

LETTER TO THE EDITOR

Cohesive properties of CaF_2 and UO_2 in the atomic sphere approximation

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Abstract. The zero-temperature equations of state of UO_2 and CaF_2 have been computed from semi-relativistic LMTO calculations. The calculated lattice parameters are 1/2% above and 5% below the experimentally determined equilibria for UO_2 and CaF_2 respectively. The computed bulk moduli are 3.0×10^{12} and 0.71×10^{12} dyn cm^{-2} and the band gap of UO_2 is found to be 5.35 eV.

The cohesive properties of fluorite structure crystals have to date been explained in terms of semi-empirical ionic models (Hodby 1974), full quantum mechanical treatment having been regarded as impractical. However, recent studies of the cohesive properties of metals (Moruzzi *et al* 1977, Skriver *et al* 1978) and compounds (Andersen *et al* 1979) by bandstructure calculations, especially the efficient linear muffin tin orbital (LMTO) technique (Andersen 1975) in the atomic sphere approximation (ASA), have been extremely successful. LMTOS may be regarded as 'tight-binding' functions from which are derived especially simple Hamiltonian and overlap matrices (Andersen *et al* 1978). They therefore make an appropriate basis set for the valence bands of ionic crystals. When the local density approximation to exchange and correlation (Hedin and Lundqvist 1971) is used, a rigorous description of ground state properties should be obtained from a self-consistent bandstructure calculation. The zero-temperature equation of state is then computed from the pressure formula (Lieberman 1971, Pettifor 1976, Nieminen and Hodges 1976, Andersen *et al* 1979) which is, in ASA, analysed according to atom type and angular momentum contributions. The pressure may also be expanded in moments of the density of states and, if moments higher than the first are neglected, is (Andersen *et al* 1979)

$$3PV = - \sum_{il} n_{il} [\delta C_{il} / \delta \ln S_i + (\bar{E}_{il} - C_{il}) \delta \ln \Delta_{il} / \delta \ln S_i] + U_{\text{MDL}} \quad (1a)$$

$$= - \sum_{il} n_{il} [\delta V_{il} / \delta \ln s_i + (\bar{E}_{il} - V_{il}) \delta \ln \Gamma_{il} / \delta \ln S_i] + U_{\text{MDL}} \quad (1b)$$

where U_{MDL} is the Madelung energy, V is the unit cell volume, C_{il} and V_{il} are the centre and square well pseudopotential of the unhybridised il band, \bar{E}_{il} is the first energy

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moment of the hybridised tl band, n_{tl} is the partial occupation number and Δ_{tl} and Γ_{tl} are bandwidth parameters:

$$\Delta_{tl} = [2m_{tl}S_t^2(S/S_t)^{2l+1}]^{-1} \quad (2a)$$

$$\Gamma_{tl} = 2(2l+1)^2(2l+3)S_t^{-2}(S/S_t)^{2l+1} \quad (2b)$$

where $S = 0.3908$, S_t is the Wigner-Seitz radius (in atomic units) for the t th atom type and m_{tl} is the band mass—proportional to the reciprocal of the square of the wavefunction at the Wigner-Seitz boundary for logarithmic derivative $-l-1$. Therefore equation (1) consists of a band centre and a bond contribution involving the first energy moment (Pettifor 1977, 1978). Whether equations (2a) or (2b) are used depends on whether the band is a 'free-electron-like' s or p band or a narrower p, d or f band (Andersen 1975).

