

Electronic and optical properties of CeO under pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 1169

(<http://iopscience.iop.org/0953-8984/1/7/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 17:45

Please note that [terms and conditions apply](#).

Electronic and optical properties of CeO under pressure

S K De and S Chatterjee

Department of Materials Science, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

Received 16 March 1988, in final form 10 August 1988

Abstract. The volume behaviour of cerium monoxide (CeO) is interesting as a function of pressure. The volume decreases rapidly up to 3 GPa and decreases more slowly above 3 GPa. In this work, we present the fully self-consistent band structure of CeO for four different values of lattice constant corresponding to four different pressures, using the linearised augmented plane-wave method. The local density formulation has been assumed for the exchange and correlation part of the potential. From the band-structure results, we have calculated the valency of Ce in CeO. The calculated valency increases from 3.0 to 3.26 with increase in pressure. From the band-structure results, the density of states, the coefficient of linear specific heat and the optical absorption spectra have been calculated.

1. Introduction

The rare-earth monoxides have been extensively studied by using high-pressure techniques (Leger *et al* 1981). These compounds crystallise in the NaCl structure and show a variety of interesting properties.

- (i) LaO, CeO, PrO and NdO are metallic with the rare earth in the trivalent state.
- (ii) EuO and YbO are semiconductors with the rare earth in the divalent state.
- (iii) SmO is metallic with Sm in an intermediate valence state close to 3.

Among these compounds, again CeO with a lattice constant of 5.089 Å is unique, as the Ce–Ce distance d_{nn} of 3.60 Å is the shortest found with Ce in the γ -like state. Hill plot correlations (Hill 1970, Pickett and Klein 1983) show that many compounds with d_{nn} less than a critical value of 3.40 Å are non-magnetic, i.e. in an α -like state while those with $d_{nn} > 3.40$ Å are magnetic, i.e. in a γ -like state. Hence the Ce–Ce distance (3.60 Å) for CeO is very close to the critical value of 3.40 Å for the occurrence of the γ to α transition where the Ce magnetic moment disappears and the volume sharply decreases. This γ to α transition in Ce metal and compounds is mainly due to the interaction of f and d electrons. To interpret the γ to α transition, two prominent models have been suggested:

- (i) a partial 4f change (Wohlleben and Rowler 1984);
- (ii) a volume-dependent Kondo interaction (Lavagna *et al* 1983, Allen and Martin 1982).

As the Ce–Ce distance in CeO is close to the critical value for the γ to α transition, the effect of a high pressure on CeO would be important in order to detect the possible

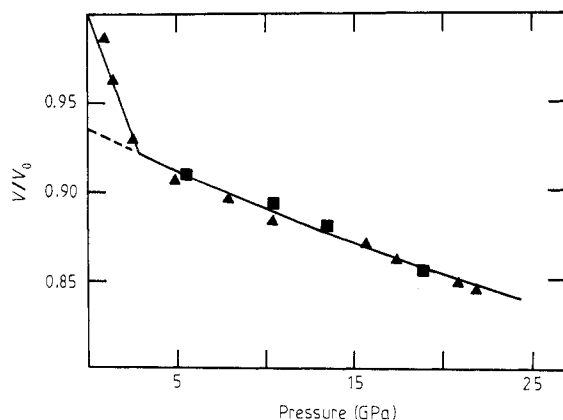


Figure 1. Relative volume of CeO as a function of pressure (Vedel *et al* 1986).

presence of a volume anomaly indicative of an electronic transition. The pressure–volume relationship was studied by Vedel *et al* (1986) up to 25 GPa at room temperature as shown in figure 1. The volume decrease strongly with pressure up to about 3 GPa and then decreases much more slowly. In the lower-pressure range below 3 GPa, the decrease in volume can be represented by the mean bulk modulus of 30 GPa (Vedel *et al* 1986). An extrapolation of the values observed for trivalent rare-earth monochalcogenides LaS or LaTe (Jayaraman *et al* 1982) indicates that the bulk modulus of CeO would be close to 125 GPa, much higher than the experimental value of 30 GPa. The lattice parameter of the high-pressure phase calculated at normal pressure is equal to 4.975 Å compared with 5.089 Å in the normal state. From the decrease in lattice parameter, Vedel *et al* (1986) estimated a valence of 3.3 in the high-pressure phase. The high-pressure value of bulk modulus (171 GPa) and its pressure derivative (4.8 GPa) above 3 GPa indicate that the valence state of 3.3 reached at 3 GPa is stable over a large pressure range.

