has only one valence electron per cell, leading to more dominant exchange-correlation effects.

Structural energy differences and shear moduli for Rb are much more difficult to assess with total-energy calculations than the properties discussed above. Considerable

TABLE I. Cohesive properties of Rb. Deviations from experimental values are shown in parentheses.

	I	II a	II b		Moruzzi *et al.*	
	bcc	bcc	bcc	fcc	(Ref. 15)	Expt.
E_{coh} (Ry)	0.0577 (-8%)	0.0623 (-0%)	0.0633 ($+1\%$)	0.0633	0.047 (-25%)	0.0626[a]
V_0 (a.u.)	580.9 (-1%)	539.5 (-8%)	531.8 (-10%)	535.5	540.7 (-8%)	589.4[b]
B_0 (Mbar)	0.034 ($+16\%$)	0.035 ($+20\%$)	0.035 ($+20\%$)	0.035	0.03 ($<18\%$)	0.0292[b]
B_0'	4.1 (0%)	3.9 (-5%)	3.9 (-5%)	3.7		4.1[b]

[a] From Kittel (Ref. 25); $T = 5$ K.

[b] From Anderson and Swenson (Ref. 26); $T = 4$ K.

numerical effort is required because the energy differences involved are very small (less than 1 mRy). In order to improve the convergence of the total-energy calculation, we use $E_{\max}=7.3$ Ry and $G_{\max}=5.4$ a.u.$\approx 2(E_{\max})^{1/2}$ for all quantities reported below, which reduces the uncertainty in the total energy to about 0.2 mRy at a volume $V=590$ a.u. At this volume the number of **G** vectors is about 1500 and the size of the Hamiltonian matrix is around 200×200. For a given $G_{\max}$ and $E_{\max}$, the number of **G** vectors and the Hamiltonian-matrix sizes decrease with decreasing volume, leading to relatively higher uncertainties at smaller volumes because of the reduced number of plane waves available for the expansion of the wave function. The main problem of convergence, however, is connected with the **k**-point sampling of the Fermi surface. Although the Fermi surface of Rb is known to be very close to spherical, it turned out to be a very delicate matter to pin down the extremely small energy differences between different structures in terms of the number of **k** points used in the calculation. In principle, one could simply increase the number of **k** points until the desired accuracy is reached for each structure, but this is too expensive. Alternatively, one can achieve high accuracy by treating different structures as similarly as possible. We therefore consider both fcc and bcc structures within a more general tetragonal unit cell such that $c/a=1$ corresponds to fcc and $c/a=1/\sqrt{2}$ to bcc.[22] Then we treat fcc structures as usual and make sure that the set of **k** points used for bcc structures corresponds exactly to the fcc set,[23] related by the tetragonal distortion from $c/a=1$ to $c/a=1/\sqrt{2}$.

In this way we improve the convergence of energy differences, with respect to the number of **k** points, to about 0.05 mRy around the equilibrium volume, with $n=10$ or 12 (see Sec. II). The convergence of the total energies of each structure alone happens to be of the same quality. At small volume, e.g., $V=260$ a.u., the uncertainty is roughly twice as large, but this causes no serious problems because the energy differences to be calculated are also larger.

Using potential II, the above-mentioned cutoff parameters, and $n=12$, which generates 273 (182) **k** points in the IBZ of the bcc (fcc) lattice,[24] we obtain the results of column IIb in Table I. From the bcc columns IIa and IIb it is obvious that the much larger numerical effort for IIb is not a necessity for the cohesive properties listed in this table, keeping in mind that another choice for the exchange-correlation functional could easily change the results more significantly than improved convergence (cf. the case of Na in Ref. 10). From this point of view the results for bcc and fcc Rb in column IIb are identical. Nevertheless, the energy difference between the two phases as a function of volume should be significant because of our effort to calculate both phases in an exactly analogous scheme.

