

Electronic Phase Transition of Cesium Metal under High Pressure

著者	Kamimura Takashi, Yamada Motohiko, Kamigaki Kazuo
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	30
page range	169-184
year	1981
URL	http://hdl.handle.net/10097/28215

Electronic Phase Transition of Cesium Metal
under High Pressure*

Takashi Kamimura**, Motohiko Yamada and Kazuo Kamigaki
The Research Institute for Iron, Steel and Other Metals

(Received August 13, 1982)

Synopsis

The isostructural phase transition of cesium metal, CsII \leftrightarrow CsIII, under pressure is discussed in terms of the crystalline energy as a function of volume. Using the augmented plane wave (APW) method and the quantum defect method, the energy bands are calculated at symmetry points in the Brillouin zone for the range of relative volume V/V_0 (V_0 : the volume at normal pressure) from 1.30 to 0.24. As the volume decreases, there appears a pronounced tendency of d-states to fall lower relative to s-states, which rise significantly at $V/V_0 \lesssim 0.6$. Besides overall rise of the band energy with decreasing volume, a small humped portion is found at $0.4 \lesssim V/V_0 \lesssim 0.5$, this being attributed to the shift of electrons into the vicinity of X. The transition beyond this portion is accompanied by a significant volume change. Thus the CsII \leftrightarrow CsIII transition is interpreted as an electronic one. A calculation using the Green's function method is also carried out and the results are compared with those by the APW method.

I. Introduction

Bridgman measured the compressibility and the electrical resistivity of cesium metal under high pressure and found phase transitions CsI \leftrightarrow CsII and CsII \leftrightarrow CsIII' ⁽²⁾. He reported for the latter transition a volume change larger than 10 percent. Since structures of both CsII and CsIII' were assigned to be close packed, this large volume change

* The 1747th report of the Research Institute for Iron, Steel and Other Metals. This work constitutes a part of the doctoral thesis submitted by T. Kamimura to the Department of Physics, Faculty of Science, Tohoku University, 1971. A short report on this work is found in ref. (1).

** College of General Education, Tohoku University.

attracted much attention. X-ray analysis by Hall et.al.⁽³⁾ (Fig. 1) indicated that this transition consisted of two successive ones, CsII (fcc) \leftrightarrow CsIII(fcc) at 42.2 kbar and CsIII \leftrightarrow CsIV(mixed crystal of fcc and hcp) at 42.7 kbar. The experimental results are summarized in Table 1.

In order to explain the isostructural phase transition CsII \leftrightarrow CsIII, Fermi first proposed that the 6s-electron was forced into the lowered 5d-level with decreasing volume. Sternheimer⁽⁴⁾ investigated this problem by calculating the energy bands using the Wigner-Seitz method. However, Ham⁽⁵⁾ has pointed out that his result for the d-band has a significant error by adopting inaccurate boundary conditions. Alekseev and Arkipov⁽⁶⁾ also discussed this transition by comparing relative positions of s- and d-levels using the Thomas-Fermi method. For expla-

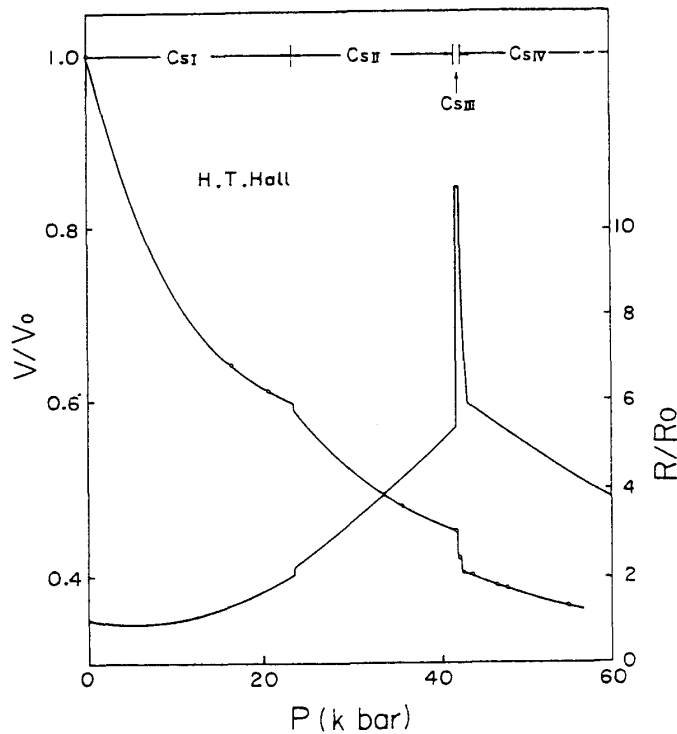


Fig. 1 Volume and electrical resistivity of cesium as a function of pressure. V_0 and R_0 are the volume and the electrical resistivity at normal pressure (from ref. (3)).

Table 1 Experimental results obtained by Bridgman⁽²⁾ and Hall et.al.⁽³⁾.
Pc: critical pressure. Vc: critical volume (normalized to the volume at normal pressure).

	P.W. Bridgman		H.T. Hall et.al.	
	Pc	Vc	Pc	Vc
CsI \leftrightarrow CsII	23 kbar	0.63 — 0.62	23 kbar	
CsII \leftrightarrow CsIII			42.2 kbar	0.46 — 0.42
CsIII \leftrightarrow CsIV	45 kbar	0.50 — 0.44	42.7 kbar	0.42 — 0.40

nation of this transition, it is necessary to obtain an accurate knowledge about the energy bands as a function of volume. In this paper, we calculate the energy bands of the fcc structure and discuss the origin of the isostructural transition on the basis of the crystalline energy which includes, besides the band energy, the electrostatic energy of electrons and the core interaction energy.

