Electronic properties of isostructural ruthenium and osmium silicides and germanides

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Electronic band structure calculations of Nowotny ''chimney-ladder'' isostructural ruthenium and osmium silicides and related germanides have been performed by the linear muffin-tin orbital method within the local density approximation. Both silicides have been found to be direct gap semiconductors with energy gaps of 0.41 and 0.95 eV in Ru_2Si_3 and Os_2Si_3, while the band gaps in the germanides have a competitive indirect-direct character with gaps of about 0.3 and 0.9 eV in Ru_2Ge_3 and Os_2Ge_3, respectively. [S0163-1829(99)05347-3]

I. INTRODUCTION

In recent years much attention has been given to semiconducting transition metal silicides due to their practical importance in new silicon-compatible devices.[1] Most important are those, which can be used for optoelectronic and thermoelectric applications. However, in comparison with well-investigated chromium and iron disilicides, there is a lack of reliable data for other compounds.

Ruthenium silicide Ru_2Si_3 is reported to be one of the promising materials for thermoelectric applications.[2] From the experimental point of view it is revealed to be a semiconductor in both modifications: low-temperature (LT) orthorhombic phase and high-temperature (HT) tetragonal one with band gaps of 0.7 and 0.44 eV, respectively.[3] Recent experimental estimations based on resistivity measurements show larger values of about 1.0 eV (Ref. 4) for the LT phase. Theoretical studies of the electronic properties of Ru_2Si_3 have been carried out by several groups. *Ab initio* electronic band-structure calculations, where the full-potential linearized augmented plane wave[5] and the linear muffin-tin orbital[6] (LMTO) methods have been applied, clearly indicate that Ru_2Si_3 is a direct gap semiconductor with an energy gap of about 0.42 eV. Unfortunately, there is almost no data for ruthenium germanide Ru_2Ge_3. From resistivity measurements the energy gap values of 0.52 and 0.34 eV have been found for the LT and HT phases, respectively.[3] The information about electronic properties of osmium silicides and germanides is practically absent except that according to resistivity measurements the band gap of Os_2Si_3 was estimated to be of 2.3 ± 0.2 eV.[7] Unfortunately, no data of the gaps based on precise optical experiments are available up to now.

The knowledge of the electronic structure of these four isostructural compounds is of great importance because of their potential applications in electronics and thermoelectrics and due to possible modifications of their semiconducting properties when ternary and quaternary compounds are considered. Recently we performed such a study for the isostructural iron and osmium disilicides.[8,9] In this paper, we present the band structures and densities of states obtained for the ruthenium and osmium silicides and germanides.

II. MODEL AND METHOD OF CALCULATION

A. Crystal structure

The isostructural Ru_2Si_3 and Ru_2Ge_3 as well as Os_2Si_3 and Os_2Ge_3 belong to a large family of transition-metal (TM) compounds known as Nowotny ''chimney-ladder'' or the so-called defect-type $TiSi_2$ structures.[10] In the LT phase they have an orthorhombic crystalline lattice with the $Pbcn$ space group. The calculations were performed using the experimental lattice parameters,[10] which are shown in Table I. The primitive unit cell of $TM_2B_3(TM = Ru, Os, B = Si, Ge)$ is rather big and complex. It contains a total of 40 atoms (16 TM and 24 B atoms). Both TM and Si (or Ge) atoms are grouped into six sets ($TM1$, $TM2$, $TM3$, Si1, Si2, and Si3) of crystallographically inequivalent sites. TM atoms occupy close to ideal positions as titanium atoms in four unit cells of the $TiSi_2$ prototype, where two unit cells are stacked one on top of the other and then doubled in the horizontal direction. But the ideal $TiSi_2$ structure has four silicon atoms in a centered rectangular, which is opposite to the TM_2Si_3 structure that has only three silicon atoms. In order to accommodate for the related Si (Ge) vacancies in the structure the remaining Si (Ge) atoms are not in the plane as

TABLE I. Lattice parameters (nm) of ruthenium and osmium silicides and germanides (Ref. 10).

	a	b	c
Ru_2Si_3	1.1057	0.8934	0.5533
Ru_2Ge_3	1.1436	0.9238	0.5716
Os_2Si_3	1.1124	0.8932	0.5570
Os_2Ge_3	1.1544	0.9281	0.5783

in the prototype. They are shifted out of the generating plane to find ideal positions between the *TM* atoms.

