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ENERGY BANDS OF THE BCC METALS RUBIDIUM AND CESIUM

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Energy bands of BCC rubidium and cesium are calculated for the first time using the full non-local but energy-independent Shaw's optimized model potential. The energy dependence of the potential is then included as first order perturbation. The effects of changing the model potential parameters and of reversing the sign of the depletion charge d are reported. The Fermi energy E_F is calculated in all cases. Our results are compared with those obtained by other authors. The band gap at N is very small for both metals, except when all model potential parameters are increased considerably (50% to 100%).

1. Introduction

In the last 25 years there are only few papers dealing with the band structure of Rb[1–4] and Cs[1–3,5] using such methods as: quantum defect QD[1], APW[2], KKRZ[3], KKR[4] and OPW[5]. The present work is the first attempt to calculate energy bands of Rb and Cs using optimized model potential[6]. We do not expect complete success of the method because both metals are too heavy for model potentials. However, due to the uncertainty in the determination of the model potential parameter A_2 of Rb and Cs, we wish to investigate what happens to the energy bands if A_2 is changed by $\pm 10\%$, or if the sign of $\mathrm{d}A_2/\mathrm{d}E$ is reversed. We study also the influence of using an effective charge $Z = 1 + d$ in the band structure computation, instead of the formal theory value of $Z = 1 - d$ where d is the depletion hole charge, since the first value leads to a correct prediction of the observed BCC structure of Rb and Cs[7]. More drastic increase of A_2 (by 100%) and of all model potential parameters A_0, A_1 and A_2 (by 50% and 100%) are also considered to investigate the effect of using much stronger potentials on the band structure of Rb and Cs.

2. *Band structure and model potential*

The model wave function is expanded in plane waves (atomic units are used):

$$\varphi_k = \frac{1}{\sqrt{V}} \sum_g C_k(g)\, e^{i(\mathbf{k}+\mathbf{g})\cdot\mathbf{r}} \tag{1}$$

where V is the volume of the crystal, $\mathbf{k}$ is a wave vector and $\mathbf{g}$ are reciprocal lattice vectors. Substituting into the model wave equation

$$(T + w)\, \varphi_k = E_k\, \varphi_k \tag{2}$$

where T is the kinetic energy and w the model potential, leads to the secular determinant for energy bands:

$$\det \left\| \left[\frac{1}{2} |\mathbf{k}+\mathbf{g}|^2 - E_k\right] \delta_{\mathbf{g}\mathbf{g}'} + S(\mathbf{g}-\mathbf{g}') < \mathbf{k}+\mathbf{g}' |w| \mathbf{k}+\mathbf{g} > \right\| = 0. \tag{3}$$

$S(g)$ is the structure factor and $\langle \mathbf{k}+\mathbf{g}' | w | \mathbf{k}+\mathbf{g} \rangle = w_E(k)$ is the screened form factor, which should be non-local and energy-dependent[6]. We have taken the non-locality into consideration, however, to save a lot of computation time, the energy dependence was ignored by putting

$$w_E(k) = w_{E_F}(k) \tag{4}$$

where E_F is the Fermi energy. Later the energy dependence Δw is added as first order perturbation. Expressions of $w_{E_F}(k)$ and Δw are given in Ref. 8.

3. *Results and discussion*

Rb and Cs both have a BCC structure with lattice constants (au): 10.552 (Rb) and 11.424 (Cs) corresponding to $k_F = 0.3694$ (Rb) and $k_F = 0.3412$ (Cs). The parameters of the ionic model potential are those of Appapillai and Heine[9], where: $A_2 = 0.384$, 0.366, $dA_2/dE = 0.526$, 0.845 and $Z = 1.1525$, 1.1953 for Rb and Cs, respectively. The linear screening was carried out using the exchange and correlation function of Singwi et al.[10]. A great deal of care should be paid to the convergence of the energy values to obtain results of acceptable accuracy from a secular determinant of reasonable order n. The convergence of the energy values (in au) of Rb and Cs at all symmetry points is given in Table 1. It should be mentioned that we use unsymmetrical sets of plane waves which are closer to the origin of the irreducible part of the Brillouin zone to achieve optimal convergence at all points. This will break the symmetry of the wave vector $\mathbf{k}$ at points of high symmetry. Consequently, a small error will appear in the values of energy of degenerate states.