II. Band structure as a function of volume

The energy eigenvalues of an electron in a periodic crystal potential have been calculated by using the augmented plane wave (APW) method⁽⁷⁾. The potential used is constant outside of APW spheres and spherically symmetric within each sphere (the muffin-tin approximation⁽⁸⁾):

$$U_c(\vec{r}) = \begin{cases} U_c(r) & r \leq r_0 \\ U_0 & r > r_0 \end{cases} \quad (1)$$

For r_0 , half of the atomic distance is used. For U_0 , we use an averaged value of the Coulomb potential $-e^2/r$ over the shell between spheres with radii r_0 and r_s , where r_s is the radius of the sphere whose volume is equal to that of the atomic polyhedron. Eigenvalues $E(\vec{k})$ for a state of given \vec{k} can be evaluated by solving the secular equation:

$$|M_{ij}| = 0 \quad (2)$$

Elements of the determinant are defined by,

$$M_{ij} = \Omega_0 (\vec{k}_j^2 - E) \delta_{ij} - 4\pi r_0^2 G^{ij} \quad (3)$$

with

$$G^{ij} = (\vec{k}_i \vec{k}_j - E) j_1(\vec{k}_{ij} r_0) / \vec{k}_{ij} - \sum_{\ell=0}^{\infty} (2\ell + 1) \times P_{\ell}(\widehat{\vec{k}_i \vec{k}_j}) j_{\ell}(\vec{k}_i r_0) j_{\ell}(\vec{k}_j r_0) R'_{\ell}(r, E) / R_{\ell}(r, E) \Big|_{r=r_0} \quad (4)$$

where Ω_0 is the volume of the atomic polyhedron, $P_{\ell}(\widehat{\vec{k}_i \vec{k}_j})$ is the Lagrange polynomial, $j_{\ell}(\vec{k}_i r_0)$ is the spherical Bessel function, $R'_{\ell}(r, E) / R_{\ell}(r, E) \Big|_{r=r_0}$ is the logarithmic derivative of the radial function at $r=r_0$, and $\widehat{\vec{k}_i \vec{k}_j}$ is an angle between \vec{k}_i and \vec{k}_j ($\vec{k}_i = \vec{k} + \vec{g}_i$, $\vec{k}_{ij} = \vec{k}_j - \vec{k}_i = \vec{g}_j - \vec{g}_i$, and \vec{g}_i is a reciprocal lattice vector for fcc). The representative

wave vectors chosen in the present calculation are defined by twenty symmetry points on cubic mesh of interval $\pi/4a$ (a : the lattice constant) in the one forty-eighth independent segment of the Brillouin zone (Fig. 2). The symmetry points of the zone are labeled according to the notation introduced by Boucheart, Smoluckowski and Wigner⁽⁹⁾.

The radial function and its derivative at $r=r_0$ are evaluated by the quantum defect method^(5,10) without constructing the potential explicitly. All elements of the determinant depend on E , either explicitly or implicitly through the radial function. Since equation (2) can not be solved analytically, for evaluating eigenvalues "interpolation method with subsidiary points"⁽¹¹⁾ has been employed. The interpolation in locating zero of the determinant was made successively until the accuracy of the obtained eigenvalue attained to better than ± 0.0002 Ry. The calculation was carried out for nine different volumes of the fcc lattice. In the following, in place of the volume a parameter $z=$

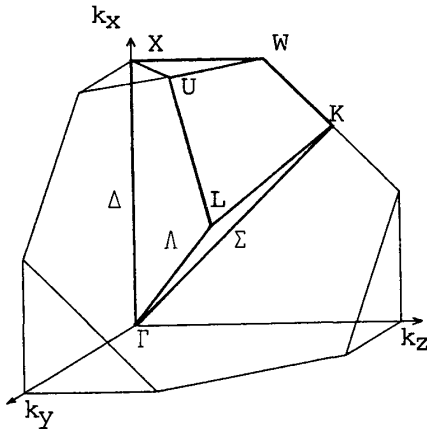


Fig. 2 One forty-eighth segment of the Brillouin zone of a fcc lattice (in heavy lines). Symmetry points are labeled according to the notation introduced by Boucheart et.al.

Table 2 Relation between the parameter z and the volume per atom V , the half of the atomic distance r_0 , etc. at which the calculation has been made. V_0 , r_0 are respectively the values of V and r_0 at normal pressure.

z	$V(\text{a.u.})$	V/V_0	$r_0(\text{a.u.})$	r_0/r_{00}
6.6	913.206	1.302	5.445	1.092
6.4	759.250	1.083	5.120	1.027
6.2	627.560	0.895	4.805	0.964
6.0	515.481	0.735	4.500	0.903
5.8	426.604	0.608	4.205	0.843
5.6	340.748	0.486	3.920	0.786
5.4	273.948	0.391	3.645	0.731
5.2	218.437	0.312	3.380	0.678
5.0	172.634	0.246	3.125	0.627

$(8r_0)^{1/2}$ is conveniently used, the correspondence between them being given in Table 2. In Table 3 are listed representative examples illustrating the convergence of eigenvalues. It is found that for the state in the valence band the trial wave function including all terms within $\ell=8$ suffices to give the eigenvalue better than ± 0.0002 Ry in its accuracy. The dimension of the determinant depends on the number of reciprocal lattice points involved $[\vec{k}_0^2 \geq \vec{k}_i^2 = (\vec{k} + \vec{g}_i)^2]$. The eigenvalues evaluated for $\vec{k}_0^2 = (2\pi/a)^2 \times 10.1$ and $(2\pi/a)^2 \times 13.1$ together with the dimensions of the determinant are shown in Table 4. For comparison, a calculation

Table 3 Examples of the convergence of energy eigenvalues at some symmetry points (see Fig. 2). ℓ_{\max} : maximum value of ℓ in eq. (4).