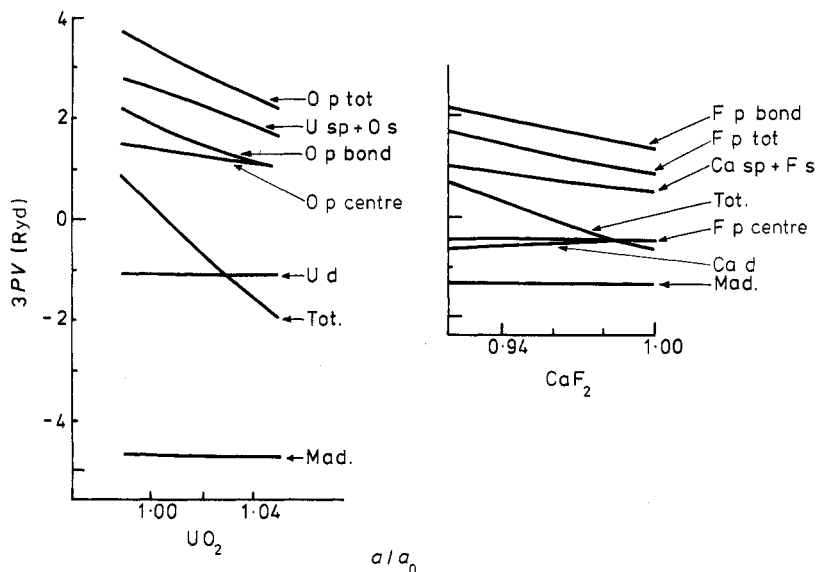


Figure 1. Equations of state of UO_2 and CaF_2 as functions of lattice parameter. a_0 is the experimental equilibrium lattice parameter. The total pressure is analysed by atomic and angular character. The anion p projected part of the valence band is further divided into centre and band contributions.

The symmetry of the fluorite lattice has been described elsewhere (Brooks and Naegele 1977). In the present work the inner cores were frozen during the entire self-consistent calculation and the outer cores were frozen for the final iterations. Some trial calculations were made with atomic starting ionicities between 0 and 2. The converged results did not noticeably depend upon starting ionicity, convincing us that inner frozen cores were quite adequate. Convergence was better than 1 in 10^4 for all of the ASA potential parameters. The relative sizes of the ASA spheres on the two types of atom were adjusted by looking for approximate continuity of potential at the sphere boundaries although the pressures were found not to be rapidly varying functions of relative sphere sizes, and alternative prescriptions have been given by others (Skriver and Andersen 1978, Jarlborg 1979). Thus, although the theory contains many approximations, there are no free parameters. The calculations were semi-relativistic, Darwin and mass velocity

terms being included, but spin-orbit coupling was used only for the f states of uranium.

The results of the calculations for UO_2 and CaF_2 are summarised in table 1 and the equations of state are shown in figure 1. For CaF_2 we obtain a lattice parameter some 5% less than the experimental value. The negative pressure contribution is primarily electrostatic but there is a sizable d contribution. It changes slowly with lattice parameter, i.e. it is soft. The short-range repulsive pressure—which is much harder—is mainly p, with some s character. We now consider what would happen if charge transfer from cation to anion were saturated—the fully ionic limit—and work backwards to explain the results we have obtained. The valence band must then be a filled unhybridised band. In this case only, the charge density is obtained from a trace since the unhybridised p valence bands form a complete set and it is possible to show analytically that the valence charge density is spherically symmetric about the anion. The proof is analogous

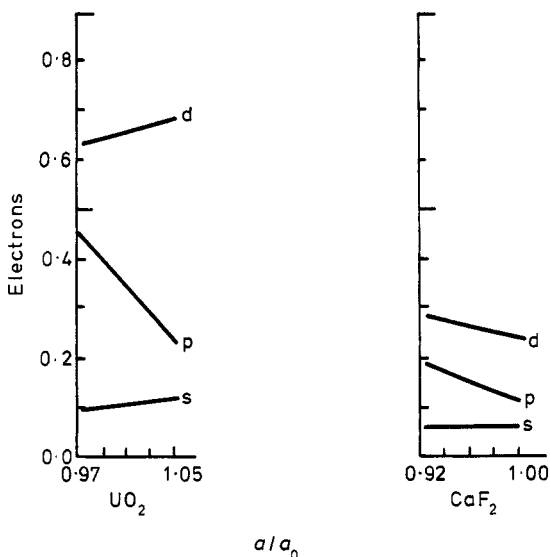


Figure 2. s, p and d character of the electron transfer from anion to cation as a function of lattice parameter.