TABLE 1.

n	26	33	42	52
Rb				
Γ_1	0.06978	0.06976	0.06973	0.06972
$\Gamma_{25'}$	0.38377	0.38343	0.38316	0.38247
N_1	0.15398	0.15386	0.15384	0.15380
$N_{1'}$	0.15983	0.15982	0.15981	0.15980
N_2	0.30729	0.30683	0.30665	0.30644
N_1	0.32050	0.31997	0.31985	0.31976
$N_{4'}$	0.33273	0.33260	0.33251	0.33247
$N_{3'}$	0.33664	0.33659	0.33659	0.33656
P_4	0.19818	0.19805	0.19805	0.19804
P_1	0.20158	0.20141	0.20138	0.20133
H_{12}	0.22982	0.22960	0.22909	0.22909
H_1	0.24649	0.24642	0.24629	0.24624
H_{15}	0.24712	0.24709	0.24703	0.24703
Cs				
Γ_1	0.06678	0.06675	0.06671	0.06665
$\Gamma_{25'}$	0.32975	0.32933	0.32902	0.32820
N_1	0.13700	0.13683	0.13678	0.13673
$N_{1'}$	0.14418	0.14418	0.14416	0.14416
N_2	0.26590	0.26536	0.26511	0.26487
N_1	0.27603	0.27534	0.27516	0.27502
$N_{4'}$	0.29062	0.29046	0.29036	0.29032
$N_{3'}$	0.29431	0.29425	0.29423	0.29421
P_4	0.17591	0.17575	0.17574	0.17573
P_1	0.17646	0.17616	0.17607	0.17600
H_{12}	0.20115	0.20090	0.20030	0.20030
H_1	0.21312	0.21296	0.21267	0.21258
H_{15}	0.21829	0.21826	0.21821	0.21820

Convergence of energy values (in au; 1au = 27.2 eV) at high symmetry points Γ, N, P and H. The results were obtained using the number of plane waves n indicated in each case.

We have chosen $n = 42$, since the convergence is very satisfactory for both Rb and Cs (less than 14×10^{-5} au = 0.28 mRy for all states in Table 1, except Γ'_{25} (1.64 mRy) and N_2 (0.48 mRy) compared with $n = 52$; 1 Ry = 13.6 eV).

Solving the 42×42 secular determinant of Eq. (3) we obtained the energy eigenvalues using the potential parameters of Ref. 9. This will be referred to as case a. The energy bands (case a) of Rb and Cs passing through the major directions in the Brillouin zone are shown in Figs. 1 and 2 relative to the bottom of the band Γ_1 (in Rydberg). The numbers given on the curves indicate the symmetry, e. g., above point N the number 1′ indicates symmetry type $N_{1'}$, and so on. The Fermi energy of Rb and Cs is calculated using the formula given by Inoue et al.[11]:

$$E_F = (3E_{100} + 4E_{111} + 6E_{110})/13 \tag{5}$$

and is plotted in Figs. 1 and 2. Here E_{100}, E_{111} and E_{110} are the energy at $|\mathbf{k}| = k_F$ in the principal directions (100), (111) and (110), respectively.

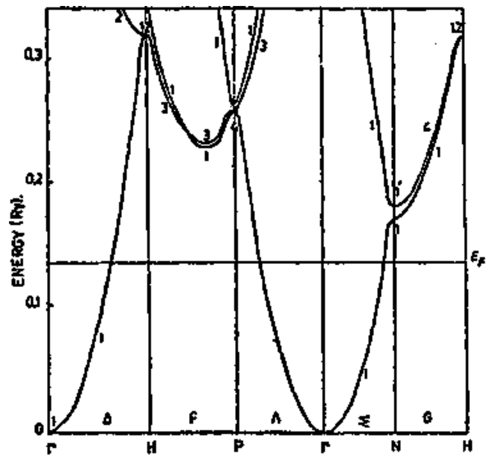

Fig. 1. Energy bands of Rb (1 Ry = 13.6 eV).