Theoretically, many band-structure calculations on Ce and its compounds have been done, but no such work on CeO has yet been carried out. As the Ce–Ce distance in CeO is nearer to the value for the γ to α transition in Ce, therefore it is highly imperative to study the band structure of CeO as a function of lattice parameter similar to that of Ce (Pickett *et al* 1981) and Pr (De and Chatterjee 1987). In this paper we report a thorough band structure calculation by self-consistent linearised augmented plane-wave (LAPW) method of CeO for four lattice constants. We have applied a general form of local density functional theory to study the electronic properties of CeO for a range of atomic volumes between that of normal pressure and a pressure of 25 GPa. From the band-structure results, the density of states (DOS), the electron–phonon coupling constant λ , the coefficient γ of linear specific heat and the imaginary part $\epsilon_2(\omega)$ of the dielectric function have been calculated.

2. Method of calculation

The details of the self-consistent semi-relativistic LAPW method have been described by many researchers (Koelling and Arbmán 1975, Koelling and Harmon 1977, MacDoland *et al* 1980, De and Chatterjee 1987). The local density approximation of Von Barth and

Hedin (1972) has been used to form the exchange and correlation parts of the crystal potential. The charge density $\rho(r)$ has been calculated by finding the crystal wavefunctions at 20 k -points inside one-fortyeighth of the Brillouin zone. The self-consistency is obtained without spin-orbit (s-o) interaction. The values of the lattice constant and the muffin-tin radius R_{MT} used in this calculation are given in table 1.

Table 1. Input parameters for LAPW calculations, lattice constant a and muffin-tin radius R_{MT} . E_F is the Fermi energy and ν is the valency of Ce.

a (Å)	$R_{MT}(\text{Ce})$ (au)	$R_{MT}(\text{O})$ (au)	E_F (Ryd)	ϵ (eV)	ν
$a_1 = 9.6182$	2.7577	2.0513	0.660	2.15	3.00
$a_2 = 9.3873$	2.6887	2.0048	0.719	2.45	3.14
$a_3 = 9.2862$	2.6522	1.9908	0.748	2.56	3.19
$a_4 = 9.1110$	2.6254	1.9300	0.792	2.71	3.26

We have only studied the effect of s-o interaction at Γ and X points. The calculated values of ξ_l^0 , ξ_l^1 , ξ_l^2 following Pickett *et al* (1981) are shown in table 2 for normal- and high-pressure phases. From table 2, it is seen that the maximum splitting occurs for the Ce p-like ($l = 1$) states which are not important since they are not in the energy range under consideration. The splitting for the O p-like state is small, however.

Table 2. Values of ξ_l^0 , ξ_l^1 and ξ_l^2 .

	l	a	ξ_l^0 (mRyd)	ξ_l^1 (mRyd)	ξ_l^2 (mRyd)
Ce	1	a_1	111.8	-3.4	0.1
Ce	1	a_4	122.7	3.1	0.08
Ce	2	a_1	5.6	2.0	0.7
Ce	2	a_4	6.1	1.7	0.5
Ce	3	a_1	3.4	2.6	2.1
Ce	3	a_4	3.5	2.3	1.6
O	1	a_1	0.9	0.4	0.1
O	1	a_4	0.9	0.3	0.1

3. Band structure and density of states

The calculated band structures for the lattice constants a_1 and a_4 corresponding to the normal- and high-pressure phases, along the major symmetry axes in the Brillouin zone are shown in figures 2 and 3. Since the s-o splitting is small as shown in table 2, we do not show this in the band-structure diagrams. The band structure consists of the occupied O 2p band and unoccupied s, d and partially occupied f bands of Ce.