ℓ_{\max}	2	3	4	5	6	7	8
z=6.4	Γ_1	-.4195	-.4195	-.4194	-.4194	-.4194	-.4194
	Δ_1	-.3606	-.3604	-.3600	-.3599	-.3599	-.3599
	X_1	-.2813	-.2913	-.2801	-.2800	-.2793	-.2793
	Γ_{25}'	-.1557	-.1558	-.1278	-.1279	-.1242	-.1242
	Δ_2'	-.2216	-.1922	-.1909	-.1872	-.1854	-.1853
	X_3	-.2344	-.2344	-.2265	-.2263	-.2246	-.2243
	z=5.4	Γ_1		-.3442	-.3434	-.3434	-.3429
Δ_1			-.2301	-.2209	-.2162	-.2160	-.2156
X_1			-.3355	-.3290	-.3290	-.3264	-.3261
Γ_{25}'			-.1228	-.0554	-.0554	-.0464	-.0463
Δ_2'			-.2039	-.2002	-.1916	-.1872	-.1871
X_3			-.2947	-.2798	-.2798	-.2755	-.2748

Table 4 Examples of the convergence of energy eigenvalues dependent on the number of the reciprocal lattice points adopted (z=6.4). Dimensions of the determinant (in eq. (2)) are given in parentheses $[\vec{k}_0^2 \geq \vec{k}_i^2 = (\vec{k} + \vec{g}_i)^2]$.

k_0^2	Γ_1	$(400)_1$	X_1	L_1	$(642)_1$
$(2\pi/a)^2 \times 10.1$	-.4194 (27)	-.3599 (43)	-.2793 (40)	-.3017 (34)	-.2661 (34)
$(2\pi/a)^2 \times 13.1$	-.4194 (59)	-.3599 (52)	-.2794 (48)	-.3018 (52)	-.2662 (52)
k_0^2	Γ_{25}'	$(400)_{2'}$	X_3	$L_{2'}$	$(642)_2$
$(2\pi/a)^2 \times 10.1$	-.1244 (27)	-.1853 (43)	-.2243 (40)	-.2233 (34)	-.2319 (34)
$(2\pi/a)^2 \times 13.1$	-.1248 (59)	-.1854 (52)	-.2243 (48)	-.2233 (52)	-.2320 (52)

using the Green's function (GF) method⁽¹²⁾ has also been carried out [see Appendix].

The results of the APW calculation for $\ell_{\max}=8$, $k_0^2=(2\pi/a)^2 \times 10.1$ and for nine values of volume are given in Table 5 and in Fig. 3. At $z=6.4$, which corresponds nearly to the volume at normal pressure, the surfaces of constant energy remain appreciably spherical except in the vicinities of the zone boundary and distortion of the Fermi surface from spherical shape is small. This trend is quite similar to that found for bcc cesium by Ham⁽¹³⁾. With decreasing volume, however, the nonspherical distortion increases significantly and occupied pockets at the zone

Table 5 Energy eigenvalues (Ry) at symmetry points [$\vec{k}=(a/4\pi)(k_x, k_y, k_z)$]

1 st

\vec{k} z	6.6	6.4	6.2	6.0	5.8	5.6	5.4	5.2	5.0
0,0,0	-.4078	-.4194	-.4284	-.4322	-.4254	-.3998	-.3429	-.2535	-.1532
2,0,0	-.3923	-.4012	-.4063	-.4048	-.3889	-.3489	-.2738	-.1719	-.0655
4,0,0	-.3572	-.3599	-.3573	-.3454	-.3181	-.2724	-.2156	-.1627	-.1192
6,0,0	-.3041	-.3037	-.3016	-.2985	-.2949	-.2920	-.2887	-.2837	-.2743
8,0,0	-.2727	-.2793	-.2873	-.2965	-.3066	-.3170	-.3261	-.3304	-.3268
2,2,0	-.3820	-.3888	-.3913	-.3854	-.3635	-.3159	-.2386	-.1453	-.0601
4,2,0	-.3453	-.3461	-.3410	-.3257	-.2941	-.2418	-.1732	-.1164	-.0740
6,2,0	-.2923	-.2894	-.2838	-.2755	-.2651	-.2529	-.2366	-.2109	-.1671
8,2,0	-.2588	-.2636	-.2688	-.2742	-.2783	-.2797	-.2737	-.2526	-.2054
4,4,0	-.3114	-.3076	-.2974	-.2768	-.2415	-.1945	-.1601	-.1385	-.1170
6,4,0	-.2620	-.2554	-.2444	-.2278	-.2127	-.2017	-.1852	-.1566	-.1083
8,4,0	-.2352	-.2385	-.2407	-.2405	-.2361	-.2237	-.1970	-.1477	-.0696
6,6,0	-.2461	-.2492	-.2526	-.2562	-.2598	-.2633	-.2662	-.2670	-.2633
2,2,2	-.3699	-.3747	-.3749	-.3664	-.3437	-.3030	-.2509	-.2005	-.1543
4,2,2	-.3349	-.3348	-.3296	-.3163	-.2929	-.2613	-.2253	-.1847	-.1378
6,2,2	-.2834	-.2796	-.2731	-.2642	-.2547	-.2464	-.2392	-.2323	-.2237
4,4,2	-.3063	-.3045	-.2996	-.2907	-.2769	-.2571	-.2279	-.1864	-.1358
6,4,2	-.2699	-.2661	-.2601	-.2505	-.2351	-.2111	-.1755	-.1296	-.0695
4,4,4	-.3001	-.3017	-.3025	-.3020	-.2990	-.2919	-.2778	-.2535	-.2164
5,5,0	-.2671	-.2603	-.2485	-.2306	-.2209	-.2181	-.2146	-.2087	-.1086
3,3,3	-.3290	-.3294	-.3260	-.3180	-.3051	-.2881	-.2666	-.2380	-.1997

2 nd

\vec{k} z	6.6	6.4	6.2	6.0	5.8	5.6	5.4	5.2	5.0
0,0,0	-.1351	-.1242	-.1139	-.1022	-.0867	-.0698	-.0463	-.0252	.0025
2,0,0	-.1514	-.1467	-.1405	-.1328	-.1230	-.1114	-.0975	-.0818	-.0637
4,0,0	-.1844	-.1853	-.1859	-.1864	-.1866	-.1868	-.1868	-.1868	-.1868

