PHYSICAL REVIEW B, VOLUME 64, 075208

Electronic and optical properties of isostructural β-FeSi$_2$ and OsSi$_2$

D. B. Migas and Leo Miglio
INFM and Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy

W. Henrion and M. Rebien
Hahn-Meitner-Institute, Kekuléstrasse 5, D-12489 Berlin, Germany

F. Marabelli
INFM and Dipartimento di Fisica "A. Volta," Università degli Studi di Pavia, via Bassi 6, 27100 Pavia, Italy

B. A. Cook
Ames Laboratory, Iowa State University, Ames, Iowa 50011-3020

V. L. Shaposhnikov and V. E. Borisenko
Belarusian State University of Informatics and Radioelectonics, P. Browka 6, 220013 Minsk, Belarus

(Received 28 February 2001; published 31 July 2001)

We present both theoretical and experimental investigations of electronic and optical properties of isostructural β-FeSi$_2$ and OsSi$_2$ by means of a full-potential linear augmented plane wave method and optical measurements. We report also ellipsometric and reflectance measurements on samples of polycrystalline osmium disilicide prepared by mechanical alloying. From *ab initio* calculations these compounds are found to be indirect band-gap semiconductors with the fundamental gap of OsSi$_2$ larger some 0.3–0.4 eV than the one of β-FeSi$_2$. In addition to that, a low value of the oscillator strength is predicted for the first direct transitions in both cases. Computed optical functions for these materials were compared to the ones deduced from optical measurements, indicating very good agreement and the presence of some anisotropic effects.

DOI: 10.1103/PhysRevB.64.075208 PACS number(s): 71.20.Nr, 78.20.−e, 78.66.−w

I. INTRODUCTION

Semiconducting silicides have been intensively studied because of their possible applications in optoelectronic and thermoelectric devices, especially β-FeSi$_2$, which is grown on and in silicon by a variety of techniques (for a recent review see Ref. 1). Actually, a light-emitting diode based on β-FeSi$_2$ precipitates and operating at 1.5 μm at low temperature has been reported by Leong *et al.*[2] Quite recently, Suemasu *et al.*[3] demonstrated room-temperature electroluminescence at 1.6 μm from β-FeSi$_2$ ball-like precipitates embedded in a Si *p-n* junction. However, continuous films of iron disilicide show just a very weak photoluminescence signal at 5 K.[4] In spite of numerous optical measurements and theoretical predictions, contradictory issues, such as the size and the nature of the fundamental band gap and the value of oscillator strength of the low-energy transitions, still remain. To this end it is worthwhile to have a closer look at OsSi$_2$, isostructural to the β phase of iron disilicide, since its electronic and optical properties are poorly studied.

Experimental investigations of iron disilicide absorption edge have shown that this compound possesses a direct band gap of 0.80–0.89 eV at room temperature[5] and that the low-temperature value increases[6] by 0.02–0.1 eV. However, there are indications[7–9] that the gap nature is indirect and a direct transition is present some tens of meV above the indirect one. This picture is confirmed by most of the theoretical calculations predicting a fundamental gap ranging from 0.44 to 0.80 eV with respect to the method applied (augmented spherical waves, linear muffin-tin orbitals, ultrasoft pseudopotentials, and full-potential linear augmented plane waves).[9–13]

At variance with respect to β-FeSi$_2$ there are only a few experimental and theoretical papers devoted to OsSi$_2$. Both isostructural materials have a base-centered orthorhombic structure, the *Cmca* space group, with four inequivalent sites (Fe-1, Fe-2 or Os-1, Os-2 and Si-1, Si-2) and the following lattice constants: $a=9.863$ Å, $b=7.791$ Å, and $c=7.833$ Å for β-FeSi$_2$ (Ref. 14) and $a=10.1496$ Å, $b=8.1168$ Å, and $c=8.223$ Å for OsSi$_2$ (Ref. 15). Preparation of osmium disilicide is difficult. Due to the peritectic formation, arc melting with subsequent annealing does not yield single-phase material. Instead a mechanical alloying technique can be used.[16] According to electrical measurements OsSi$_2$ is characterized by an energy gap of 1.8 eV (Ref. 17) or 1.4 eV (Ref. 18). By reflectivity measured on polycrystalline samples an optical band gap of 2.0 eV was estimated.[17] The nature of the gap was not deduced from the experiments, still the calculations by a linear muffin-tin orbital method predict an indirect gap: its size is estimated to be 0.95 eV by Filonov *et al.*,[19] whereas van Ek *et al.*[20] have found a surprisingly small value (0.06 eV). To our knowledge there are no data on the optical functions of OsSi$_2$. In this paper we present the results of full-potential *ab initio* calculations, which are compared to existing optical measurements on β-FeSi$_2$ (epitaxial films and single crystals), and ellipsometric data on polycrystalline OsSi$_2$.