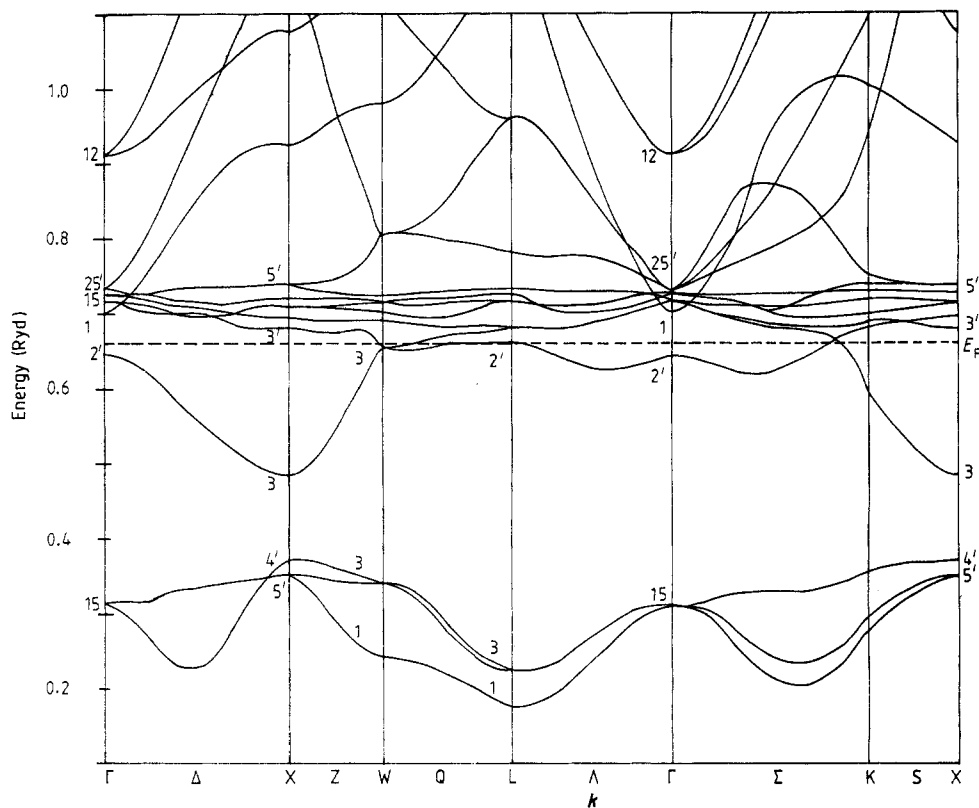


Figure 2. Band structure of CeO for the lattice constant a_1 , along the symmetry points and axes. E_F is the Fermi energy.

Some important features can be observed from the general behaviour of the bands throughout the range of the atomic volume. The f bands, with the Δ_2' singlet lying lowest, lie about 5 eV above the 2p-derived valence band of oxygen. The triplet Γ_{15} and Γ_{25} state of f bands lies above the Fermi level E_F . The d and s bands are broad conduction bands. The f bands are therefore immersed in a sea of s-d conduction bands. There exists a gap between the 2p valence bands and the f-d-s conduction bands. Hybridisation is strongest between the Δ_1, Δ_5 (from Γ_{15} at Γ) f and 2p bands, the Δ_2' f and d bands and the Δ_1, Δ_5 (from Γ_{15} at Γ) f and 2p bands, the Δ_2' f and d bands and the Δ_1 2p and d (from Γ_{12} at Γ) bands. The first of these interactions produces bonding and anti-bonding Γ_{15} states and pushes the anti-bonding Γ_{15} triplet above the Γ_{25} triplet, inverting the f crystal-field levels. The interaction between Δ_2' f and d singlet states produces a bonding band that lies almost entirely in the gap. The interaction between the Δ_1 2p and d bands pushes the anti-bonding band up at X so that it is no longer the lowest lying of the conduction band states. The results of s-o splitting are shown in table 3 at the Γ and X points for a_1 and a_4 . The important effect of s-o splitting is to increase the f-band width W_f from 83 to 97 mRyd for a_1 and from 119 to 130 mRyd for a_4 .

An investigation of the charge distribution for a_1 and a_4 in each LAPW sphere in table 4 shows that, in the lowest three bands, the O 2p state is dominant. In these three bands, (Ce f-state mixes), for example the f component in the Γ_{15} state of 2p state is 10% of the

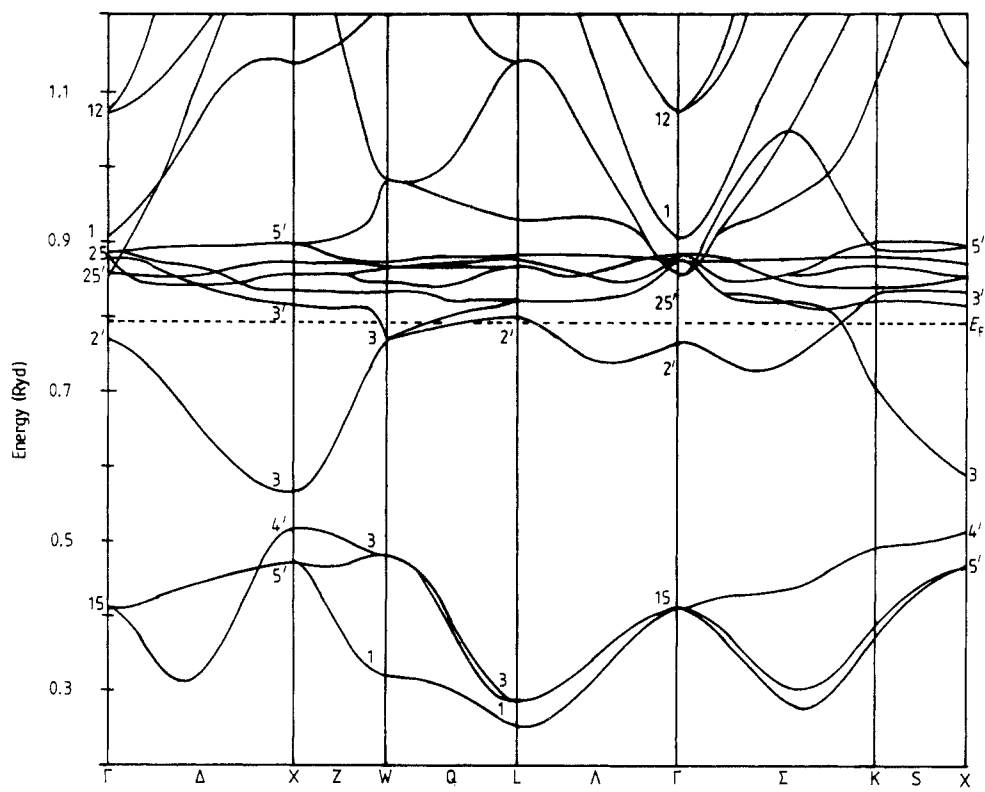


Figure 3. Band structure of CeO for the lattice constant a_4 , along the symmetry points and axes. E_F is the Fermi energy.

