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Band structures of NaCl structure uranium compounds

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Résumé. — Des calculs de structure de bande ont été accomplis pour les monpnictures d'uranium ainsi que pour US. Les structures de bande ont été calculées en utilisant la méthode semi-relativiste LMTO. Les largeurs des bandes non hybridées et hybridées issues des électrons f ont été étudiées et une corrélation entre l'augmentation de la largeur de bande f non hybridée et la diminution de la constante de réseau a pu être mise en évidence. Les résultats de la structure de bande complète ont été comparés avec ceux obtenus en photoémission.

Abstract. — Non self-consistent band structure calculations have been made for the uranium monpnictides and for the monochalcogenide US. The band structures were calculated using the semi-relativistic LMTO method. f-electron unhybridized and hybridized bandwidths have been studied, and a correlation between increasing unhybridized f-electron bandwidth and decreasing lattice constant has been found. The full band structure results have been compared with available photoemission data.

1. Introduction. — The actinide elements form a large number of compounds with elements from groups IV, V and VI of the periodic table. Many of these compounds crystallize with the NaCl type crystal structure. We present here the results of electronic band structure calculations on a number of actinide compounds of this type, specifically the uranium monpnictide series UN, UP, UAs, USb and UBi together with the uranium monochalcogenide US. Previous investigations of this kind have been made by Adachi and Imoto [1] and Davis [2] non-relativistically and by Freeman and Koelling [3] fully relativistically.

In order to calculate the electronic structure of these compounds we have used the linear muffin tin

orbital (LMTO) method of Andersen in the atomic sphere approximation [4], in non self-consistent form. The bands obtained are paramagnetic in that no attempt has been made to calculate band splittings due to magnetic interactions and semi-relativistic in the sense that Darwin and mass-velocity shifts are included although spin-orbit interactions have been so far omitted in order to reduce the size of the problem.

2. Exchange approximation and atomic configuration. — In non self-consistent band structure calculations one is faced with a number of uncertainties concerning the modelling of the crystal potential. We begin, then, by investigating the effects

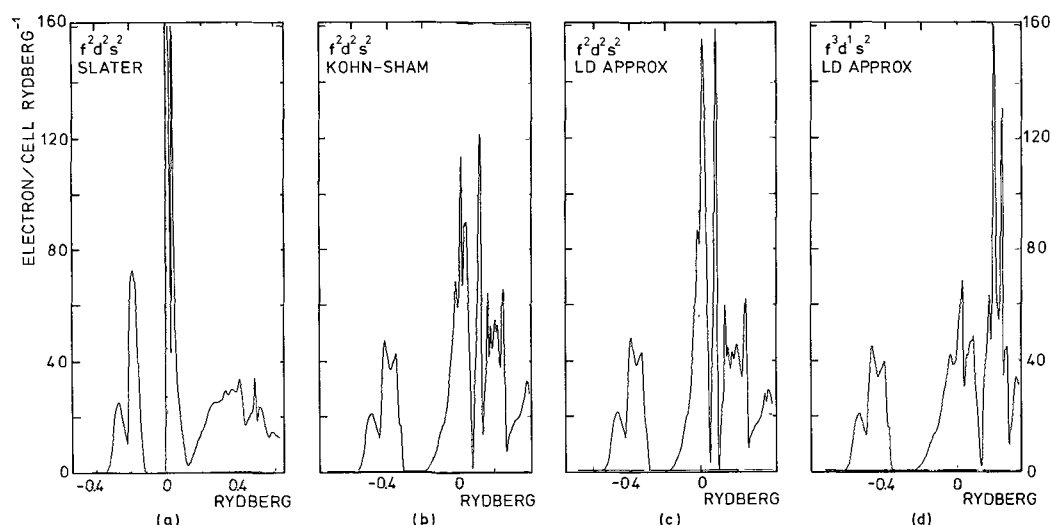


Fig. 1. — Density of states curves for US : In 1a, 1b and 1c a uranium atomic configuration $f^2 d^2 s^2$ has been used with respectively the Slater, Kohn-Sham and LD approximations to the exchange. In 1d the uranium configuration is $f^2 d^1 s^2$ and we have used the LD approximation to the exchange.

on the calculated band structures of two of these *uncertainties*, namely *a*) the choice of exchange approximation, and *b*) the choice of atomic configuration. Figure 1 shows three density of states curves for US calculated from the LMTO eigenvalues at twenty points in the irreducible wedge (1/48th) of the Brillouin zone. In each case we have assumed a uranium free atom configuration of the form $f^2 d^2 s^2$ and the exchange contribution has been calculated using the Slater $\rho^{1/3}$ approximation ($\alpha = 1$) [5], the Kohn-Sham approximation [6] ($\alpha = 2/3$) and a local density (LD) approximation [7] (curves (a), (b) and (c) respectively).

We have observed that reducing the exchange contribution to the model potential in going from the Slater to the Kohn-Sham approximation has little effect on the relative positions of the s and p-like bands, but raises the level of the f-bands relative to the p's by about 0.2 to 0.3 Rydbergs. The f-bands are also apparently broader in the case of the lower exchange.

The LD approximation yields a band structure quite similar to that obtained in the Kohn-Sham approximation.