In Fig. 1, $\Delta E(V)=E_{\mathrm{tot}}(\mathrm{fcc})-E_{\mathrm{tot}}(\mathrm{bcc})$ at $T=0$ K is shown for two sets of **k** points ($n=10$ and 12) with a solid line drawn as an averaging guide to the eye. This curve suggests two phase transitions between bcc and fcc Rb, one very clearly at small volume and another at the margin of convergence of the calculation around the equilibrium volume. The calculated transition pressure at small volume (determined in various ways from both data sets) is (52 ± 1) kbar; the bcc transition volume equals (301 ± 1) a.u., with a volume decrease of 1% during the transition from bcc to fcc. The other transition would occur at a negative pressure of about -1 to -2 kbar starting at a bcc volume ≈ 533 a.u., with a volume increase of less than 1%.

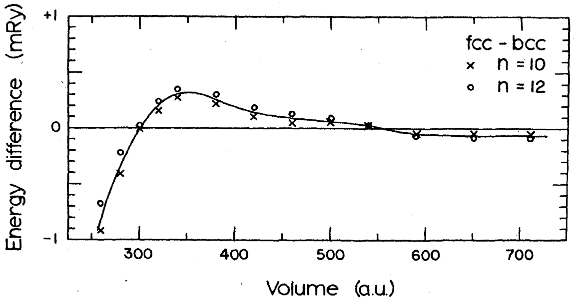

FIG. 1. Total-energy differences between fcc and bcc Rb vs volume. As a guide to the eye, an averaging line is drawn between the two sets of results, with different numbers of **k** points generated from $n=10$ and 12, respectively.

Comparing the individual contributions to the total-energy differences at $V=260$ and 340 a.u., the cause of the transition from bcc to fcc structure can be traced to a stronger gain in the nonlocal potential energy (associated with the nonlocal parts of the pseudopotential) in the fcc structure with decreasing volume, i.e., occupying p and d states in the fcc structure becomes energetically more favorable (-16 mRy). This gain in energy is accompanied by an increase in kinetic energy ($+13$ mRy) and a smaller increase in the (local) potential energy of the charge density ($+2$ mRy). The other energy terms are far less important, especially the exchange-correlation term, which contributes only -0.07 mRy to the total difference of ≈ -1 mRy. Therefore, the transition volume $V_t\approx 300$ a.u. should be fairly independent of the choice for the exchange-correlation functional. The total-energy curves for both phases do not exhibit any special features in the transition region; they simply cross each other with increasing d character of the valence electrons. For the possible transition at small negative pressure, however, the differences in exchange-correlation energy are no longer negligible and the transition pressure and volumes—if not the mere existence of this transition—could well depend on the approximation used for the functional for exchange and correlation.

Given the very small energy difference (≈ 0.02 mRy) between the two phases at their equilibrium volumes, one would like to know what kind of energy barrier might exist between these two structures. Of course, there are many ways to deform bcc and fcc structures into each other, and, in general, it is difficult to find the path with the lowest barrier. A reasonable path is certainly a deformation within the tetragonal unit cell mentioned above, with a continuous variation of c/a from 1 (fcc) to $1/\sqrt{2}$ (bcc) with the volume kept constant. Near equilibrium, the barrier appears to be very small and near the limit of the accuracy of the calculation. Our results for the energy along this deformation are strongly fluctuating even with $n = 12$ (468 **k** points in the IBZ of the tetragonal lattice), indicating that still more **k** points would be necessary for an accurate determination of the barrier. The numerical data suggest that the barrier height might be of the order of 0.05 mRy for $V = 539.5$ a.u. At the small volume of $V = 260$ a.u., however, the behavior of E_{tot} versus c/a could be determined unambiguously: We found a minimum for the fcc structure and a maximum for the bcc structure without a barrier between them. Hence, bcc Rb is unstable rather than metastable in this regime. Just below the transition ($V = 340$ a.u.) there is a very small barrier ($\approx 80\ \mu$Ry) separating fcc from bcc (see Fig. 2).