Table 3. Eigenvalues at Γ and X, showing the effect of including the s-o interaction.

	Eigenvalue (mRyd) at Γ				Eigenvalue (mRyd) at X			
	a_1		a_4		a_1		a_4	
	No s-o	s-o	No s-o	s-o	No s-o	s-o	No s-o	s-o
Γ_{15}	315	311 318	408	401 411	348	335 351	468	456 474
$\Gamma_{2'}$	643	641	764	763	485	485	565	565
$\Gamma_{25'}$	728	725 732	852	847 855	678 691 708	675 686 703	816 835 854	814 831 849
Γ_{25}	710	700 712	875	866 876	720 737	725 732 746	869 894 903	873 888 903
Γ_{15}	726	722 738	883	881 893	922 1075 1160	922 1074 1155	1135	1134
Γ_1	698	698	905	905		1166		
Γ_{12}	909	910	1073	1074				

Table 4. Valence charge distribution of some selected states.

	States	Energy (Ryd)	Ce sphere	O sphere	Interstitial
a_1	Γ_{15}	0.315	0.10(f)	0.75(p)	0.12
a_1	$\Gamma'_{2'}$	0.643	0.87(f)		0.12
a_1	X'_5	0.348	0.05(p), 0.05(f)	0.76(p)	0.12
a_1	X'_4	0.365	0.12(p)	0.75(p)	0.12
a_1	X_3	0.485	0.45(d)		0.51
a_1	W_1	0.242	0.07(d)	0.69(p)	0.17
a_1	W_3	0.345	0.09(p)	0.71(p)	0.14
a_1	W_3	0.650	0.18(p), 0.53(f)		0.24
a_1	L_1	0.175	0.07(s), 0.08(d)	0.54(p)	0.30
a_1	L_3	0.223	0.13(d)	0.69(p)	0.17
a_1	L'_2	0.662	0.89(f)		0.09
a_4	Γ_{15}	0.408	0.11(f)	0.71(p)	0.13
a_4	Γ'_2	0.764	0.84(f)		0.15
a_4	X'_5	0.468	0.08(p), 0.07(f)	0.72(p)	0.12
a_4	X'_4	0.515	0.15(p)	0.74(p)	0.10
a_4	X_3	0.565	0.43(d)		0.53
a_4	W_1	0.318	0.08(d)	0.67(p)	0.19
a_4	W_3	0.480	0.13(p)	0.70(p)	0.12
a_4	W_3	0.772	0.20(d), 0.47(f)		0.28
a_4	L_1	0.253	0.07(s), 0.09(d)	0.52(p)	0.30
a_4	L_3	0.290	0.14(d)	0.66(p)	0.18
a_4	L'_2	0.791	0.87(f)		0.10

total and that in the $X_{5'}$ state is 5%. This p-f mixing occurs only along the ΓX direction. The occupied $\Gamma_{2'}$ state is purely f character. The f character of 87% at the $\Gamma_{2'}$ state of the $\Delta_{2'}$ band decreases along ΓX and this becomes purely d (45%) character at the X point. Thus this band hybridises strongly with another $\Delta_{2'}$ band derived from $\Gamma_{25'}$ of the d state along the ΓX axis. From table 4, we also observe that the p character of the lowest three bands decreases and the f character increases on reduction in the volume. This indicates that the p-f mixing along the ΓX direction has a tendency to increase with increase in pressure.

The behaviour of the eigenvalues at the Γ and X points on reduction in the volume is shown in figure 4. The Γ_1 s state is extremely sensitive to volume, moving upwards rapidly as the volume is decreased. The f-band width increases from 83 to 119 mRyd on increase in pressure for the normal pressure to about 25 GPa. The f-band energies also increase as the volume decreases, pulling E_F with them and increasing the separation between the valence bands and the Fermi level. From figure 4, we also observe that the X_3 point is also more sensitive than the other X points. The gap between the $X_{4'}$ and X_3 states decreases from 120 to 50 mRyd on reduction in volume. This is due to the increased hybridisation between Δ_1 p and f bands and $\Delta_{2'}$ f and d bands on increase in pressure. The $L_{2'}$ state, which is at E_F at normal pressure, moves up 10 mRyd from E_F at high pressures.