In figure 1d we show the US density of states in which the assumed uranium atomic configuration is $f^3 d^1 s^2$ with an exchange contribution calculated using the LD-approximation. The principal effect of the extra f-electron is to raise the f-bands on the energy scale (by 0.27 Rydbergs) relative to a largely unchanged s and p band structure. Such sensitivity of the f-band location to the choice of exchange and atomic configuration has been previously observed in NaCl structure actinide compounds by Davis [2] and in the actinide metals by Freeman and Koelling [8].

In compounds in the presence of inequivalent sites, additional configuration changes can occur due to interatomic charge transfer. We have modelled such a charge transfer by calculating the band structure for a $(U^{1+})(S^{1-})$ configuration. The effect was to raise the sulphur p-bands relative to the uranium bands to the extent that the p-band not only touched but compressed the f-band. Similar modelling has been attempted by Freeman and Koelling [3] for UC. More quantitatively reliable information about charge transfer effects will only be obtained from self-consistent band structure calculations.

3. LMTO band structures. — Of the possible combinations of atomic configuration and exchange approximation considered, the atomic configuration $f^2 d^2 s^2$ together with the LD approximation or Kohn-Sham exchange agrees best with the photoemission data of Eastman and Kuznietz [9] for US. A comparison is shown in figure 2. In view of this we have calculated the LMTO band structures for the entire series of uranium monpnictides using the $f^2 d^2 s^2$ configuration and the LD approximation to the ex-

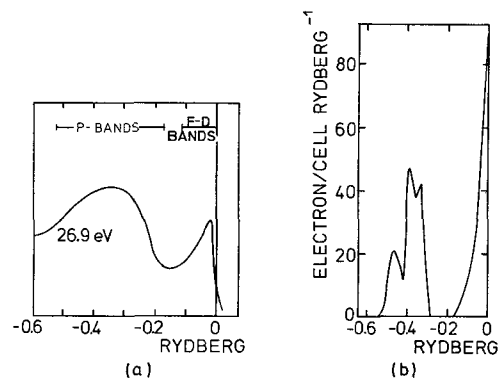


Fig. 2. — 2a shows the photoemission results of Eastman and Kuznietz [9] for US. 2b shows the calculated density of states.

change. Figure 3 shows the band structures for UN, UP and USb along the Γ -X symmetry direction in the Brillouin zone. The three results are broadly similar in structure and in the ordering of the bands on the energy scale. A most striking feature however is the general narrowing of the bands with increasing pnictogen atomic number, an effect observed through the entire pnictide series. As pointed out by Davis [2] this band narrowing may be largely due to the increase of lattice parameter with increasing pnictogen atomic number.

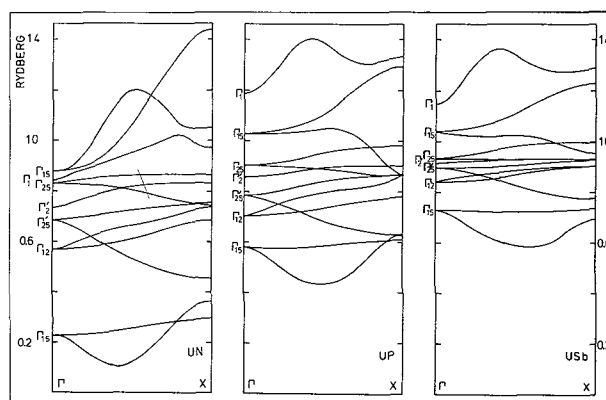


Fig. 3. — The LMTO band structures for UN, UP and USb along the Γ -X symmetry direction.

Of particular significance is the width of the unhybridized 5f bands since this is a measure of the localization of the f-electrons which in turn determines the extent to which correlation effects neglected in band structure calculations might be important. In figure 4 we show the calculated unhybridized 5f bandwidth, along with lattice constant, as a function of pnictogen atomic number. A clear correlation is observed between the variation in lattice constant and f-bandwidth in support of Davis' suggestion [2] that the increasing lattice constant is the predomi-

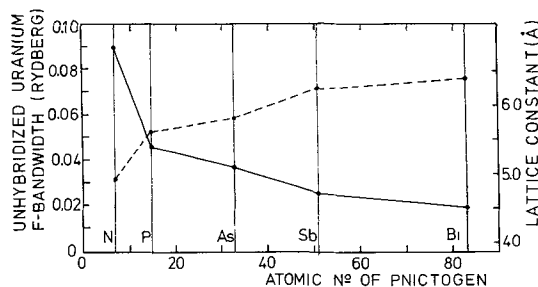


Fig. 4. — Unhybridized uranium f-bandwidth and lattice constant (broken line) as a function of pnictogen atomic number.

nant factor in the f-band narrowing as the pnictogen atomic number is increased.

Finally we note that examination of the normalized LMTO eigenvectors reveals strong hybridization of the uranium 5f with the pnictogen p and d bands in the uranium pnictides considered, as ob-

served by Lander *et al.* [10]. The 5f bands are substantially broadened, particularly on the higher energy side of the unhybridized band centre, by this hybridization.

4. Conclusion. — It has been found that an $f^2 d^2 s^2$ uranium configuration combined with the LD approximation to exchange produces electronic band structures in reasonable agreement with photoemission data on US.

The trends in the pnictide series are similar to those found by Davis [2] although the details of the band structures are often different, a fact that might be explained by the introduction of relativistic effects. A recent comparison of photoemission experiments on USb with the present results is given by Baptist, Naegele and Baer [11].

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