In principle, the shear modulus $\mu' = 1/2(c_{11} - c_{12})$ can also be obtained from the total energy at c/a ratios close to the cubic structures. However, again because of the unusually small value for this material, a converged result has not been achieved. The other shear modulus $\mu = c_{44}$ has been successfully determined to be (0.023 ± 0.004) Mbar, with the quoted uncertainties derived from the calculations with $n = 10$ and 12. In the calculation an orthorhombic unit cell (rather than a triclinic one with lower symmetry) has been used, in which the usual bcc cube is tilted by 45°; $n = 10$ (12) generates 500 (864) **k** points in the IBZ.

IV. DISCUSSION

Some of our results can be compared with the all-electron calculation of Moruzzi, Janak, and Williams,[15] which is also *ab initio*, employing the same exchange-correlation functional (see Table I). Their equilibrium volume V_0 and bulk modulus B_0 basically agree with our calculations that included the nonlocal d part in the potential (column II). The agreement for the cohesive energy E_{coh} is still good in an absolute sense (within 15 mRy$\approx$0.2 eV), but not on a relative scale (25%). This discrepancy may be related either to the muffin-tin approximation,[15] or to the fact that the all-electron calculation has to deal with much larger energies than the pseudopotential calculation, e.g., the total energy of the Rb atom is almost 6000 Ry, whereas that of the pseudoatom is 10 000 times smaller. Other quantities, such as B_0', shear moduli, and structural energy differences, have not yet been calculated by other *ab initio* methods.

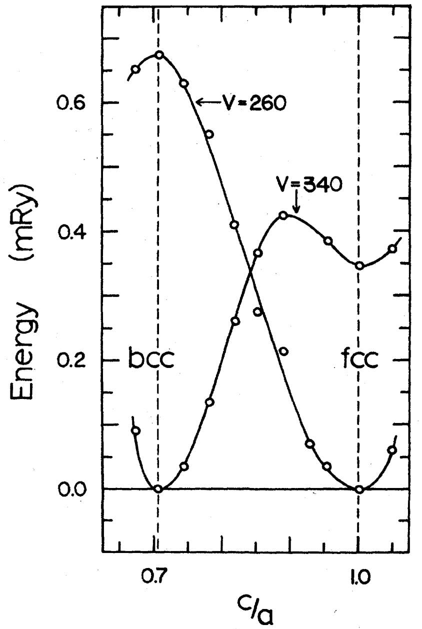

FIG. 2. Energy vs c/a distortion of the tetragonal unit cell below ($V = 340$ a.u.) and above ($V = 260$ a.u.) the bcc-fcc transition calculated with 468 **k** points in the IBZ ($n = 12$). The zero of energy is set at the minimum of each curve. The solid lines are guides to the eye; the dashed lines indicate the c/a values for bcc and fcc structures.

The agreement of our results with experiment is on the same level as the corresponding Na calculation by Louie, Froyen, and Cohen,[10] with the same Hedin-Lundqvist exchange-correlation formula. As in the case of Na,[10] another functional for correlation (e.g., Wigner's[27]) would probably improve the agreement with experiment for Rb too. A correction due to the zero-point motion derived from a Debye model by Froyen and Cohen[28] with a Debye temperature of 56 K (Ref. 29) would slightly shift (in the bcc column II b) E_{coh} by $E_{\text{zero}} = 0.4$ mRy, V_0 by 3.3 a.u., and B_0 by 0.8 kbar closer to the experimental values. Our result for the shear modulus $\mu = 0.023$ Mbar compares well with the experimental value 0.0222 Mbar.[30] The other shear modulus, $\mu' = 0.0027$ Mbar,[30] is almost 10 times less than μ, and therefore would require increased numerical effort to calculate. We expect no principal difficulty in this respect because the shear moduli of Rb have been calculated with local empirical pseudopotentials (see, e.g., Refs. 31 and 32). The results which depend on the screening functions used range from 0.0193 to 0.0213 Mbar for μ and from 0.0012 to 0.0038 Mbar for μ'.