to that for free atoms where a filled shell is also spherically symmetric. However, this situation may only be realised if the cation core occupies negligible volume. The width of the unhybridised tl band, for an idealised square well density of states, is given by (Anderson 1975, Andersen *et al* 1979)

$$W_{tl} = [12N_t^{-1}M_{tl}^{tl}]^{1/2}\Delta_{tl} \quad (3)$$

in terms of $N_{tl} = N_t(2l + 1)$ where N_t is the number of type t atoms in the primitive cell and M_{tl}^{tl} is an average over the structure constants (Andersen *et al* 1978). The factor inside the square root depends only upon structure and for fluorite structures we calculate $M_{td}^{td} = 229$; $M_{tp}^{tp} = 818$; $M_{Ap}^{Cd} = 3230$ (C = cation, A = anion). Hence

$$W_{Cad} = 1.6 \text{ eV}, \quad W_{Fp} = 4.7 \text{ eV}$$

for the d states of the cation and the p states of the anion respectively. We now introduce weak hybridisation between, for simplicity, just anion p states and cation d states. The shift of the tl band by weak hybridisation with the $t'l'$ band is

$$\delta_{tl} = M_{t'l'}^{tl} \Delta_{tl} \Delta_{t'l'} / [N_{tl}(C_{tl} - C_{t'l'})] \quad (4)$$

and the number of electrons transferred from the entire tl band as a result of weak hybridisation into type t' spheres with local angular momentum l' is given by (Andersen *et al* 1978)

$$N_{t'l'}^{tl} = 2N_{tl} \delta_{tl} / (C_{tl} - C_{t'l'}). \quad (5)$$

For CaF_2 we calculate

$$\delta_d = 0.35 \text{ eV} \quad \delta_p = -0.30 \text{ eV} \quad N_{\text{Cad}}^{\text{Fp}} = 0.24$$

for the shifts of the two bands and for the electron transfer from the filled anion p states to the cation d states. Thus, because the cations are of finite size, the original spherically symmetric valence band must be expanded about the cation centres in the cation sphere producing a cation s, p, d mixture in the valence band. The weak hybridisation limit is not so accurate for s and p states and the full energy band analysis is required. The results of this analysis are shown in figure 2.

The partial pressures may be analysed in a similar manner. Estimates of the pressure may be made from the approximate expressions (Andersen *et al* 1979)

$$\delta C_{tl} / \delta \ln S_t = -n_{tl}(C_{tl} - \phi_t^l) / M_{tl}, \quad \delta V_{tl} / \delta \ln S_t = -(2l + 3)(V_{tl} - \phi_t^l) \quad (6)$$

$$\delta \Delta_{tl} / \delta \ln S_t = -(2l + 1) - 1/m_{tl} + 2(C_{tl} - \phi_t^l) S_t^2 a_{tl}, \quad \delta \Gamma_{tl} / \delta \ln S_t = -2 \quad (7)$$

where

$$\phi_t^l = V_c^t + \epsilon_{xc}^t$$

V_c^t is the value of the Coulomb potential at the Wigner-Seitz sphere and ϵ_{xc}^t is the exchange and correlation energy. It is normally possible to estimate quite well by approximating the change in Δ_{tl} by $2l + 1$, but the second and third terms are required in the present problem since the potential parameters a_p , a_d (0.2) are especially large. V_c^t is always within about 1 eV of zero, even for ionic materials, since the Madelung potential cancels the Coulomb potential of the ion at the sphere boundaries. The d bond pressures may be evaluated immediately since the occupied centre of the d band coincides approximately with the valence band centre; hence $E_{\text{Cad}} - C_{\text{Cad}} = C_p - C_d = -1.07$. The centre term depends upon $\epsilon_{xc}^t = -0.55$ Ryd for CaF_2 , whence (in Ryd)

$$(3PV)_{\text{Cad}}(\text{bond}) = -0.77; \quad (3PV)_{\text{Cad}}(\text{centre}) = 0.16; \quad (3PV)_{\text{Cad}} = -0.61$$