6,0,0	-.2091	-.2141	-.2197	-.2261	-.2336	-.2423	-.2521	-.2626	-.2743
8,0,0	-.2179	-.2243	-.2317	-.2403	-.2502	-.2618	-.2748	-.2885	-.3005
2,2,0	-.1653	-.1608	-.1546	-.1461	-.1343	-.1180	-.0952	-.0621	-.0128
4,2,0	-.1893	-.1879	-.1850	-.1805	-.1731	-.1619	-.1442	-.1035	-.0438
6,2,0	-.2085	-.2100	-.2109	-.2108	-.2090	-.2043	-.1942	-.1747	-.1393
8,2,0	-.2156	-.2183	-.2206	-.2223	-.2225	-.2205	-.2134	-.1968	-.1634
4,4,0	-.1986	-.1937	-.1855	-.1721	-.1599	-.1375	-.0786	-.0124	.0718
6,4,0	-.2181	-.2146	-.2128	-.2078	-.1880	-.1477	-.0918	-.0241	.0511
8,4,0	-.2095	-.2015	-.1905	-.1735	-.1484	-.1131	-.0659	-.0040	.0744
6,6,0	-.2303	-.2275	-.2233	-.2157	-.2024	-.1796	-.1431	-.0892	-.0161
2,2,2	-.1807	-.1756	-.1677	-.1556	-.1361	-.1031	-.0465	.0394	.1400
4,2,2	-.2040	-.1994	-.1912	-.1774	-.1531	-.1163	-.0837	-.0541	-.0147
6,2,2	-.2241	-.2216	-.2166	-.2078	-.1930	-.1692	-.1323	-.0779	-.0032
4,4,2	-.2249	-.2159	-.1999	-.1738	-.1419	-.1191	-.0977	-.0706	-.0303
6,4,2	-.2392	-.2319	-.2202	-.2051	-.1898	-.1746	-.1562	-.1272	-.0867
4,4,4	-.2387	-.2233	-.1965	-.1532	-.0892	-.0021			
5,5,0	-.2182	-.2182	-.2177	-.2145	-.1902	-.1416	-.0739	.0119	
3,3,3	-.2151	-.2064	-.1908	-.1634	-.1173	-.0463			

3 rd

\vec{k} z	6.6	6.4	6.2	6.0	5.8	5.6	5.4	5.2	5.0
0,0,0									
2,0,0									
4,0,0									
6,0,0									
8,0,0	-.1951	-.1708	-.1335	-.0788					
2,2,0	-.1332	-.1233	-.1108	-.0947	-.0742	-.0479			
4,2,0									
6,2,0									
8,2,0	-.1998	-.1812	-.1529	-.1121	-.0559				
4,4,0	-.1859	-.1823	-.1775	-.1720	-.1522	-.1215	-.0762		
6,4,0									
8,4,0	-.1699	-.1430	-.1130	-.0792	-.0407				
6,6,0	-.2020	-.1869	-.1638	-.1298	-.0821	-.0180			
2,2,2	-.1271	-.1178	-.1057	-.0917	-.0728	-.0500	-.0229	.0084	.0435
4,2,2									
6,2,2									
4,4,2									
6,4,2	-.1776	-.1729	-.1638	-.1456	-.1112	-.0568	.0168		
4,4,4	-.1418	-.1354	-.1274	-.1173	-.1045	-.0891	-.0710	-.0505	-.0295
5,5,0	-.2037	-.1946	-.1803	-.1585	-.1265	-.0807	-.0183	.0624	
3.3.3	-.1368	-.1294	-.1201	-.1085	-.0940	-.0762	-.0556	-.0319	

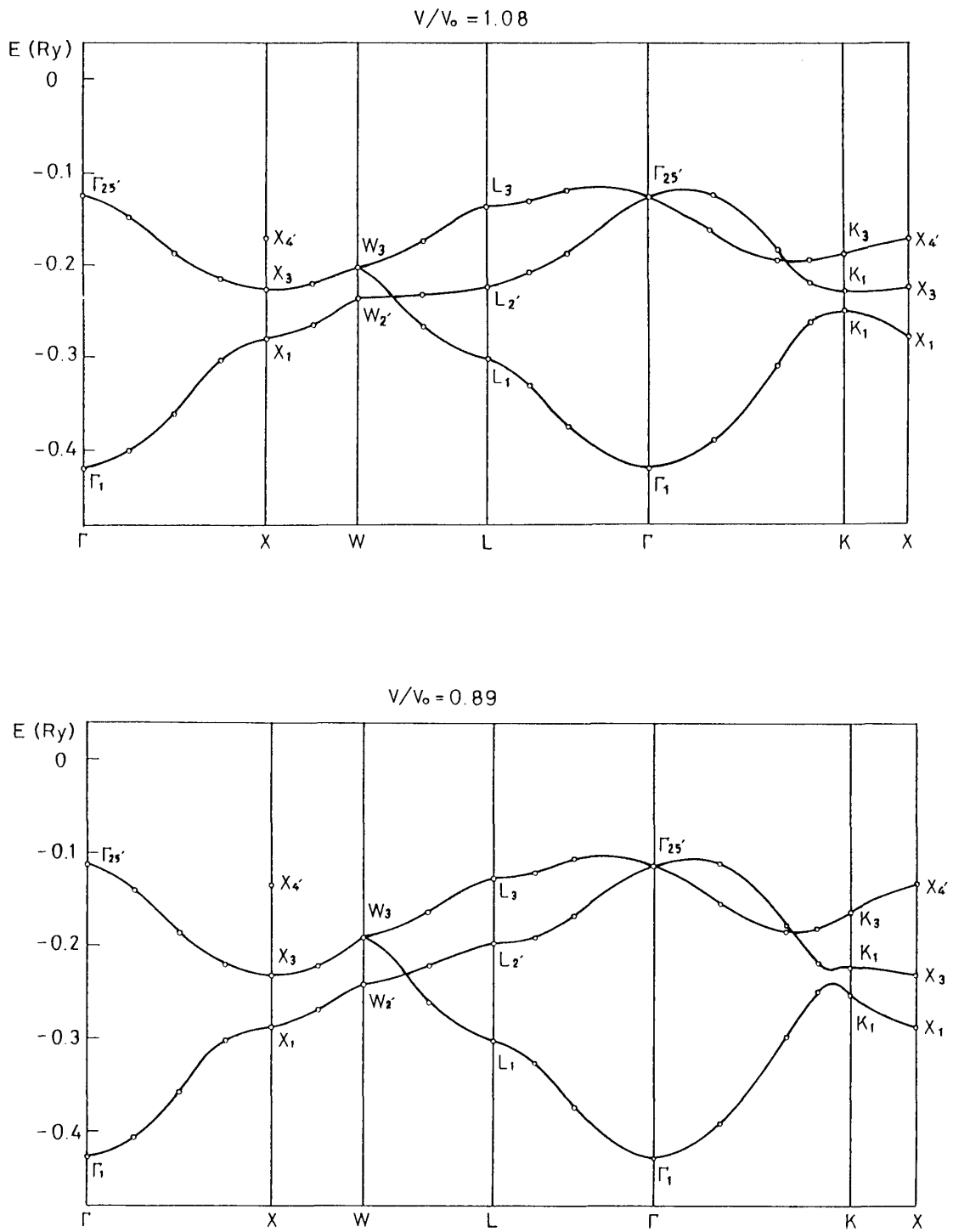


Fig. 3 Calculated energy bands for various volumes.

