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Structural stability, electronic structure and f hybridization of PuM_3 and Pu_3M (M = Ge, Sn, Pb) intermetallic compounds

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Abstract

The ground-state equilibrium properties, the electronic structure and the structural stability of PuM_3 and Pu_3M (M = Ge, Sn, Pb) compounds are studied using density functional theory in the presence and in the absence of spin–orbit coupling (SOC). The calculated lattice parameters are in good agreement with the experimental values. The results for the electronic density of states (DOS) show that the Fermi level is situated in a "pseudogap" as a common feature for all these compounds, similar to what has been found for the PuTe system. The reason for the creation of the "pseudogap" is due to the strong pdf hybridization. The most unusual feature in the DOS of Pu_3M compounds is the presence of a gap at the interval from –7.5 to −4 eV, which is absent in the DOS of $PuGe_3$ and $PuSn_3$ and is smaller for $PuPb_3$. In addition to that there is a strong hybridization between Pu 6d and M p orbitals in both PuM_3 and Pu_3M compounds. Also the cohesive energy calculations show that Pu_3M structures are more stable than PuM_3 structures.

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1. Introduction

The physics of plutonium and its compounds is mainly determined by two competing factors, one the degree of the itinerancy of the 5f electrons associated with the chemical bonding in the compound, and the other the on-site localization of these electrons. Pu is the last element in actinide series in which the 5f electrons still have some contributions in the bonding, while in the next element, Am, 5f electrons retract from bonding and become localized. The degree of itinerancy of the 5f electrons is quite sensitive to small variations in the chemical environment. Pu compounds in which Pu–Pu distance is greater than the Hill critical spacing [1] (3.40 Å for Pu) favor 5f localization, because beyond this distance the direct 5f–5f overlap of Pu atoms is too weak to enable 5f band formation. On the other hand, the bonding interaction between Pu and ligand atoms favors hybridization between Pu 5f, and the p states of the ligand atoms, and thus could itself result in 5f delocalization. Much work has already been done in order to understand the behavior of 5f electrons in plutonium compounds [2–4].

The binary PuM_3 and Pu_3M series (whit M = some elements from Group IIIA or IVA), exhibit a relatively wide variety of physical properties [4–6]. They all have the $L1_2$ Strukturbericht [7] (Cu_3Au) structure, in which Au and Cu atoms are located, respectively, on the vertices and on the face centers of the cubic unit cell. $PuSn_3$ is reported to be a temperature-independent paramagnetic compound [5]. And to our knowledge there is no experimental report on the magnetic properties of $PuPb_3$, $PuGe_3$ and any of Pu_3M compounds. Recently we have reported on the calculated electronic structure and electric field gradient in Pu_3Sn and $PuSn_3$ compounds [6] and have found that there is a strong hybridization between Sn 5p with Pu 5f and Pu 6d orbitals in both compounds.

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In this work, we present the cohesive energy calculated for all PuM_3 and Pu_3M (M = Ge, Sn, Pb) compounds. For this, we have first calculated the band structure of Pu_3Ge, $PuGe_3$, Pu_3Pb and $PuPb_3$; and for $PuSn_3$ and Pu_3Sn, we have used the results presented in our previous work [6].

In Section 2 the details of the electronic structure calculations are presented. Section 3 contains the results and their discussion. A brief conclusion of this work is given in Section 4.

2. Computational details

The electronic structure and total energies are calculated using the all-electron full potential linearized augmented plane wave (FP-LAPW) method [8,9] within the density functional theory (DFT) with the generalized gradient approximation (GGA) [10] for the exchange-correlation energy functional. The unit cell is partitioned into spheres (with a muffin-tin radii R_{MT}) centered at the atomic positions and an interstitial region. In the latter, the Bloch wave functions are expanded using plane waves that are augmented by atomic-like functions (numerical radial functions multiplied by spherical harmonics) inside the spheres [9,11]. The starting radial basis functions inside the atomic spheres were obtained as scalar-relativistic solutions of the Dirac equation in the spherical part of the effective potential. The SOC was included subsequently via a second variational step [12]. In the first step of this approach, the scalar relativistic part of the Hamiltonian is diagonalized on a basis adopted for each of the spin projections separately. In the second step the full Hamiltonian matrix is constructed on the basis of eigenfunctions of the first step Hamiltonian. Only a limited number of eigenstates of the first step Hamiltonian is necessary to construct the basis used in the second step. The size of the second step basis is controlled by an energy cutoff. We have neglected the SOC in the interstitial region. And in the atomic spheres only the spherical part of the effective potential has been considered for it.