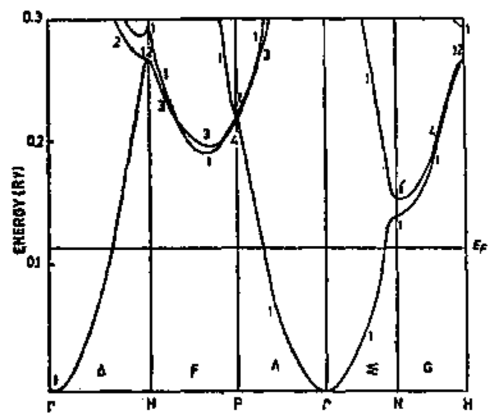

Fig. 2. Energy bands of Cs (1 Ry = 13.6 eV).

In addition to case a, the energy bands and E_F of Rb and Cs are calculated seven times as follows:

b — with A_2 increased by 10%, i. e. $A_2 = 0.4224$ (Rb) and 0.4026 (Cs)
c — with A_2 decreased by 10%, i. e. $A_2 = 0.3456$ (Rb) and 0.3294 (Cs)
d — using dA_2/dE with a reversed sign, i. e. $dA_2/dE = -0.526$ (Rb) and -0.845 — (Cs)
e — using the effective charge $Z = 1 + d$, i. e. $Z = 0.8475$ (Rb) and 0.8047 (Cs), which leads to a correct prediction of the observed BCC structure for both Rb and Cs[7])
f — with A_2 doubled, i. e. $A_2 = 0.768$ (Rb) and 0.732 (Cs)
g — with the model potential parameters A_0, A_1 and A_2 all increased by 50% and
h — with the model potential parameters A_0, A_1 and A_2 all doubled.

It is obvious that the charge d of the depletion hole should be recalculated for each of the above cases, except e. This was done and the corresponding values obtained for $Z = 1 - d$ for Rb and Cs are: b 1.1526, 1.1955, c 1.1522, 1.1949, d 1.1529, 1.1959, f 1.1527, 1.1956, g 1.0505, 1.0638 and h 1.0223, 1.0280 compared to 1.1525 and 1.1953 of the original calculation a for Rb and Cs, respectively.

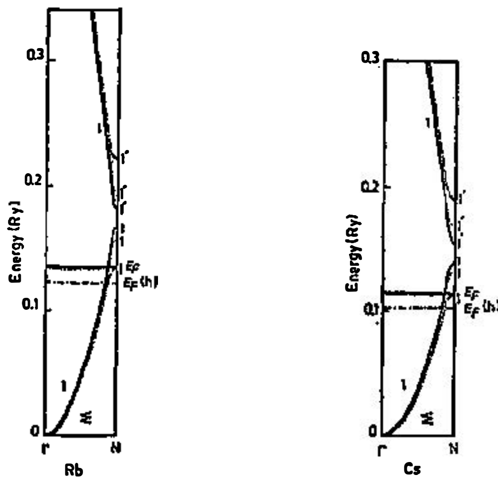

Fig. 3. Energy bands of Rb and Cs in direction $\Gamma - N$.

(——— case a ······· case g ·-·-·- case h)

The calculations b, c, d and f are carried out to investigate the influence of the uncertainty in the model potential parameters A_2 and dA_2/dE[6,9] on the band structure. Cases g and h are included to examine the energy eigenvalues obtained using much deeper model potential wells. The change of the energy bands of Rb and Cs in the direction $\Gamma - N$ is shown in Fig. 3 for the cases g and h compared to case a. It is obvious that the gap at N increases considerably if the potential is raised. The present results calculated with and without the energy dependence of the potential and those of other authors are compared in Table 2. $\Gamma - N$ is the width of the lowest band, i. e. $E(N_1) - E(\Gamma_1)$, where N_1 is the lowest N state. $N_1 - N_{1'}$ indicates the energy gap $E(N_1) - E(N_{1'})$ at point N. Finally, $E_F - \Gamma_1$ gives the width of the occupied band. Ea, Eb etc. indicate the present results obtained when the energy dependence of the potential is included in cases a, b, etc. The result obtained with 10% decrease in A_2, case c, or using $Z = 1 + d$, case e, are not given in Table 2 because they bring only a very small change of about ± 1 mRy, which is practically neglegible.