The calculation of the energy difference between bcc and fcc Rb near equilibrium yields very small values much less than 1 mRy (Fig. 1). This is in general agreement with several calculations for the heavy alkali metals using empirical pseudopotentials,[33-38] although some of them favor the hcp (Refs. 33 and 35) rather than the bcc structure (Refs. 36—38). (Compared to K and Cs, Rb tends to give the smallest fcc—bcc energy difference.) Upadhyaya, Wang, and Moore[36] claim that van der Waals and perhaps Born-Mayer interactions between the cores should be taken into account. Including van der Waals interactions changes their lowest-energy structure from hcp (Ref. 35) to bcc (Ref. 36). van der Waals interactions between the cores are beyond both the local-density approximation for exchange and correlation and the frozen-core approximation which is implied by the pseudopotential. Therefore they are not included in the present calculation. Rather than discussing this question in detail, we remind ourselves that the problem of structural stability not only involves energy differences between different structures, but also requires positive total-energy derivatives with respect to arbitrary distortions. In addition, for a structure to be in thermodynamical equilibrium at zero temperature, its (absolute) minimum of the total energy in configurational space should be separated from other local minima by barriers higher than the zero-point energy.

Considering a zero-point energy of about 400 μRy and a barrier of only ≈ 50 μRy (Ref. 39) between structures which perhaps differ by ≈ 20 μRy, the observed structure is most likely determined by external factors such as stress, or by grain-boundary energies and the history of the sample, or even by impurities, unless the difference in zero-point energy is unusually high or one of the structures considered is unstable. (The effects of entropy and temperature on the free-energy difference are negligible below 5 K, probably less than 1 μRy.) The experimental situation for zero-pressure and zero-temperature Rb is still unclear, but the observation of a shock-induced (martensitic?) transition by Templeton[4] at 4.2 K and below seems to indicate that bcc is not necessarily the most stable structure.

The transition from bcc to fcc structure at 70 kbar and room temperature is experimentally well established.[40,5] The transition volume V_t is 0.478 times the equilibrium volume at room temperature, i.e., 299 a.u., with a relative volume change ΔV_t of $(1.5\pm0.8)\%$. The first attempt to predict this transition quantitatively was made by Eremenko and Zarochentsev[34] in 1979 using a local two-parameter pseudopotential of the Animalu-Heine type fitted to equilibrium volume and shear modulus μ, and including short-range core-core repulsion in Born-Mayer form. Their $T=0$ K results ($p_t=37$ kbar, $V_t=365$ a.u., and $\Delta V_t \approx 0.2\%$) depend strongly on the parameters for the Born-Mayer repulsion.[34,40] However, the main deficiency of their method is the lack of a nonlocal d part in the pseudopotential, which has proved essential to this transition in our analysis in Sec. III. It is interesting to note that Eremenko and Zarochentsev[34] report a behavior similar to Fig. 1 for their difference in Gibbs free energy, except that they do not consider negative pressures. According to Takemura and Syassen,[40] the bcc-fcc phase boundary of Rb is fairly independent of temperature, and they suggested that a more rigorous *ab initio* calculation has to be done to achieve a better agreement with experiment. Our results for $T=0$ K ($p_t=52$ kbar, $V_t=301$ a.u., and $\Delta V_T=1\%$) are much closer to the experimental values. Hence, it appears that repulsive core-core interactions do not play a dominant role for this transition. Nevertheless, a low-temperature measurement of the transition is desirable for a more detailed comparison with the present calculation.

In summary, we conclude that the *ab initio* pseudopotential approach within the local-density approximation is able to reproduce cohesive properties of Rb and the transition from bcc to fcc under pressure with reasonable accuracy. The energy differences between different structures at zero pressure and zero temperature appear to be extremely small, and further investigations, both experimental and theoretical, are required.

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This can save up to a factor of 2 in computing time.

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