B. Method

For the electronic property simulation we employed the self-consistent LMTO method in its scalar relativistic form with combined correction terms described in detail elsewhere.[11] Exchange and correlation contributions to both atomic and crystalline potentials were included using the local density approximation (LDA) of von Barth-Hedin.[12] In the calculation we used basis functions including angular momenta up to $l=2$ for all the elements entering the system. As it was shown earlier for d-metal silicides[13] the inclusion of virtual f states did not influence much on the resulting band spectrum in the energy region of interest. This is due to the fact that the contribution of f states in this region is negligible. They define high energy states of the conduction band far above the Fermi level. The results obtained within the LMTO method are crucially sensitive to the choice of the atomic-sphere radii ratios. It is not a trivial task if one deals with a lot of chemically inequivalent atoms in the unit cell. But making the choice properly one can get the results not worse in accuracy that could be obtained within other LDA schemes. The electronic property calculations of iron disilicide, which have been performed by LMTO and full potential LAPW methods (which may be nowadays the most powerful and accurate approach within LDA and as a result is not so sensitive to the choice of atomic sphere radii), gave similar band structures with the difference of main gaps at higher symmetry points of some tens meV.[8,14]

Unfortunately, there are no exact rules how to choose atomic-sphere radii ratios for the LMTO method. One often used criterion is the condition of a minimum electron pressure of the system calculated, which is directly related to the sum of the one-electron energies and at zero temperature equals to the volume derivative of the total energy.[11] Practically, zero of electron pressure (minimum of the total energy) corresponds to the structure at equilibrium volume. But we did not perform optimization of the lattice constant, we just used the experimentally determined set of the structural parameters. Therefore, we have an electron pressure which is not equal to zero (usually LDA underestimates lattice constants). In this case the criterion of minimum pressure is the best possible choice because an incorrect ratio will result to a large electron pressure. It is not simple to minimize a function of six variables taking into consideration six chemically
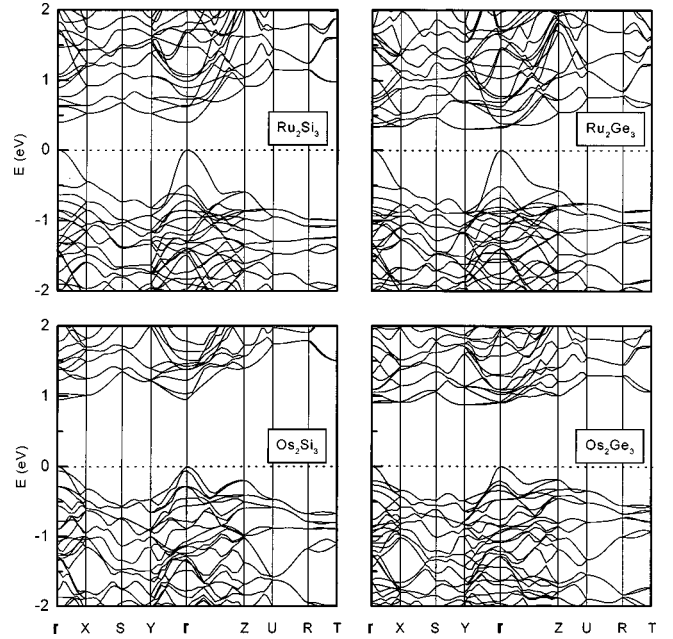

FIG. 1. Band structures of ruthenium and osmium silicides and germanides along some high-symmetry directions. Zero of the energy scale corresponds to the Fermi energy.

inequivalent atom types for these isostructural compounds. But here we conventionally divided them only into two types: metal and nonmetal atoms.

