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ARTICLE *in* PHYSICA STATUS SOLIDI (B) · JULY 1979

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A Preliminary Study of the Electronic Structure of Uranium Chalcogenides and Pnictides Using a Relativistic Single-Site Scattering Model

By

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Resonant differential Friedel summands for uranium monopnictides and monochalcogenides are calculated using a fully relativistic single-site scattering model. It is found that relativistic effects are important in discussing the electronic structure of these compounds, especially for those with heavy non-metal atoms. The bonding between the uranium and non-metal constituents is predicted to have considerable covalent character, which increases with atomic number and is particularly important for the heavier group Vb elements. The calculations indicate that the uranium f-electrons form a narrow well-localized band.

Die differentiellen Resonanz-Friedel-Summanden für Uran-Monopniktide und -Monochalkogenide werden mit Hilfe eines voll relativistischen „single-site“-Streumodells berechnet. Wie sich zeigt, sind relativistische Effekte wichtig, um die elektronische Struktur dieser Verbindungen zu charakterisieren. Das trifft insbesondere auf Verbindungen des Urans mit schweren nichtmetallischen Atomen zu. Für die Uran-Nichtmetall-Bindung wird ein erheblicher kovalenter Anteil vorausgesagt. Der kovalente Charakter der Uran-Nichtmetall-Bindung nimmt mit steigendem Atomgewicht zu, besonders in Verbindungen mit Vb-Elementen. Aus den Berechnungen folgt, daß sich die Uran-f-Elektronen in einem engen, wohldefinierten Band befinden.

1. Introduction

The electronic structure of UNMe compounds, where NMe is a group Vb or group VIb element, is of interest not only because of the importance of these compounds in nuclear fuel technology, but also because of their unusual physical properties such as high melting points, extreme hardness, and metallic conductivity (see Dell [1]). A relativistic single-site scattering model, previously employed to discuss VC, NbC, and UC by Weinberger [2], has been used to obtain a qualitative characterization of the electronic structure and a qualitative understanding of the bonding in these compounds. Although the model used here is non-self-consistent and cannot account for neighbour interactions, a recent self-consistent relativistic KKR calculation on UC [3] has indicated that the overall features of the individual phase shifts and their interrelation do not change much in the self-consistency process, and in addition, the changes that do occur are likely to be monotonic down a group.

2. Calculations

Relativistic single-site scattering from a spin-independent muffin-tin potential is described by phase shifts defined as

$$\tan \delta_{\kappa}(E) = \frac{cf_{\kappa}(r, E) j_l(Kr) - K \operatorname{sign}(\kappa) j_l(Kr) g_{\kappa}(r, E)}{cf_{\kappa}(r, E) n_l(Kr) - K \operatorname{sign}(\kappa) n_l(Kr) g_{\kappa}(r, E)}; \quad (1)$$

$$K = (E + c^{-2}E)^{1/2}, \quad E > 0, \quad c = 137.037 \text{ Ryd},$$

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where $j_l(Kr)$ and $n_l(Kr)$ are spherical Bessel and Neumann functions, and $f_\kappa(r, E)$ and $g_\kappa(r, E)$ are the usual large and small component of the solutions of the radial Dirac equation [4]. The quantum numbers κ , l , and \bar{l} are defined as follows:

$$\left. \begin{aligned} \kappa &= \begin{cases} -l-1; & j = l + \frac{1}{2}, \\ l; & j = l - \frac{1}{2}, \end{cases} \\ l &= \begin{cases} \kappa; & \kappa > 0, \\ -\kappa-1; & \kappa < 0, \end{cases} \quad \bar{l} = \begin{cases} \kappa-1; & \kappa > 0, \\ -\kappa; & \kappa < 0. \end{cases} \end{aligned} \right\} \quad (2)$$

The relativistic single-site differential density of states is then given by

$$\frac{dN(E)}{dE} = \frac{dN_0(E)}{dE} + 2\pi^{-1} \sum_j (2j+1) \frac{d\delta_\kappa(E)}{dE}, \quad (3)$$

Table 1

Lattice parameters, exchange parameters, muffin-tin radii, and constant potentials

UNMe	NMe at. No.	lattice parameter (at. units)*	α_{NMe}	R_{U} (at. units)	R_{NMe} (at. units)	constant potential (Ryd)
UN	7	9.222	0.75118	2.639171	1.971824	-1.647819
UP	15	10.564	0.72569	2.822997	2.458858	-1.264293
UAs	33	10.904	0.70630	2.900100	2.551834	-1.183226
USb	51	11.698	0.70029	3.035781	2.812999	-1.028672
UBi	83	12.019	0.69265	3.114591	2.894819	-0.961427
UO	8	9.298	0.74367	2.703573	1.945217	-1.558998
US	16	10.356	0.72460	2.787223	2.390697	-1.287648
USE	34	10.866	0.70606	2.889816	2.543219	-1.159599
UTe	52	11.641	0.70007	3.011843	2.808592	-1.018791

$\alpha_{\text{U}} = 0.69152$, U at. No. = 92.