which is in quite good agreement with the computed result (figure 1). Clearly the bond term is negative if \bar{E}_{tl} is less than C_{tl} and, for a filled valence band, in the absence of hybridisation ($\bar{E}_{tl} = C_{tl}$) it vanishes. From the self-consistent calculations we find that \bar{E}_{2p} lies above C_{2p} for both CaF_2 and UO_2 . This is due to hybridisation with the cation outermost core p states and the anion outermost core s state, which produces a large valence band distortion. With \bar{E}_{Fp} from table 1 one finds, using equations (1), (6) and (7),

$$(3PV)_{\text{Fp}}(\text{bond}) = 1.75, \quad (3PV)_{\text{Fp}}(\text{centre}) = -0.55, \quad (3PV)_{\text{Fp}} = 1.2$$

where the centre term is negative because C_{2p} lies below ϵ_{xc} . Again the agreement with

Table 1. Parameters required for an analysis of the partial pressure contributions to the equation of state of UO_2 and CaF_2 at the calculated equilibrium lattice parameter. Energies are in Ryd; radii are in au.

	S_i		m_{it}	C_{it}	V_{it}	E_{it}	ϵ_{xc}	a_{it}	K
U	2.6728	7s	0.24		0.55	-0.33	-0.62	0.08	$3.0 \times 10^{12} \text{ dyn cm}^{-2}$
		7p	0.27		1.81	-0.22		-0.01	
		6d	0.70	0.81		-0.30		0.13	
O	2.8134	2p		-0.32		-0.24	-0.44	0.25	
			4s	0.25		0.32	-0.63	-0.55	
Ca	2.4454	4p	0.26		0.52	-0.58		-0.01	
		3d	1.80	0.46		-0.59		0.19	
		2p	2.88	-0.61		-0.56	-0.40	0.25	

figure 1 is good. The positive pressures of the high lying cation s and p states and anion s state may be understood by observing that V_{it} lies so far above the potential at the Wigner-Seitz sphere boundary that the positive band centre term dominates. This, like the positive valence band pressure, is a core repulsion effect since the square well pseudo-potential of the s and p conduction bands is determined by the cation cores via orthogonality constraints. Again, using table 1, we find

$$(3PV)_{\text{Cap}}(\text{bond}) = -0.6; \quad (3PV)_{\text{Cap}}(\text{centre}) = 1.0; \quad (3PV)_{\text{Ca3p}} = 0.4$$

since $V_{\text{Cap}} - \epsilon_{xc} = 1.0$ Ryd. The calcium s pressure is much less, due to the small s occupation number.

It is remarkable that the d contribution to the pressure has almost the same slope as the Madelung contribution. Also, the sum of the d and Madelung terms ($3PV = -1.95$) is the same as the Madelung contribution that would be obtained if the 0.28 d electrons were transferred to the fluorine ions ($3PV = -2.03$). There appears to be a compensation between the covalent and ionic parts of the bond (at least for very ionic compounds) which we believe underlies the success of the ionic model for calcium fluorite.

The lattice parameters of the actinide oxide series ThO_2 – CmO_2 do not show the parabolic trend typical of the filling of a transition metal band (Friedel 1969), although it is believed that the f shell fills monotonically along the series. Our conclusion is that there is no large f band contribution to bonding in these oxides. Andersen *et al* (1979) have recently shown that it is possible to reduce the bonding contribution of a band by spin polarising although this is most effective for a half-filled band and the Fermi surface may remain in other cases. Since UO_2 is an insulator with—according to the experimental evidence (Lander *et al* 1976)—an integral number (two) of f electrons we have used a simple approximate solution by leaving the f states out of the band structure and treating them as resonant orbitals. Thus they were allowed to contribute to the valence charge density, their number set equal to two, their logarithmic derivative at the uranium sphere boundary made equal to the resonant state value of -4 , but all hybridisation was suppressed—leaving a level that is allowed to relax but not a band. A summary of the results is shown in table 1 and the equation of state is plotted in figure 1(b). The computed lattice parameter is within $\frac{1}{2}\%$ of the experimental value.