Inspection of Table 2 shows that:

1. In cases a, b, d, f: Increase of A_2 with 10% to 100%, or change of the sign of dA_2/dE does not affect the quantities $\Gamma - N$, $N_1 - N_{1'}$ and $E_F - \Gamma_1$ calculated using the original values of A_2, dA_2/dE in both Rb and Cs. The present value of $\Gamma - N$ is very close to Ref. 4 for Rb and to Ref. 5 for Cs. The occupied band width is 10% smaller than[3] for Rb and[2] for Cs. Unfortunately,

TABLE 2.

Ref.	Method	$\Gamma - N$	$N_1 - N_{1'}$	$E_F - \Gamma_1$
Rb				
Present	Ea, Eb, Ed, Ef	0.198	−0.014	0.159
4)	KKR	0.170	−0.054	0.158
1)	QD	0.163	−0.063	0.150
3)	KKRZ	0.158	−0.043	0.145
2)	APW	0.157	−0.044	0.143
Present	Eg	0.167	−0.042	0.141
Present	a, b, d, f	0.168	−0.012	0.135
Present	g	0.157	−0.040	0.133
Present	Eh	0.138	−0.088	0.125
Present	h	0.135	−0.086	0.122
Cs				
Present	Ea, Eb, Ed, Ef	0.175	−0.019	0.143
5)	OPW	0.142	−0.039	0.126—0.129
Present	Eg	0.143	−0.039	0.122
2)	APW	0.127	−0.069	0.125
1)	QD	0.123	−0.085	0.122
3)	KKRZ	0.112	−0.067	0.122
Present	a, b, d, f	0.140	−0.015	0.114
Present	g	0.133	−0.036	0.113
Present	Eh	0.117	−0.082	0.105
Present	h	0.113	−0.079	0.102

Bandwidth $\Gamma - N$, energy gap at point N and occupied bandwidth (all in Ry; 1Ry = = 13.6 eV) compared with other theoretical results of Rb and Cs. Ea, Eb, etc. indicate the present results when the energy dependence of the potential is taken into account in cases a, b, etc.

the gap at N is very small for both Rb and Cs, being only 20% to 25% of other theoretical values. However, N_1 is lower than $N_{1'}$ like all other results[1–5]. This is different from the case of potassium where the present method[12] yielded $E(N_1) > E(N_{1'})$, contrary to other available results of potassium. The derivations in $N_1 - N_{1'}$ of other authors are very large for Cs (more than 100%) and are considerable for Rb (46%). Also the $\Gamma - N$ results for Rb lie closer together than those of Cs.

2. In calculation g, 50% increase of A_0, A_1 and A_2 reduces $\Gamma - N$ slightly, leaves $E_F - \Gamma_1$ unchanged but causes a considerable increase of $\Delta = |N_1 - N_{1'}|$ against case a, so that it comes very close to other theoretical results:[2,3] for Rb and[5] for Cs. $\Gamma - N$ is identical with that of Refs. 2 and 3 for Rb and very close to that of Ref. 2 for Cs. On the other hand, $E_F - \Gamma_1$ of both Rb and Cs, is 10% smaller than that of Ref. 3 for Rb and Ref. 2 for Cs.

3. Further increase of the potential parameters A_0, A_1 and A_2 by 100%, case h, leads to even more reduction in both $\Gamma - N$ and $E_F - \Gamma_1$ and to a rather drastic increase of Δ (more than doubled compared to case g). This yields unacceptable results for Rb. However, in case of Cs, $\Gamma - N$ is almost identical with that of Ref. 3 and Δ is very close to Ref. 1, although $E_F - \Gamma_1$ is 20% smaller than in Refs. 1 and 3.