*) Values taken from Wyckoff [6].

Table 2

Peak widths and line separations (in Ryd)

UNMe	U-d ^{3/2} width	U-d ^{5/2} width	U-f ^{5/2} width	U-f ^{7/2} width	U-f ^{5/2} -NMe-p ^{1/2} separation
UN	0.76	0.85	0.056	0.071	0.73
UP	0.49	0.57	0.020	0.029	0.43
UAs	0.42	0.49	0.015	0.022	0.37
USb	0.31	0.37	0.007	0.012	0.28
UBi	0.28	0.33	0.004	0.008	0.26
UO	0.71	0.79	0.046	0.059	0.80
US	0.52	0.59	0.024	0.033	0.53
USE	0.42	0.51	0.015	0.023	0.44
UTe	0.32	0.38	0.008	0.013	0.33

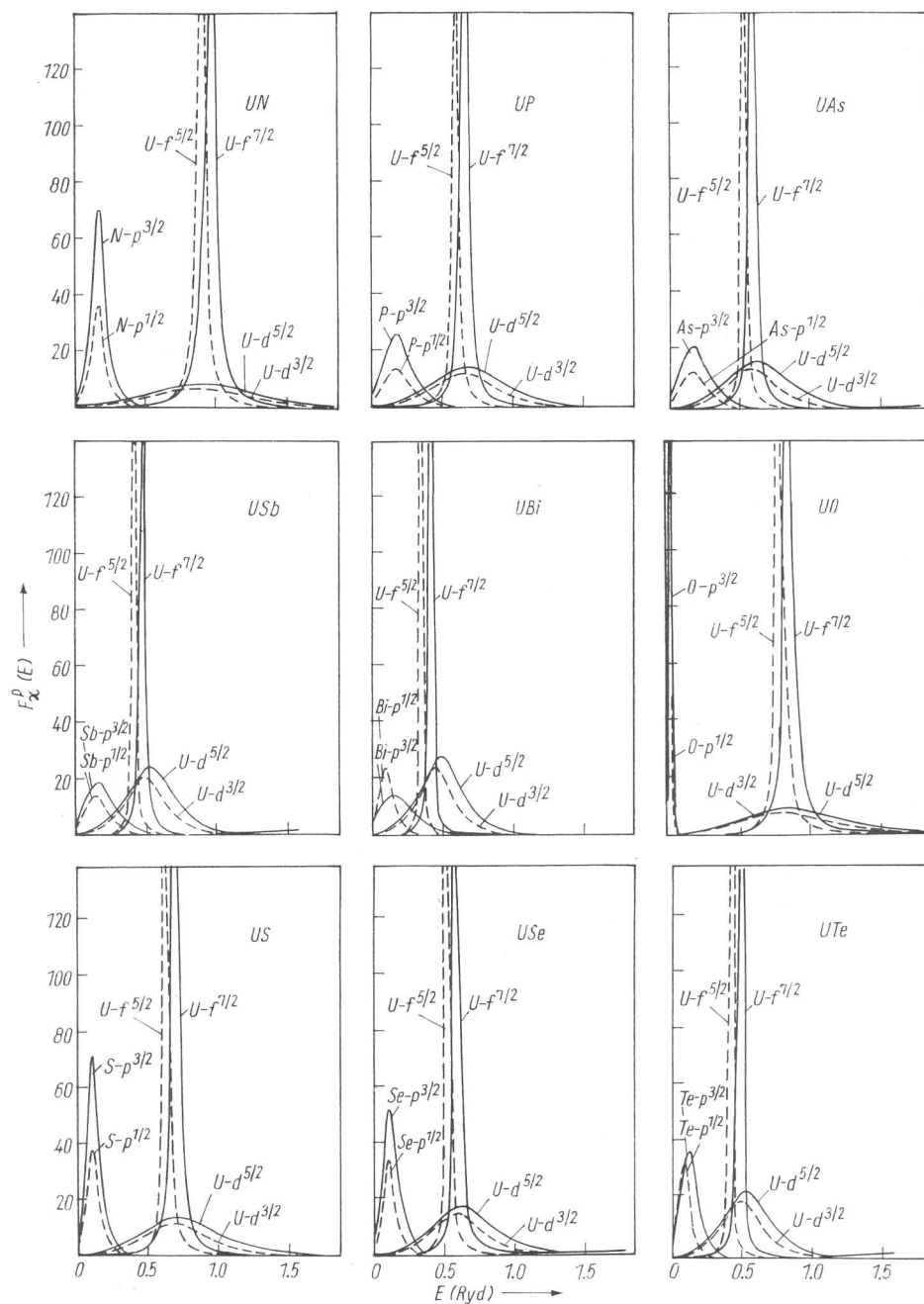


Fig. 1. Resonant α -like Friedel summands (4) for uranium and the non-metal in UN, UP, UAs, USb, UBi, UO, US, USE, and UTe

where $dN_0(E)/dE$ is the free-electron contribution and the second term is the differential Friedel sum made up of components

$$f_j(E) = (2j + 1) \frac{d\delta_j(E)}{dE}. \quad (4)$$

The Friedel summands given in (4) have been calculated for the compounds UN, UP, UAs, USb, UBi, UO, US, USe, and UTe, and the results for resonant scattering states are shown in Fig. 1. The potentials for use in the radial Dirac equation were generated from relativistic atomic charge densities calculated with the X_α -approximation [5] by superimposing the charge densities of four shells of neighbours. The atomic sphere radii were calculated from the intersection of the potential curves of the two constituent atoms in the (111) direction. The values of the muffin-tin radii were taken as the nearest radial grid points below the sphere radii. Table 1 gives the lattice parameters, exchange parameters, muffin-tin radii, and constant interstitial potentials for all the compounds studied here. In Table 2 the linewidths and peak separations derived from Fig. 1 are given.

3. Discussion

The first point to emerge from Fig. 1 is that relativistic effects are important for all compounds studied. The $p^{1/2}$ - $p^{3/2}$ peak separation of the non-metal component increases monotonically down the group for both group V b and group VI b, the effect being particularly marked for bismuth. The qualitative change at Bi, caused by a jump in atomic number of 32 (almost an arsenic nucleus), results in the $p^{1/2}$ - $p^{3/2}$ separation doubling from 30 mRyd for antimony to 60 mRyd for bismuth. In addition, the lineshapes of the two p-resonances differ considerably for both the Friedel summands and the phase shifts.