The DOS has been calculated by the tetrahedron method (Jepsen and Andersen 1971, Lehman and Taut 1972). For this purpose, first-principles eigenvalues are calculated at 89 points and are interpolated linearly within each tetrahedron. The results of these calculations are shown in figure 5. The DOS consists of a huge peak arising from the f

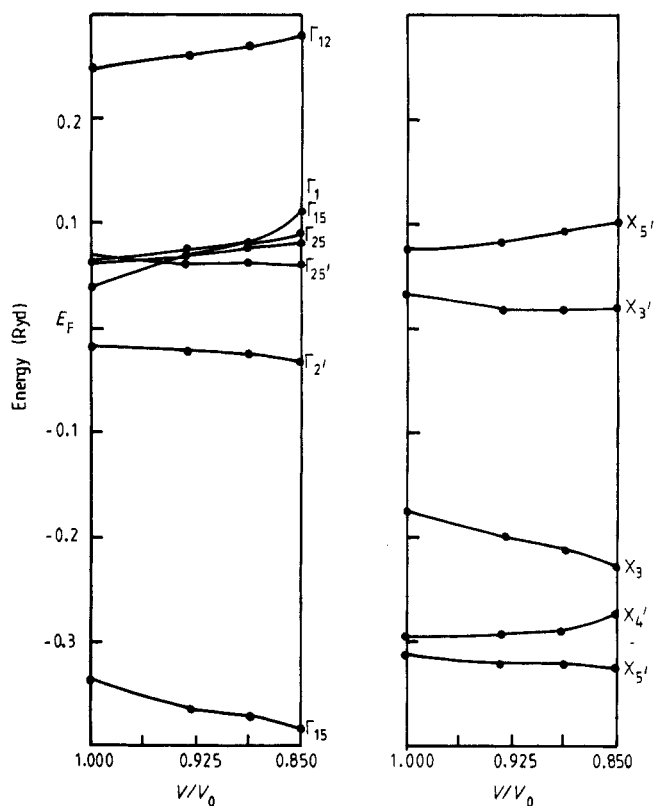


Figure 4. Behaviour of eigenvalues at Γ and X on reduction in volume: ●, calculation results for the four lattice constants listed in table 1.

bands. The DOS at E_F decreases from 29.89 states Ryd^{-1} to 17.46 states Ryd^{-1} . Throughout the range of the atomic volume, the occupied part of the DOS exhibits three peaks. The first peak below E_F is due to the Ce f states and the second and third peaks are due to the O p. The height of the second peak decreases more rapidly than does that of the third peak on increase in pressure, as observed in figure 5. The energy positions of these peaks do not change appreciably on increase in pressure. The unoccupied part of the DOS consists of mainly three peaks. These peaks are mainly derived from Ce d states.

The angular-momentum-decomposed DOS at E_F and the corresponding charges inside the spheres are shown in table 5. The Ce 6s electrons are mainly distributed between the muffin-tin spheres. The number of Ce d electrons increases and the number of O p electrons decreases on increase in pressure. The number of f electrons decreases from 0.994 to 0.926 on increase in pressure. Thus f-to-d-electron transfer occurs since the f band increases in energy relative to the conduction d band.

The valency determination of rare earths is of great importance. The valency of rare earths depends on the position of the f band in the conduction band and the hybridisation of f and d states. The strong hybridisation between f and d states occurs along the singlet Δ_2 band derived from the $\Gamma_{2'}$ state. Hence the parameter $\varepsilon = \varepsilon(\Gamma_{2'}) - \varepsilon(X_3)$ is important for the determination of valency. Since there is no theoretical first-principles formula for valency ν as a function of ε for the rare earths, we use the empirical relation obtained