II. EXPERIMENT

Polycrystalline osmium disilicide has been grown by mechanical alloying. The annealed samples contained 0.5-wt. %

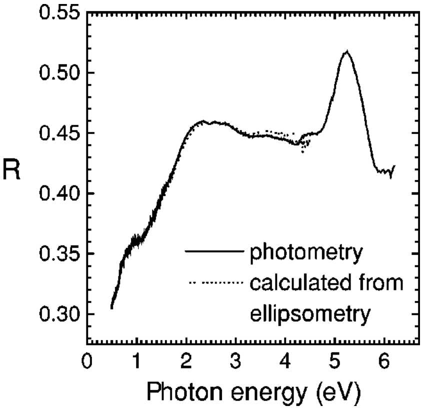

FIG. 1. Directly measured reflectivity (solid line) in comparison with the reflectivity values calculated from the ellipsometric spectra using the model described in the text (dashed line).

aluminum yielding *p*-type conductivity with a carrier concentration of 9.3×10^{20} cm^{-3}. X-ray diffraction measurements revealed the samples to be mostly in orthorhombic structure (b-FeSi$_2$ structure type), with weak diffraction lines with the *Cmca* structure (β-FeSi$_2$ structure type), with weak diffraction lines indicating approximately 5% of OsSi$_2$ in the OsGe$_2$ structure (for structural details see Ref. 18). Optical measurements were performed on a slab of 150 μm thickness.

Room-temperature reflection spectra from 0.5 to 6.2 eV were measured using a commercial double-beam spectrophotometer. The specular and diffuse light was recorded by an integrating sphere. Due to the high absorption of the samples no transmission spectra could be measured. Spectroscopic ellipsometry measurements at room temperature were carried out on a Woollam VASE rotating analyzer ellipsometer over the photon energy range 0.75–4.5 eV, at an angle of incidence of $77.00°\pm0.02°$. In order to extract the bulk dielectric function from the ellipsometry data we need to take into account the native oxide overlayer (a native oxide layer consisting mainly of SiO$_2$ is commonly observed on silicon-rich metal silicide surfaces[21]), microscopic surface roughness, and small voids present on the polished sample surface. Actually, an average void volume fraction of 0.0127 and an average void depth of 3.78 nm were determined from atomic force microscopy (AFM) measurements on different regions on the sample. We then applied a three-layer model assuming semi-infinite bulk of OsSi$_2$, a 4 nm OsSi$_2$ bulk with 1.5% voids, and a 2 nm SiO$_2$ on top. Using SiO$_2$ instead of voids yields only minor variations: SiO$_2$ optical constants were taken from tabulated data.[22] Such a model can be considered as an effective representation of the oxidized rough surface of the sample, as confirmed by the AFM measurements (here not reported). Employing this model from the ellipsometric spectra the dielectric function of OsSi$_2$ has been extracted numerically. These data were then used to calculate the normal incidence reflectivity and to compare with spectrophotometric measurements. The comparison of both rather different types of measurement is shown in Fig. 1. Near-normal incidence reflectance measurements are much less influenced by the native oxide overlayer. Therefore, the excellent agreement between the spectrum directly measured at near-normal incidence and the one calculated for bulk material at normal incidence from the ellipsometric data determined at a large angle of incidence confirms our modeling procedure.