Total and projected densities of states have been calculated by the tetrahedron method.[15] First iterations of a self-consistent procedure were performed using the 27 k-point set. Then it has been continued on the grid of 125 k points uniformly distributed in the irreducible part of the orthorhombic Brillouin zone till complete self consistency was achieved. Further increase of the k points' number does not lead to any noticeable changes in the eigenvalues. For the band structure representation we choose up to 30 k points within the segments along the high-symmetry directions and the final density of states were calculated using 256 k points in the irreducible part of the Brillouin zone.

III. RESULTS AND DISCUSSION

A. Electronic band structures

Fragments of the calculated band structures of the ruthenium and osmium silicides and germanides along the high-

TABLE II. Eigenvalues (eV) of the top of the valence (Ev) and bottom of the conduction (Ec) bands at the high-symmetry points of the orthorhombic Brillouin zone.

		Γ	Y	S	X	Z	U	R	T
Ru$_2$Si$_3$	E_v	0.00	−0.81	−0.73	−0.45	−0.59	−0.83	−0.98	−1.00
	E_c	0.41	0.53	0.68	0.53	0.91	1.15	1.16	0.98
Ru$_2$Ge$_3$	E_v	0.00	−0.88	−0.77	−0.53	−0.57	−0.75	−0.87	−0.85
	E_c	0.33	0.31	0.48	0.35	0.55	0.76	0.78	0.67
Os$_2$Si$_3$	E_v	0.00	−0.47	−0.57	−0.32	−0.20	−0.47	−0.67	−0.67
	E_c	0.95	1.22	1.35	1.01	1.40	1.74	1.79	1.50
Os$_2$Ge$_3$	E_v	0.00	−0.49	−0.49	−0.34	−0.19	−0.34	−0.56	−0.57
	E_c	0.91	0.88	1.06	0.92	1.00	1.29	1.28	1.07

symmetry directions of the Brillouin zone are presented in Fig. 1. The systems contain 224 valence electrons each and the gap is being formed between the 112th and 113th bands. Corresponding eigenvalues of the valence/conduction band maximum/minimum at the high-symmetry k points are presented in Table II.

The band structures of Ru_2Si_3 and Os_2Si_3 are characterized by a direct transition at the Γ point of the Brillouin zone. It is worthwhile to note that there is only one couple of distinct extrema in the band structure obtained. Our gap value of 0.41 eV correlates very well with the results of other theoretical calculations.[5,6] The band spectra of Ru_2Si_3 and Os_2Si_3 are quite similar. One of additional features is that in osmium silicide the 112th band moved down to the 111th band so that the difference between the first and the second direct transitions at the Γ point constitutes less than 0.1 eV, while in the ruthenium silicide this difference is about 0.5 eV.

Unlike the situation in the silicides, where a direct transition at the Γ point exists, an indirect character of the band structures of Ru_2Ge_3 and Os_2Ge_3 has been revealed. As in the silicides the maximum of the valence band is located at the Γ point, while the minimum of the conduction one is shifted to the Y point. The lowest conduction band near the Y point is almost flat in the Γ-Y and Γ-X directions. For the ruthenium germanide the band gap value is of 0.31 eV and the direct transition energy at the Γ point is about 0.33 eV. For the osmium germanide the values are 0.87 and 0.91 eV, respectively for indirect and direct band gaps. As the difference of direct and indirect band gaps in the germanides is very small (some tens of meV), which is comparable with the LMTO method's accuracy, it is difficult to say unambiguously about the nature of the gap, so it makes sense to speak about competitive indirect-direct gap character. If the band spectra of the silicides and germanides are compared, one can see that the valence band behavior near the Fermi energy (i.e. band's dispersion, relative to each other position etc.) remains practically the same and the main differences take place in the conduction band, where eigenvalues at the Y point are shifted down on the energy scale for the germanides as compared to the silicides.