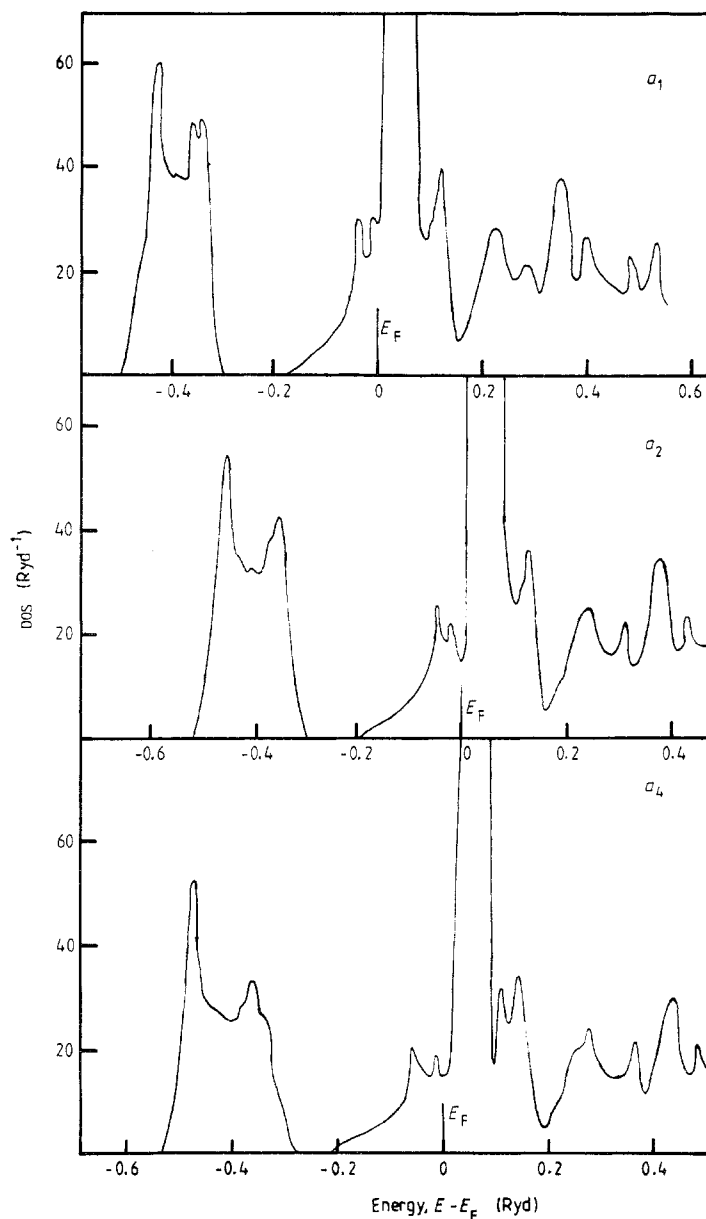


Figure 5. DOSs for the three lattice constants a_1 , a_2 and a_4 as a function of energy.

by Forberovich *et al* (1984) for TmS. Following these workers, if we assume the relation to be

$$v = 2 + \varepsilon/2.15 \quad (1)$$

we find a v -value of 3 for Ce in CeO at normal pressure. To study the effect of pressure on v , we substituted the value of ε in equation (1) from our band-structure calculation; the values of v are shown in table 1. The value of v obtained at high pressures is 3.26

which is in good agreement with the experimental value of 3.30 (Vedel *et al* 1986). However, the ν estimated from equation (1) relates very poorly to the changes in the f occupation number given in table 5. To obtain better agreement, however, one would require better theoretical understanding of the problem. From the occupation numbers given in table 5, we observe that the number of f electrons decreases while the number of d electrons increases on increase in pressure. This indicates that the valency of Ce in CeO increases on increase in pressure; this is also found experimentally (Vedel *et al* 1986).

Table 5. Angular-momentum decomposed muffin-tin DOS $N_i(E_F)$ at E_F and corresponding charges Q_i .

	Ce					O			Interstitial	Total	
	s	p	d	f	g	s	p	d			
$N_i(E_F)$	a_1	0.001	0.235	1.465	23.681	0.017	0.041	0.213	1.465	2.774	29.892
$N_i(E_F)$	a_2	0.001	0.213	1.421	18.949	0.017	0.034	0.219	0.158	3.634	24.646
$N_i(E_F)$	a_3	0.001	0.213	1.395	16.544	0.018	0.035	0.222	0.156	3.533	22.117
$N_i(E_F)$	a_4	0.001	0.196	1.240	12.744	0.017	0.034	0.181	0.126	2.925	17.464
Q_i	a_1	0.075	0.229	0.824	0.994	0.013	0.007	4.178	0.033	1.647	8.000
Q_i	a_2	0.072	0.273	0.837	0.955	0.013	0.009	4.119	0.036	1.686	8.000
Q_i	a_3	0.071	0.295	0.828	0.935	0.013	0.010	4.110	0.038	1.700	8.000
Q_i	a_4	0.074	0.335	0.855	0.926	0.015	0.013	4.023	0.037	1.722	8.000

4. Specific heat

We have calculated the linear contribution to the specific heat γ at normal and high pressures. The value of γ has been calculated from the relation

$$\gamma = (\pi^2 k_B^2/3)(1 + \lambda)N(E_F) \quad (2)$$

where k_B and λ are Boltzmann's constant and the electron-phonon coupling constant respectively. Since the atomic mass M_{Ce} of Ce is much greater than the atomic mass M_O of oxygen, λ is given in terms of Ce and O sites by (Klein and Papaconstantopoulos 1976)

$$\lambda = \eta_{Ce}/M_{Ce}\langle\omega^2\rangle_{Ce} + \eta_O/M_O\langle\omega^2\rangle_O \quad (3)$$

where $\langle\omega^2\rangle_\alpha$ is the mean squared phonon frequency for atom α . Owing to this separation the heavy Ce atom vibrates mainly in the acoustic range of frequencies while the light O atom vibrates in the optical range. Neglecting the contribution of electron-optical phonon interaction to λ , we have

$$\lambda \approx \eta_{Ce}/M_{Ce}\langle\omega^2\rangle_{Ce}. \quad (4)$$

The electron-ion interaction constant η_α has been calculated using the rigid muffin-tin approximation of Gaspari and Gyorffy (1972):

$$\eta_\alpha = \frac{2E_F}{\pi^2 N(E_F)} \sum_l (l+1) \sin^2(\delta_{l+1}^\alpha - \delta_l^\alpha) \frac{N_l^\alpha N_{l+1}^\alpha}{N_l^{(1)\alpha} N_{l+1}^{(1)\alpha}}. \quad (5)$$

In this expression, δ_l^α are the scattering phase shifts, $N_l^{(1)\alpha}$ are the single-scatterer DOSS and N_l^α are the DOSS for atom α and angular momentum l at E_F .