We note the increased steepness of the equation of state compared with CaF_2 leading to a much greater bulk modulus (table 1). In fact the bulk modulus is some 40% larger than the experimental value, which may in part be due to the freezing of the extended

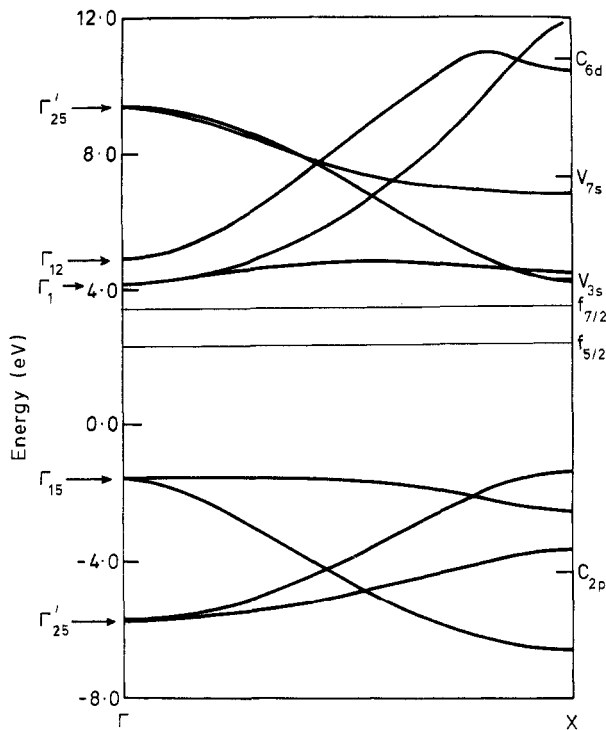


Figure 3. Band structure of UO_2 . The f orbital energies are drawn in the band gap and their spin-orbit splitting is 1.1 eV.

$\text{U}(6p)$ core charge densities. The charge transfer (70%) is farther from saturation than in CaF_2 (75%), as one would expect for an oxide, but is larger than in the 3d transition metal oxides (Andersen *et al* 1979). For the reasons stated above in connection with CaF_2 , one would expect the cohesive properties to be simulated quite well by an ionic model. Table 1 and figure 2 reproduce all the information required to estimate the partial pressure contributions shown in figure 1, and the band structure of UO_2 is shown in figure 3. The f orbital energy falls in the band gap, which is found to be 5.35 eV at the theoretical equilibrium lattice parameter. The occupied part of the band structure is in excellent agreement with XPS and UPS experiments (Veal and Lam 1974, Baer and Schoenes 1980, Naegele 1979, Norton *et al* 1980). The eigenvalue spectrum from cluster calculations (Gubanov *et al* 1977) is similar but with valence bands less than 3 eV wide and a greater energy gap. There have been several recent non-self-consistent bandstructure calculations for fluorites (e.g. Albert *et al* 1977, Starostin and Shepilov 1975) using the Slater X_α method. We find broader valence bands than those obtained by other authors, since the long range p-p interactions are better handled by LMTOS than by normal tight-binding calculations. The experience of the authors (Kelly *et al* 1979) with the X_α method in complex cases such as UO_2 is that by changing X_α it is possible to fit almost any optical spectrum. In particular the f orbital energy may be shifted relative to the valence band by almost 1 Ryd. The self-consistent results therefore fulfil an especially sensitive test without the necessity of any fitting. The optical properties of UO_2 , in particular the band gap, have been under some discussion in the literature (Naegele *et al*

1976, Brooks and Naegele 1977, Schoenes 1978, Naegele 1979, Lachere and Bonnelle 1980). The band gap of 5.3 eV is very close to the 5.0 ± 0.4 eV observed in the recent Bremsstrahlung Isochromat Spectroscopy (BIS) experiment of Baer and Schoenes (1980).

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