4. If the energy dependence of the potential is taken into consideration, an increase of the band widths $E_F - \Gamma_1$ and $\Gamma - N$ will result in as explained in Refs. 12 and 13. For Rb, this increase reaches 18% (case Ea), 6% (case Eg) and 2.5% (case Eh) over the cases a, g and h, respectively. The corresponding values for Cs are 25%, 8% and 3%. This makes $\Gamma - N$ in calculation Ea too large for both Rb and Cs, while $E_F - \Gamma_1$ of Rb is identical with Ref. 4 and that of Cs is again too high. Among present results Eg is the closest one to those of other authors, namely, Refs. 2 and 3 for Rb and to Ref. 5 for Cs.

We conclude that the present OMP calculation gives only a qualitative picture, not a quantitative one, of the band structure of Rb and Cs when compared to more sophisticated methods like APW or KKR. Changes of -10% to $+100\%$ in A_2 and of the sign of dA_2/dE, or the use of $Z = 1 + d$, do not practically influence such quantities as lowest bandwidth or energy gap at N or occupied bandwidth. However, the energy gap at N remains too small, unless the potential is increased by at least 50% (Rb) and 50% to 100% (Cs). Of course, if the potential is raised the resulting energy bands become more flat or narrow. This explains the reduction of band widths $\Gamma - N$ and $E_F - \Gamma_1$ in cases g and h. If the energy dependence of the potential is taken into consideration our Eg results of Table 2 are close to those of APW[2] and KKR[3] methods for Rb and are almost identical with those of OPW[5] method for Cs. In general, the agreement of energy values at points of high symmetry in our calculation and those published for Rb and Cs is not satisfactory.

References

1) F. S. Ham, Phys. Rev. **128** (1962) 82;
2) J. F. Kenney, MIT Quart. Progr. Report **53** (1964) 38;
3) M. J. Lawrence, J. Phys. F **1** (1971) 836;
4) V. L. Moruzzi, J. F. Janak and A. R. Williams, *Calculated Electronic Properties of Metals*, Pergamon, New York, (1978) p. 108;
5) S. D. Mahanti and T. P. Das, Phys. Rev. **183** (1969) 674;
6) R. W. Shaw. Phys. Rev. **174** (1968) 769;
7) A. M. Radwan, to be published in Cryst. Res. and Technol. **1** (1988);
8) A. M. Radwan, Proc. Math. Phys. Soc. Egypt **54** (1982) 35;
9) M. Appapillai and V. Heine, Technical Report No. 5, Solid State Theory Group, Cavendish Laboratory, Cambridge (1972);
10) K. S. Singwi, A. Sjoelander, M. P. Tosi and R. H. Land, Phys. Rev. **B1** (1970) 1044;
11) S. T. Inoue, S. Asano and J. Yamashita, J. Phys. Soc. Japan **30** (1971) 1546;
12) A. M. Radwan, Egypt. J. Phys. **14** (1983) 63;
13) A. M. Radwan and M. Taut, Phys. Stat. Sol. (b) **76** (1976) 605.

ENERGETSKE VRPCE U VCK METALIMA RUBIDIJU I CEZIJU

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Energetske vrpce volumno centriranih kubičnih kristala rubidija i cezija po prvi put su izračunate koristeći potpuno nelokalni ali energetski nezavisan Shaw-ov optimizirani modelni potencijal. Energetska ovisnost potencijala uključena je zatim u prvom redu računa smetnje. Razmatran je utjecaj promjene parametara modelnog potencijala. Fermijeva energija izračunata je u svim slučajevima. Dobiveni rezultati uspoređeni su s rezultatima drugih autora. Energetski procijep u točci N je vrlo mali za oba metala, osim ako se parametri modelnog potencijala znatno ne povećaju (50 do 100%).