Butler (1977) has found that $\langle \omega \rangle^{1/2} = 0.69\theta_D$, θ_D being the Debye temperature. Since there is no experimental value of θ_D , we have calculated θ_D from the relation (Hama and Watanabe 1986)

$$\theta_D = (\hbar V/k_B R_e) \left[-\frac{5}{2} (1/M_{Ce} + 1/M_O) (P' + 4P/3V) \right]^{1/2} \quad (6)$$

where R_e is the intra-atomic distance of CeO at volume V and P' is the first derivative of P with respect to V . P' has been calculated from the experimental value of the bulk modulus (Vedel *et al* 1986). The values of P' are $-30.00/V_0$ GPa below a pressure of 3 GPa and $-201.176/V_0$ GPa above a pressure of 3 GPa. The calculated values of θ_D at normal and high pressures ($V = 0.85V_0$, V_0 being the volume at normal pressure) are found to be 301.2 K and 646.3 K, respectively.

Table 6. Phase shifts δ_l and contribution $\eta_{l,l+1}$ to η .

		l	δ_l	$\eta_{l,l+1}$ (eV Å ⁻²)	η (eV Å ⁻²)
a_1	Ce	0	-1.371		
a_1	Ce	1	-0.748	0.170	
a_1	Ce	2	0.649		0.580
a_1	Ce	3	0.674	0.410	
a_1	Ce	4	0.0005		
a_1	O	0	-1.311	0.006	
a_1	O	1	-0.804	0.160	0.166
a_4	Ce	0	-1.552	0.001	
a_4	Ce	1	-0.893	0.341	
a_4	Ce	2	0.633		0.908
a_4	Ce	3	0.579	0.566	
a_4	Ce	4	0.0007		
a_4	O	0	-1.426	0.010	
a_4	O	1	-0.888	0.237	0.254
a_4	O	2	0.016	0.005	

The values of δ_l^α and the contribution to η up to the transitions with $l = 3 \leftrightarrow 4$ for Ce and $l = 1 \leftrightarrow 2$ for O atoms are shown in table 6. The main contribution to η_{Ce} comes from $p \leftrightarrow d$ and $f \leftrightarrow g$ transitions in Ce atoms at both normal pressure and high pressures. The calculated values of λ and γ are 0.054 and 5.45 mJ mol⁻¹ K⁻² at normal pressure and 0.017 and 3.07 mJ mol⁻¹ K⁻² at high pressure. Since there is no experimental value of γ , we are unable to compare the γ -value with experiment but the values of γ are quite near to the value observed for CeN (Danan *et al* 1969).

5. Optical properties

The optical absorption spectra $\varepsilon_2(\omega)$, the imaginary part of the dielectric function, is given by

$$\varepsilon_2(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{n_f(\text{occupied})} \int_{B_2} |P_{fi}|^2 \delta[En_f(\mathbf{k}) - En_i(\mathbf{k}) - \hbar\omega] d^3k \quad (7)$$

where $\hbar\omega$ is the energy of incident light and $P_{\mathbf{\hat{n}}}$ is the optical matrix element. The \mathbf{k} -space integral over the delta function alone yields the joint density of states (JDOS). Thus, if the matrix elements $P_{\mathbf{\hat{n}}}$ are assumed to be constant throughout the Brillouin zone, then

$$\varepsilon_2(\omega) \propto \text{JDOS}/\omega^2. \quad (8)$$

We have calculated the JDOS by the tetrahedron method in a similar way to the DOS calculation.

The calculated $\varepsilon_2(\omega)$ spectra at normal and high pressures are shown in figure 6. As there are no experimental results so far, we cannot compare our calculated $\varepsilon_2(\omega)$ with experiment, but we can explain the peaks and structures observed in $\varepsilon_2(\omega)$ spectra in terms of inter-band transitions. The peak at around 1 eV is due to the transition from around $\Gamma_{2'}$ to around $\Gamma_{25'}$. The small structure around 3.5 eV arises from the transition around X_3 to f bands. The large peak at around 5.5 eV originates due to the transition from the second band along the Δ axis, the third band along the Σ axis, the second and third bands along the Z axis and the second band along the Λ axis to f bands. The small structure at around 7 eV is due to the transition at around L_1 to f bands. From figure 6, we observe that the positions of peaks and structures shift towards higher-energy positions on increase in pressure. The reason for this shift towards a higher energy is that the Fermi energy rises owing to the increase in the number of conduction electrons with increasing pressure. We also find that the large peak at around 5.5 eV becomes broader on increase in the pressure.