Fig. 3 (continued)

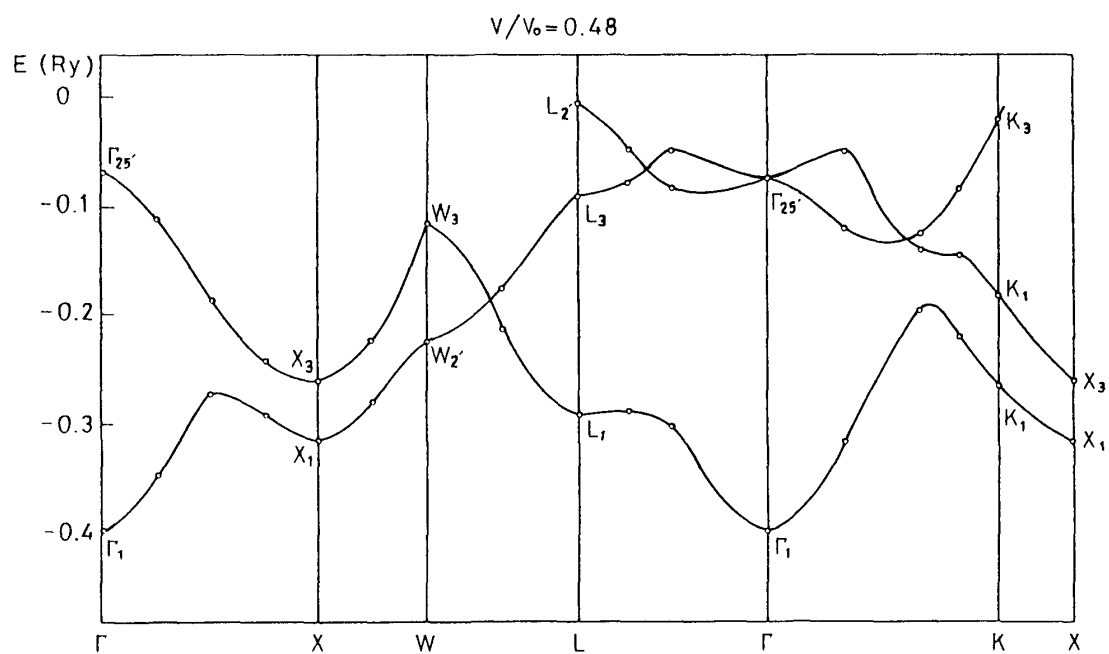
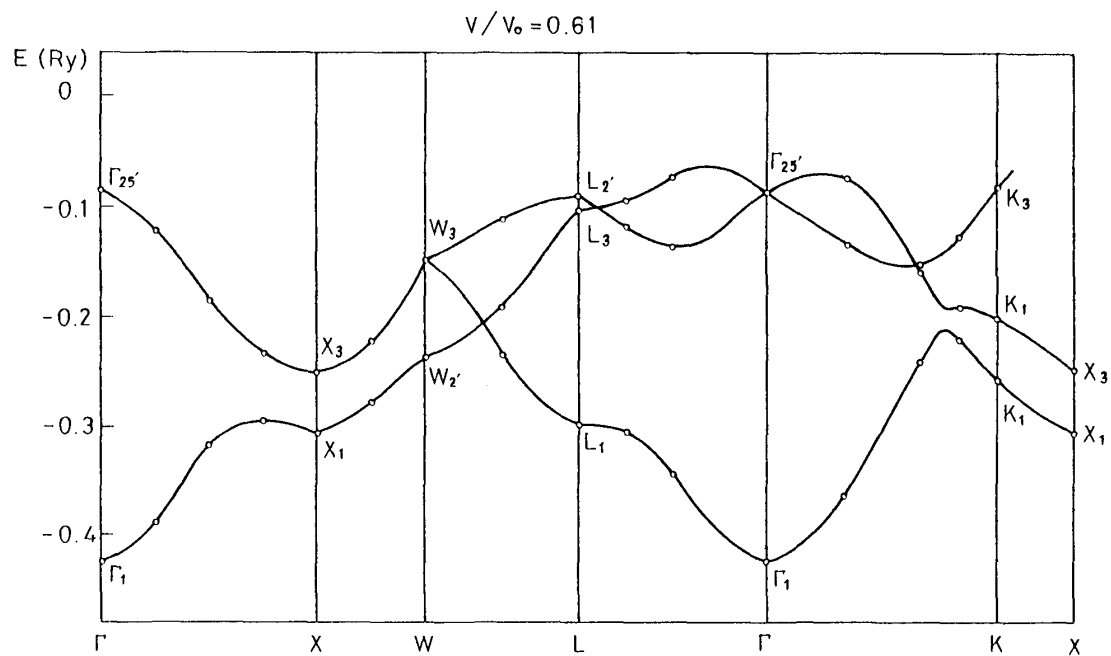
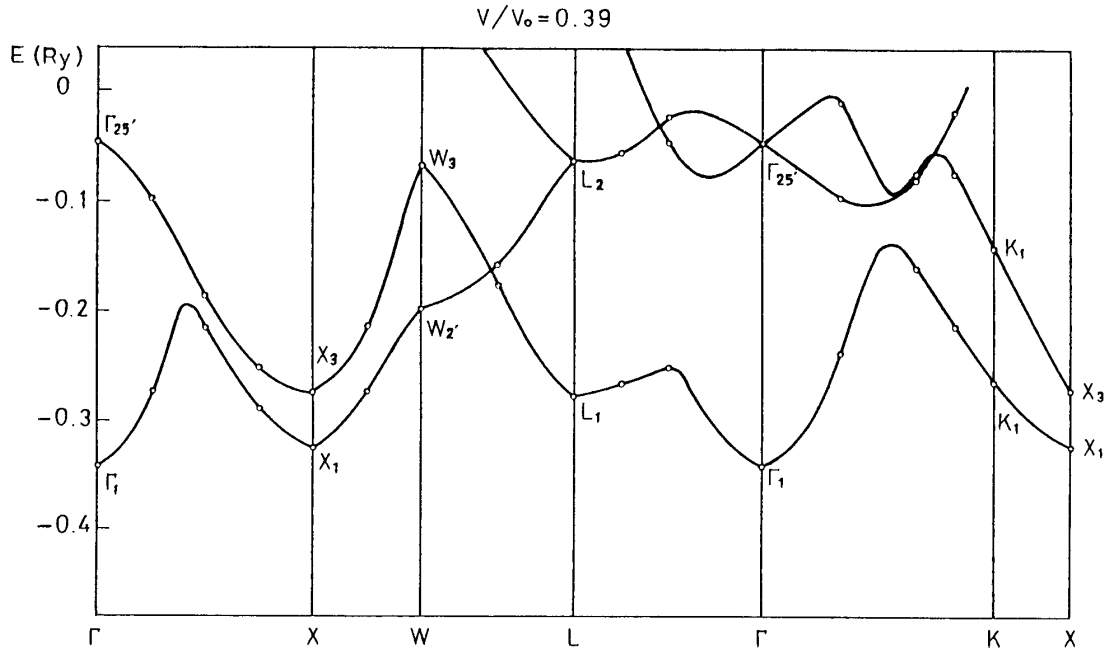