The linewidth of the uranium d- and f-levels decreases down a group, due to the increasing confinement of charge in the U muffin-tin sphere. The f-levels are not affected as much as the d-electrons, since they are less involved in bonding with the non-metal. There is no clear trend in the linewidths of the non-metal p-resonances, although the second-row elements (N and O) have much sharper resonances than the heavier elements of the same group.

The overlapping of the uranium and the non-metal resonances suggests that there will be extensive covalent bonding in both the chalcogenides and the pnictides. As one can see from Fig. 1 and Table 2, the p-d overlap increases down the group for both group V b and group VI b, being especially marked for the former. The covalent bonding between the non-metal p- and uranium f- and d-levels is expected to increase as the non-metal component becomes heavier, as the decreasing sharpness of the p-resonances in going down a group indicates. Since the p-d and p-f overlap is more marked in group V b than group VI b, the pnictides are expected to be rather more covalent than the chalcogenides, with typical non-metal bands being narrower in the latter case. The f-electrons are likely to form a narrow band, which will not be completely localized in the uranium sphere since the f-resonance width does depend on the non-metal component, though the resonances are very sharp and the $f^{5/2}$ - $f^{7/2}$ separation is constant and independent of the non-metal component.

It should be noted that the discussion above is qualitative in character and cannot give quantitative statements on the electronic structure or on bonding in these compounds. However, single-site scattering models, owing to their close relationship with multiple-scattering approaches, are suited to give a comprehensive characterization of the electronic structure to be expected from tedious self-consistent relativistic band structure calculations. In this sense they are extremely useful to discuss trends for groups of compounds such as the uranium chalcogenides and pnictides.

Acknowledgements

All computations were performed using the facilities of the Computing Centre of the Technical University of Vienna. We also wish to thank Prof. A. Neckel for his interest in this work. One of us (C.P.M.) gratefully acknowledges a Research Fellowship from the Royal Society (London) under the European Science Exchange Program.

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(Received March 14, 1979)