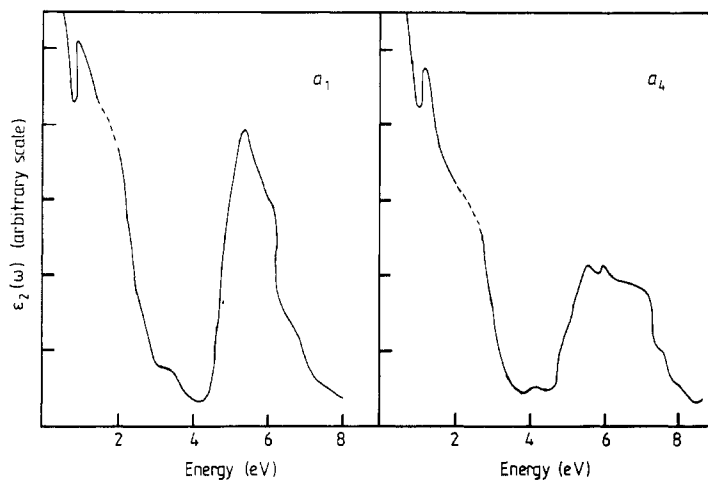


Figure 6. $\varepsilon_2(\omega)$ spectra for two lattice constants a_1 and a_4 .

6. Conclusion

Vedel *et al* (1986) found experimentally a volume decrease of 8% between the normal pressure and 3 GPa. This volume decrease is about half the value of 17% observed in the γ -to- α transition of Ce. From our band-structure calculation, we find that between normal pressure and 3 GPa the change in 4f-band width is about 12% which is about one fifth of the value found at the γ -to- α transition of Ce (Pickett *et al* 1981) and about one

quarter of the value found at the Pr(III)-to-Pr(IV) transition (De and Chatterjee 1987). Thus the 4f shell of Ce in CeO is not very delocalised compared with the volume change. We also find that the 4f–5d hybridisation increases slightly on increase in the pressure. Thus the pressure–volume behaviour of CeO may not be due to the increased 4f–5d hybridisation. However, the valency of Ce in CeO calculated from the band-structure results increases from 3.0 at normal pressure to 3.26 at high pressures.

The valency obtained at high pressures is in good agreement with the experimental value of 3.3 (Vedel *et al* 1986). Thus the pressure–volume behaviour of CeO can be interpreted by a continuous increase in valence similar to the explanation of the γ -to- α transition suggested by Wohlleben and Rowler (1984). However, we believe that the volume-dependent Kondo effect (Lavagna *et al* 1983) may also be responsible for this behaviour, but a study of this is beyond the scope of the present work.

References

- Allen J W and Martin R C 1982 *Phys. Rev. Lett.* **49** 1106
Butler W H 1977 *Phys. Rev. B* **15** 5267
Danan J, de Novin C and Lallement R 1969 *Solid State Commun.* **7** 1103
De S K and Chatterjee S 1987 *J. Phys. F: Met. Phys.* **17** 2057
Forberovich O V, Nizhnikova G P, Vlasov S V and Domashevskaya E P 1984 *Phys. Status Solidi b* **121** 241
Gaspari G P and Gyorffy B L 1972 *Phys. Rev. Lett.* **28** 801
Hama J and Watanabe M 1986 *Phys. Lett.* **115A** 287
Hill H H 1970 *Nucl. Metall.* **17** 2
Jayaraman A, Batlogg B, Maines R G and Bach H 1982 *Phys. Rev. B* **26** 3347
Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
Klein B M and Papaconstantopoulos D A 1976 *J. Phys. F: Met. Phys.* **6** 1135
Koelling D D and Arbman G O 1975 *J. Phys. F: Met. Phys.* **5** 2041
Koelling D D and Harmon B N 1977 *J. Phys. C: Solid State Phys.* **10** 3107
Lavagna M, Lacroix C and Cyrot M 1983 *J. Phys. F: Met. Phys.* **13** 1007
Leger J M, Yacoubi N and Loriers J 1981 *J. Solid State Chem.* **36** 261
Lehman G and Taut M 1972 *Phys. Status Solidi b* **54** 469
MacDoland A H, Pickett W E and Koelling D D 1980 *J. Phys. C: Solid State Phys.* **13** 2675
Pickett W E, Freeman A J and Koelling D D 1981 *Phys. Rev. B* **23** 1266
Pickett W E and Klein B M 1983 *J. Less-Common Met.* **93** 219
Vedel I, Redon A M and Leger J M 1986 *J. Phys. C: Solid State Phys.* **19** 3549
Von Barth U and Hedin L J 1972 *J. Phys. C: Solid State Phys.* **5** 1629
Wohlleben D and Rowler J 1984 *J. Appl. Phys.* **55** 1904