Fig. 3 (continued)



faces appear in addition to the greatly warped central portion of the Fermi surface⁽¹⁴⁾.

To evaluate the density of states, $N(E)$, the energies at 512 points in the one forty-eighth independent segment of the zone were determined by linear interpolation between the evaluated values tabulated in Table 5. The band energies thus obtained against volume are listed in Table 6 and plotted in Fig. 4. As seen in the figure, the main feature of the band energy vs. volume curve is the initial gradual fall followed by the rapid rise with decreasing volume, the minimum being in the neighborhood of the volume at normal pressure ($V/V_0=1$). In addition, there appears a small humped portion at $0.4 \leq V/V_0 \leq 0.5$. This behavior of the band energy can be understood in terms of the energies of individual states (Fig. 5): With decreasing volume, the energy of Γ_1 , which has the s-character, initially decreases but rises substantially for $V/V_0 \leq 0.6$. The rapid rise of the energy at the bottom region of this valence band reflects the gain of the kinetic energy in the condensed lattice. Thus the nature of these states determines the main feature of the band energy vs. volume curve. The energies of X_1 and X_3 both approximately of the d-character fall monotonically with decreasing volume. This is due to the reduction of the potential energy. (A slight rise of energy

for X_1 at $V/V_0 \leq 0.3$ is attributable to the s-like character possessed by this state.) The change in the relative height of energy values induces a shift of electrons into the vicinity of X, this giving rise to the hump of the band energy at $0.4 \lesssim V/V_0 \lesssim 0.5$. The volume dependence of the band energy derived here plays a leading role in the CsII \leftrightarrow CsIII phase transition.

Table 6 Energies as dependent on z. E_b : band energy. E_{el} : electrostatic energy. E_{core} : core interaction energy. $E_{crys}(=E_b+E_{el}+E_{core})$: crystalline energy.

z	E_b	E_{el}	E_{core}	E_{crys}
6.6	-.3290	-.0165	-.0007	-.3462
6.4	-.3300	-.0152	-.0009	-.3461
6.2	-.3268	-.0137	-.0010	-.3415
6.0	-.3173	-.0118	-.0008	-.3299
5.8	-.2993	-.0096	.0005	-.3084
5.6	-.2736	-.0070	.0041	-.2765
5.4	-.2455	-.0040	.0137	-.2358
5.2	-.2203	-.0003	.0367	-.1839
5.0	-.1918	.0040	.0878	-.1000

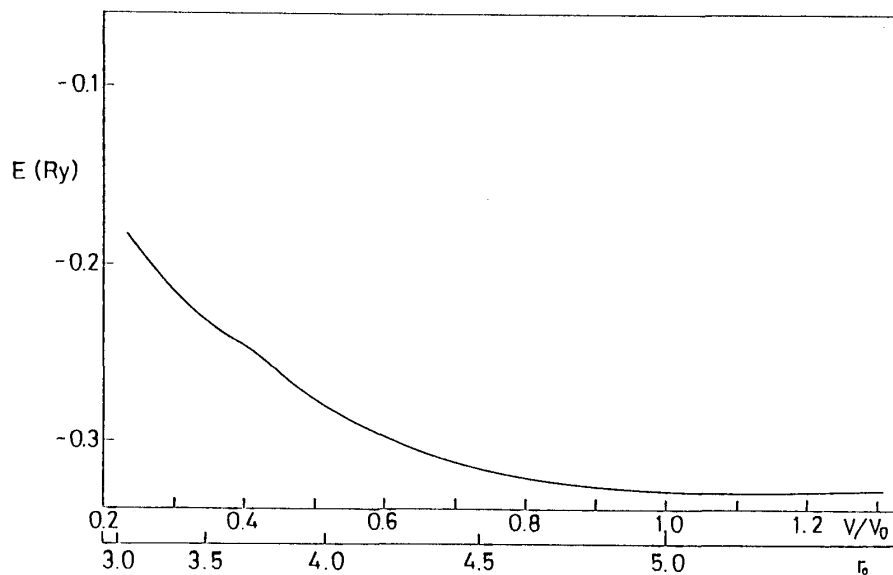


Fig. 4 Calculated band energy (Ry) as a function of V/V_0 . Half of the atomic distance r_0 is also shown.