Table III summarizes orbital compositions of the extreme states in the valence and the conduction bands of all isostructural compounds considered. The eigenstates of the conduction-band minima at the Γ and Y points are mainly defined by d-like states of metal atoms. An interesting feature is that the contribution of Ru3 (Os3) d states at the Γ point is about 60% while d states from the two other types of metal atoms are much smaller participating. The same situation was also observed in Ref. 5. The very different composition has the valence band maximum at the Γ point. The appropriate eigenfunctions contain less than 10% of metal d states with large admixture of p states of metal (about 20%) and Si or Ge (about 60%). About 80% of metal d states defines the minimum of the conduction band at the Y point in both ruthenium and osmium germanides. The analysis of the 111th band eigenstates at the Γ point shows the domination of metal d states (about 70%) in all compounds. The eigenstates are close in their compositions to the conduction band minimum and differ from the valence-band maximum at this point.

TABLE III. Projected occupancies (in %) of the states around the gap at some high-symmetry points. The sum of the contributions of TM s and Si (Ge) s and d states constitutes less than 20%.

Band N		Y 113	111	Γ 112	113
			Ru_2Si_3		
Ru1	p	1	2	8	0
	d	5	37	6	7
Ru2	p	1	0	3	0
	d	2	11	2	5
Ru3	p	1	5	7	0
	d	51	20	3	61
Si1	p	3	4	11	2
Si2	p	15	5	26	9
Si3	p	10	8	14	6

Band N		Y 113	111	Γ 112	113
			Os_2Si_3		
Os1	p	0	0	6	0
	d	24	29	3	2
Os2	p	0	0	4	0
	d	5	21	2	2
Os3	p	0	5	8	1
	d	48	22	1	48
Si1	p	2	2	15	2
Si2	p	4	3	28	17
Si3	p	5	3	14	11

Band N		Y 113	111	Γ 112	113
			Ru_2Ge_3		
Ru1	p	0	1	3	0
	d	33	15	1	8
Ru2	p	0	0	3	0
	d	7	38	2	5
Ru3	p	0	3	6	0
	d	44	16	4	64
Ge1	p	3	4	13	2
Ge2	p	2	4	34	7
Ge3	p	5	7	13	4

Band N		Y 113	111	Γ 112	113
			Os_2Ge_3		
Os1	p	1	1	3	0
	d	38	23	1	7
Os2	p	0	0	5	0
	d	2	25	2	4
Os3	p	0	5	10	0
	d	40	24	10	67
Ge1	p	2	3	13	1
Ge2	p	2	4	29	8
Ge3	p	5	5	11	4

FIG. 2. Total and projected density of states in Ru_2Si_3 and Os_2Si_3.
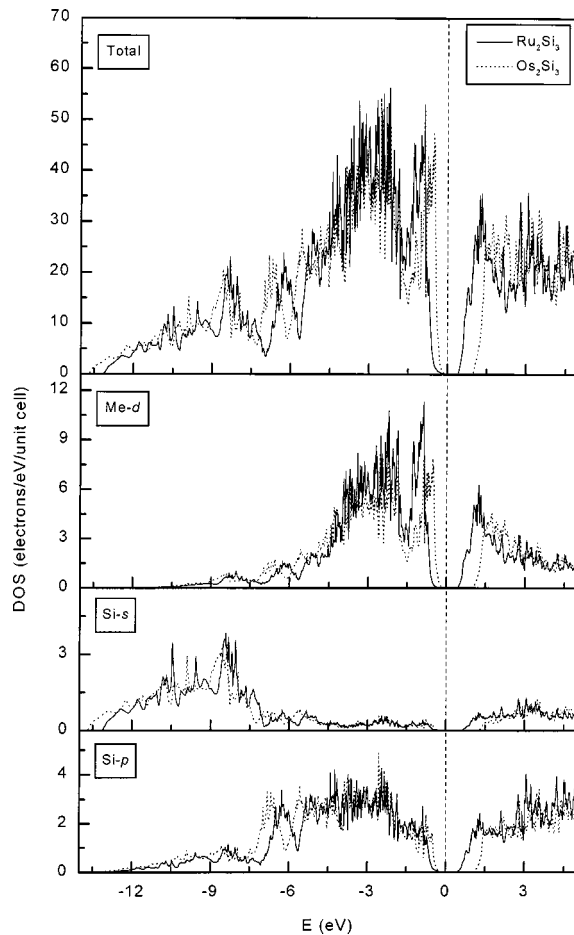