In order to obtain better flexibility in the radial basis functional and to decrease the basis set size, new local orbitals (APW + lo) for 5f partial waves of Pu are included. The basis sets are standard and include 6s, 6p, 7s, 7p, 6d and 5f partial waves for Pu, and 3d, 4s, 4p for Ge, and 4d, 5s, 5p for Sn, and 4f, 5d, 6s, 6p for Pb. The electronic states with energy of at least 7.5 Ry below the Fermi-energy were considered as core states. For Pu the muffin-tin radius was chosen as $R_{Pu} = 2.7$ a.u., while for M a radius of $R_M = 2.4$ a.u was used. The maximum angular momentum quantum number as a cutoff for expanding the Kohn–Sham wave functions in terms of lattice harmonics inside the muffin-tin spheres was confined to $L_{max} = 10$. The wave functions in the interstitial region were expanded in plane waves with a cutoff of $K_{max} = 7/R_M$. The charge density and the potential were Fourier expanded in the interstitial region up to $G_{max} = 16$, while they were expanded inside the atomic spheres, in crystal harmonics up to $L_{max} = 6$. During the iterations to self-consistency, the Brillouin zone was sampled using 120 special k points in the irreducible wedge of the zone.

3. Results and discussion

3.1. Ground-state equilibrium properties

We have determined the equilibrium lattice parameter (a_{eq}), bulk modulus (B_0) and its pressure derivation (B'_0) of PuM_3 and Pu_3M compounds (with M = Ge, Pb) by minimizing the total energy curves that have been calculated using the GGA [10] in density functional formalism. The calculated total energy vs. volume has been fitted to the standard Murnaghan equation of state [13]. This procedure has been carried out both in scalar-relativistic (without SOC) and in full relativistic (with SOC) FP-LAPW method. The results are given in Table 1 together with the available experimental results and the results for $PuSn_3$ and Pu_3Sn compounds, from our previous work [6] for comparison. We have found that the equilibrium lattice parameters calculated in GGA + SOC are in better agreement with the available experimental values compared to GGA. It is worth mentioning that from the E vs. unit cell volume curves (which for the sake of brevity we have not been included here) it may be seen that the SOC reduces the total energy.

For Pu_3Pb, the agreement between our unpolarized calculated lattice parameter with the experimental value is rather poor; we have also performed the calculation in (ferromagnetic) spin-polarized state, which has led to major improvement. The results are also given in Table 1.

To our knowledge there is no experimental report on the lattice parameter of Pu_3Ge. Our calculated result for this compound (which is the first report) fits well within the expected trend, namely the decreasing of the lattice parameter with the decrease in the size of M atom [14].

We have found that the bulk modulus for both series PuM_3 and Pu_3M (M = Ge, Sn, Pb) decreases with increasing atomic number in a column of the periodic table. Similar behavior is also reported for NpX_3 and UX_3 (X = Ge, Sn) [14]. Comparing the values of the bulk modulus for $PuGe_3$ ($PuSn_3$), $NpGe_3$ ($NpSn_3$) and UGe_3 (USn_3) compounds, we have found that they fit properly in the expected inequalities B_0 (UGe_3) > B_0 ($NpGe_3$) > B_0 ($PuGe_3$), and B_0 (USn_3) > B_0 ($NpSn_3$) > B_0 ($PuSn_3$) [15]. It is also seen that the calculated bulk modulus of Pu_3M compounds at ambient pressure is greater than that of the corresponding PuM_3 compound.

3.2. Density of states

The partial density of states (DOS) is calculated by tetrahedron method [16]. These are shown in Figs. 1–4 for $PuGe_3$, Pu_3Ge, $PuPb_3$ and Pu_3Pb respectively. The most prominent difference in the DOS curves for Pu_3M and the corresponding PuM_3 compounds is the presence of a gap at