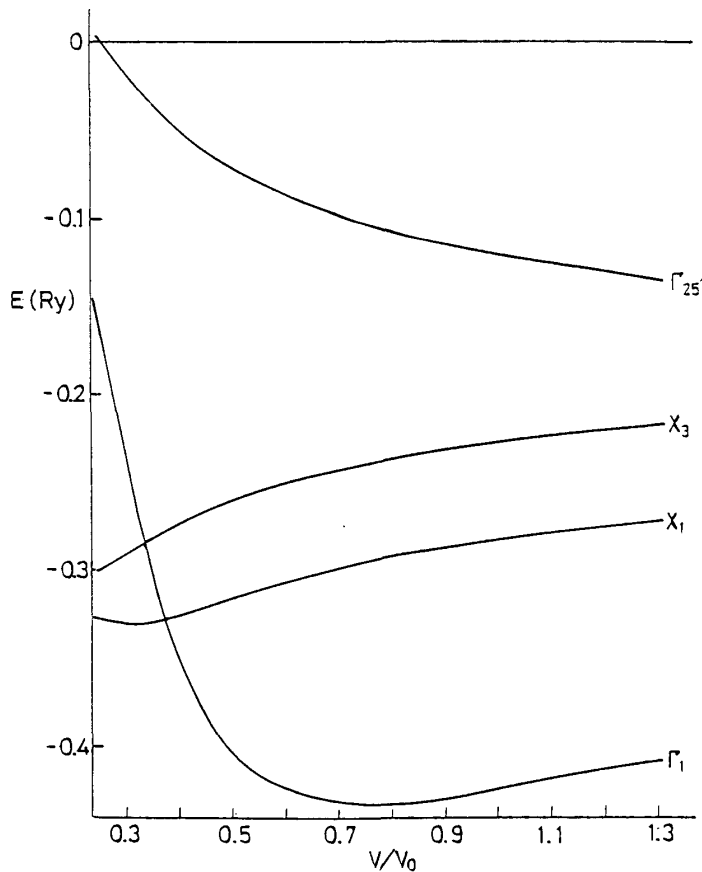


Fig. 5 Energies of the states, Γ_1 , X_1 , X_3 , and $\Gamma_{25'}$ as dependent on V/V_0 .

III. Discussion

For discussing the transition in detail, it is also necessary to take account of the electrostatic interaction energy, E_{el} , of the electron distribution⁽¹⁵⁾ and the ion core interaction energy, E_{core} . For E_{el} (per electron), we used the following expression.

$$E_{el} = 1.2/r_s - 0.916/r_s - 0.88/(r_s + 7.79) \quad (5)$$

The terms on the right side of this equation are respectively the self-energy, the exchange energy, and the correlation energy*. The core interaction energy consisting of the exchange interaction energy and the electric dipole interaction energy between two neighboring cores is

* As yet, the correlation energy has not been calculated successfully in the region of electron densities appropriate to real materials. Several authors have discussed the problem of interpolating the energy between the low and high density limits. The agreement between the various interpolations is only fair but the volume dependences of these values agree fairly well⁽¹⁶⁾. We used Wigner's expression⁽¹⁷⁾ in eq.(5).

expressed as

$$E_{\text{core}} = 12\{A\exp((2r_i - 2r_0)/\rho) - C/(2r_0)^6\} \quad (6)$$

with $A=1.25 \times 10^{-12}$ erg, $\rho=0.345$ Å, $r_i=1.455$ Å, and $C=100 \times 10^{-12}$ ergÅ⁶. Numerical values for constants in eq. (6) have been obtained by Huggins and Mayer⁽¹⁸⁾ in the study of the compressibility and the lattice constant of cesium. The energies E_{el} and E_{core} together with the band energy, E_{b} , constitute the crystalline energy, E_{crys} . Calculated values of these energies are tabulated in Table 6. Over the volume examined, E_{el} is a slowly varying function of the volume, but E_{core} increases rapidly at $V/V_0 \leq 0.4$. It is also observed that the volume dependence of E_{crys} is determined essentially by E_{b} and the repulsive energy E_{core} .

Now, the pressure dependence of the equilibrium volume is discussed. The crystalline energy vs. volume curve in Fig. 6 has an almost linear portion (indicated by arrows). This portion corresponds to the hump of the band energy in Fig. 4. It can be shown that with changing pressure a transition takes place between two volumes corresponding to both ends of this portion.⁽¹⁾ As has been discussed, this transition is of electronic origin. The CsII \leftrightarrow CsIII phase transition found by Bridgman et.al. is ascribed to this transition. Calculated critical volumes and the amount of volume change ($V/V_0 \approx 0.45 \leftrightarrow 0.4$) are in fairly good agreement with the experimental values. However, the calculated critical pressure

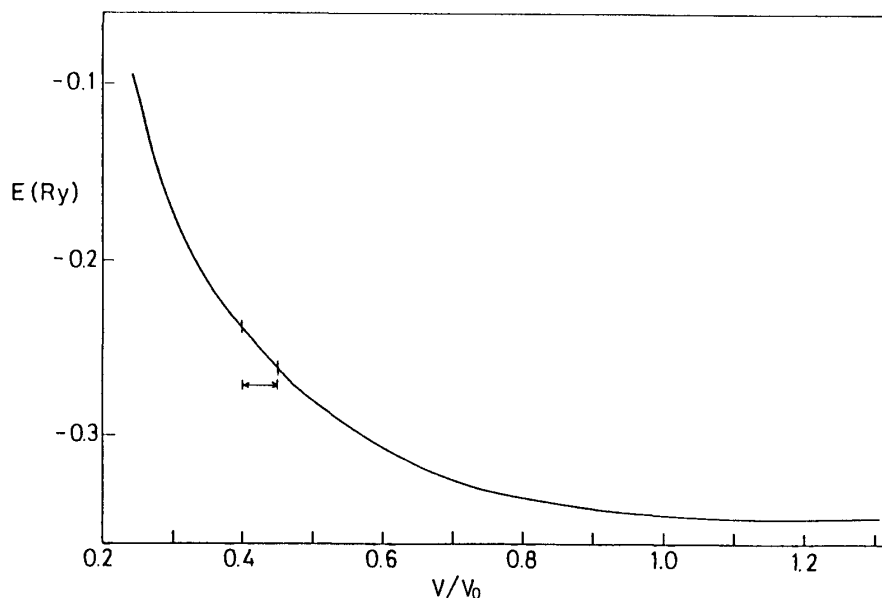


Fig. 6 Calculated crystalline energy (Ry) as a function of V/V_0 . The phase transition occurs between the volumes indicated by arrows.

($P_c = -dE_{\text{crys}}/dV \approx 88$ kbar) is considerably larger than the observed one. For the crystal potential, we assumed the Coulomb potential at $r \approx r_0$. With decreasing volume, however, the potential acting on the valence electron becomes more attractive by the "outer shielding effect" of the electron oozed out from the ion core. This effect has a tendency to reduce the band energy and hence may lower the theoretical P_c value.