FIG. 3. Total and projected density of states in Ru_2Ge_3 and Os_2Ge_3.

As the orbital composition of the valence-band maximum and conduction-band minimum at the Γ point for Ru_2Si_3 and Os_2Si_3 (which corresponds to direct transition) consists of metal d with the strong admixture of p states, one can expect the oscillator strength to be of sizable magnitude and these direct-gap semiconducting compounds may have interesting and promising optical properties.

B. Densities of states

The total densities of states (DOS) and projected densities of states (PDOS) versus energy for the ruthenium and osmium silicides and germanides are shown in Figs. 2 and 3, respectively. The PDOSs of chemically inequivalent types of metal or silicon/germanium atoms are practically the same, so we plotted them only for the first type of atoms. The valence band of the compounds extends down to about -13 eV. The first energy region from the bottom of the valence band up to about -7 eV is attributed to practically pure silicon/germanium s-like states due to Si-Si (Ge-Ge) s-s hybridization. The second wide region arises between about -7 eV to about 0 eV from the direct Ru-Ru $4d$-$4d$ (Os-Os $5d$-$5d$) overlap forming the d-d bonding and antibonding states. These states are broadened by the hybridization with the Si $3p$ (Ge $4p$) states, which are spread over the wide-energy region from -7 eV to about 5 eV. For all the compounds considered the common feature of the DOS's is the
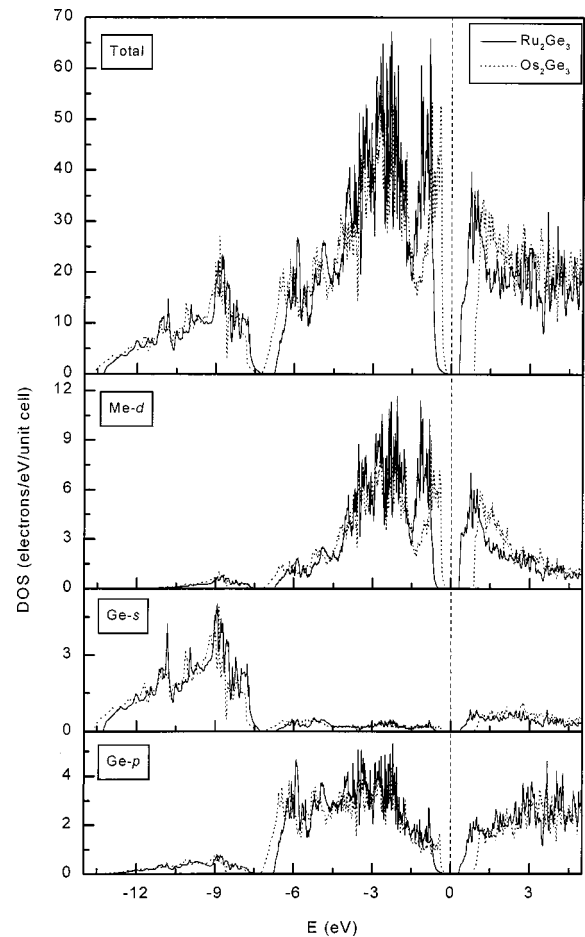
domination of the TM d states. As the TM atomic number is increased the center of gravity of the Si $3p$ (Ge $4p$) states moves to the higher binding energy following of the corresponding shift of the d metal states. The similar behavior was observed for a group of $3d-5d$ TM silicides both theoretically and experimentally.[16] In general, the characters of the DOS's and PDOS's for the ruthenium and osmium silicides and germanides are quite similar over the energy region considered. One of the differences is that, in the case of the germanides, there is a distinct gap within the valence band near -7.0 eV just between the region of Ge s states and the one composed by bonding germanium p and metal d states (Fig. 3). For the silicides we have obtained only a considerable drop of the DOS's in this energy region (Fig. 2). The results for Ru_2Si_3 are in good agreement with the general DOS and PDOS's behavior observed in other theoretical calculations.[5]

C. Band-gap related problems

It is necessary to note that for the compounds analyzed there are some discrepancies in the energy gap values theoretically predicted and experimentally measured. E.g., for Ru_2Si_3 our results as well as other LDA calculations[5,6] give the gap value of about 0.4 eV versus experimental values of 0.7 (Ref. 3) and about 1.0 eV.[4] In order to explain this fact one has to account for the following reasons. It is well known that, normally, band-gap values calculated within the

LDA should be underestimated with respect to the ones derived from experiments. The value of such underestimation depends on the shift of eigenvalues in the energy range analyzed due to the so-called correlation effects. Nevertheless, unlike the situation with sp bonding semiconductors, band gap predictions obtained within LDA approaches for transition metal silicides are often quantitatively correct. For example, in the case of semiconducting iron disilicide we also obtained very good agreement between theoretically predicted and experimental values.[8,14] We ascribed that to the fact that the corresponding eigenfunctions at the extremum points of the band structure were mainly composed of d-electron states of iron atoms. So, they undergo an almost equal shift. The same situation was obtained for the indirect band gap of semiconducting chromium disilicide.[17] However, in our cases, like in $OsSi_2$,[9] where the maximum of the valence and minimum of the conduction bands were mainly defined by different electron states ($p-d$ gap), correlation effects can cause more pronounced discrepancy between the theory and experiments. The silicides and germanides considered have similar configurations of the valence-electron shells and orbital compositions. The same self-consistent procedure and exchange-correlation potentials have been applied for all the compounds. So one can expect the underestimation of the energy gaps to be of the same order for all materials. For instance, according to the experimental data based on resistivity measurements the band gap in Os_2Si_3 is more than 2 times higher than that in Ru_2Si_3. It can be also seen in the theoretical results. In order to clarify these contradictions precise optical experiments should be made on high-quality crystals and thin films. Moreover, it is also nec-essary to mention that the gap values obtained for the ruthenium silicide and germanide are close to those for the tetragonal high-temperature phase examined in Ref. 3.

IV. CONCLUSION

The isostructural orthorhombic silicides Ru_2Si_3 and Os_2Si_3 were found to be direct-gap semiconductors with the similar band structures and energy-gap values of 0.41 and 0.95 eV, respectively. The analysis of isostructural germanides Ru_2Ge_3 and Os_2Ge_3 which are similar to the silicides show the energy gap values in the region of 0.3 and 0.9 eV, and the difference between indirect and first direct gap to constitute of some tens meV. Thus, our results follow the general tendency, indicating that a germanide has a lower band gap value with respect to the isostructural silicide of the same metal. As the orbital composition of the extreme states of the direct transition in Ru_2Si_3 and Os_2Si_3, consists of metal d states with strong admixture of p states, one can expect that the oscillator strength will be of sizable magnitude. Moreover, ternary and quaternary compounds on the basis of the material considered look indeed promising for a wide range energy gap engineering.

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