We have shown the good convergence of the APW method. The accuracy of the evaluated band structure obviously depends on the potential used. We have not attempted to improve the self-consistency of the potential beyond that of the Wigner-Seitz assumption and the quantum defect method. Because to do so would largely remove the advantages of the latter method in dealing with all of the volumes on the same basis. Accordingly we have no estimate of uncertainty arising from this source in the present calculation. Another uncertainty in the present calculation is concerned with the energy interpolation in evaluating the density of states: It is evident that the interpolation schemes for nearly spherical bands^(13,19) or narrow d-bands⁽²⁰⁾ can not be utilized in the present case. To estimate an error introduced by the interpolation used here, it is necessary to compare with the results evaluated at more than just the symmetry points in the zone.

The volume dependence of energies of s- and d-states as shown in Fig. 5 should be qualitatively the same as those for the other alkali metals, rubidium and potassium. From the spectroscopic data⁽²¹⁾ on free atoms, however, the energy difference between s- and d-levels is the smallest for cesium ($\Delta E_{\text{Cs}} = E_{5d} - E_{6s} = 0.132$ Ry, $\Delta E_{\text{Rb}} = 0.176$ Ry, and $\Delta E_{\text{K}} = 0.196$ Ry). Hence the volume at which electrons are forced into d-states must be the largest for cesium. The sharp rise in the electrical resistivity of rubidium at about 200 kbar⁽²²⁾ may correspond to the electronic phase transition as discussed in this paper.

Acknowledgments

The authors wish to express their sincere thanks to Professor T. Hirone for suggesting the problem and for guidance during this work. Thanks are also due to Professor A. Morita for valuable comments and encouragement, and to Dr. S. Wakoh for supplying his structure constant data. One of the authors (T.K.) wishes to thank Professor T. Iwata for his continuous encouragement. This work was partially supported by the Grant-in-Aid from Ministry of Education.

Appendix

In GF calculation, the muffin-tin potential is also used. The boundary condition required is satisfied by the Green function. The structural and the atomic properties are segregated in terms of the determinant, so that they can be evaluated separately. Once the "structure constants" are calculated as functions of the energy and \vec{k} , the computation of the band structure as a function of volume can be done with reasonable ease. Some of energies at symmetry points obtained by APW and GF methods are compared in Table 7. Numerical agreement between them is impressive.

Table 7 Comparison of energy eigenvalues using the GF method ($l \leq 2$) and the APW method.

z		6.4	6.0	5.4
Γ_1	APW	-.4194	-.4322	-.3429
	GF	-.4194	-.4321	-.3429
X_1	APW	-.2793	-.2965	-.3261
	GF	-.2793	-.2966	-.3262
L_1	APW	-.3017	-.3020	-.2778
	GF	-.3018	-.3022	-.2780
K_1	APW	-.2492	-.2562	-.2662
	GF	-.2488	-.2555	-.2653

References

- (1) T. Kamimura and M. Yamada, Bulletin Japan Inst. Metals, 10 (1971), 407 [in Japanese].
- (2) P. W. Bridgman, Proc. Am. Acad. Arts Sci., 56 (1921), 61. 60 (1925), 385. 76 (1948), 55. Phys. Rev., 72 (1947), 533.
- (3) H. T. Hall, L. Merrill, and J. P. Barnet, Science, 146 (1964), 1297.
- (4) R. Sternheimer, Phys. Rev., 78 (1950), 235.
- (5) F. S. Ham, "Solid State Physics", Ed. by F. Seitz and D. Turnbull, (Academic Press, New York, 1955), vol. 1 p. 27.
- (6) E. S. Alekseev and R. G. Arkipov, Sov. Phys.-Solid State, 4 (1962), 795.
- (7) J. C. Slater, Phys. Rev., 51 (1937), 846. J. H. Wood, Phys. Rev., 126 (1962), 157. T. Loucks, "Augmented Plane Wave Method", (Benjamin Inc., New York, 1967).
- (8) W. E. Rudge, Phys. Rev., 181 (1969), 1024, 1033.

- (9) L. P. Bourcheart, R. Smolckowski and E. Wigner, *Phys. Rev.*, 50 (1936), 58.
- (10) T. S. Kuhn and J. H. van Vleck, *Phys. Rev.*, 79 (1950), 382.
T. S. Kuhn, *Phys. Rev.*, 79 (1950), 515. H. Brooks and F. S. Ham, *Phys. Rev.*, 112 (1958), 344. H. Brooks, *Phys. Rev.*, 91 (1953), 1027.
- (11) W. S. Raymond and L. D. Samuel, "Digital Computation and Numerical Methods" (McGraw-Hill, Inc., New York, 1965).
- (12) W. Kohn and N. Rostoker, *Phys. Rev.*, 94 (1954), 1111. J. C. Slater, *Phys. Rev.*, 145 (1966), 599.
- (13) F. S. Ham, *Phys. Rev.*, 128 (1962), 82, 2524.
- (14) J. Yamashita, S. Wakoh, and S. Asano, *J. Phys. Soc. Jpn.*, 27 (1969), 1153. J. Yamashita and S. Asano, *J. Phys. Soc. Jpn.*, 29 (1970), 264.
- (15) J. Callaway, "Energy Band Theory" (Academic Press, New York, 1964).
- (16) V. M. Born and J. E. Mayer, *Z. Phys.*, 75 (1932), 1.
- (17) E. Wigner, *Phys. Rev.*, 46 (1934), 1002.
- (18) M. L. Huggins and J. E. Mayer, *J. Chem. Solid*, 1 (1933), 643.
- (19) J. E. Cornwell and E. P. Wohlfarth, *Nature*, 186 (1960), 379.
- (20) L. C. Allen, *Phys. Rev.*, 98 (1955) 993. J. C. Phillips, *Phys. Rev.*, 112 (1958), 685.
- (21) "Atomic Energy Levels" Ed. by C. E. Moore, (National Bureau of Standards, Washington, 1971).
- (22) H. G. Drickmer and R. A. Stager, *Phys. Rev.*, 132 (1963), 124.