The ellipsometric and reflectivity data for mainly *a*-oriented β-FeSi$_2$ thin films epitaxially grown on Si(001) have been already published (for details see Ref. 23) and we report them here for the sake of comparison to the new calculated spectra. The single crystals of β-FeSi$_2$ used for ellipsometry measurements are the same as in Ref. 24. They were obtained by chemical vapor transport growth in form of needles and plaquets; the latter have a well-defined orientation with the *b* and *c* axes lying on the surface ($\sim 2\times2$ mm^2). The needles (3×0.1 mm^2 on average dimensions) show the *a* axis perpendicular to the needle axis, but *b* and *c* axes can both occur along this direction. Then, only qualitative indications can be drawn from measurements on such needle samples. Spectroscopic ellipsometry measurements were performed with the plane of incidence aligned along the main crystallographic axes lying on the measured surface. Since ellipsometry results are a complicated function of the (anisotropic) complex refraction index parallel and perpendicular to the plane of incidence, a numerical inversion of the ellipsometric results, combining pairs of measurements on the same surface, was used in order to extract the anisotropic dielectric function of β-FeSi$_2$.

III. COMPUTATIONAL DETAILS

We have applied a full-potential linear augmented plane wave method (package WIEN97) described in detail elsewhere.[25] The exchange and correlation potentials were included using the generalized gradient approximation of Perdew, Burke, and Ernzerhof.[26] The muffin-tin radii R_{MT} of Fe, Os, and Si have been chosen as 2.25, 2.35, and 2.10 a.u., respectively. The corresponding plane-wave cutoff of $R_{\mathrm{MT}}K_{\mathrm{max}}$ was equal to 8. A self-consistent procedure was performed on a grid of 24 *k* points uniformly distributed in the irreducible part of the Brillouin zone (IBZ). Further increase in the cutoff value and *k*-point number did not lead to any noticeable changes in the eigenvalues. The relaxation of the atomic positions was obtained by calculating the forces on the atoms and using the Newton dynamics, which has been iterated until the forces were less than 0.001 eV/Å. For the band structure representation we choose up to 40 *k* points for any high-symmetry directions. The dipole matrix elements were computed in the onsite-transition approximation on a dense mesh of 432 *k* points in the IBZ. We used the random-phase approximation in order to calculate the interband contribution to the imaginary part of the dielectric function (ε_2) and the Kramers-Kronig relation to obtain the corresponding real part (ε_1).

IV. RESULTS AND DISCUSSION

A. Electronic structure

The band structure of β-FeSi$_2$, shown in Fig. 2, is characterized by an indirect transition of 0.68 eV between the valence band maximum (VBM) at the *Y* point and the conduction band minimum (CBM) situated along the Γ-Z direction (approximately at $0.6\times\Gamma$-Z, conventionally denoted

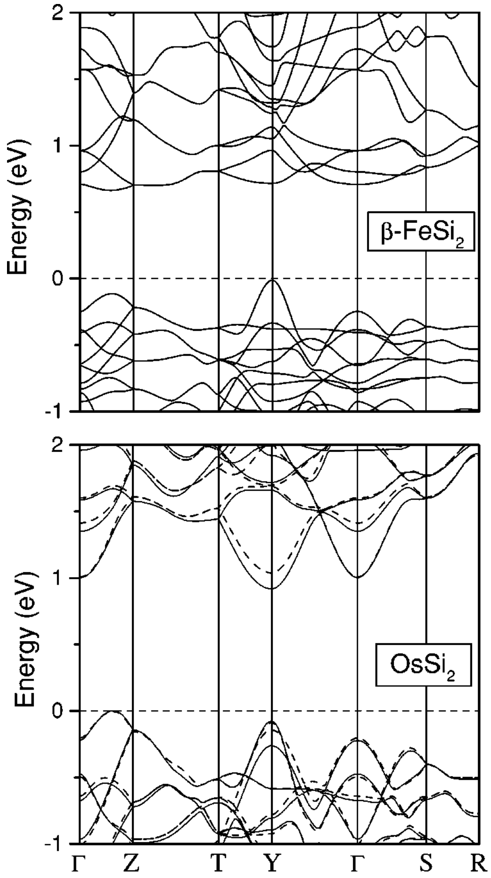

FIG. 2. Band structures of isostructural β-FeSi$_2$ and OsSi$_2$ calculated along the high-symmetry directions of the base-centered orthorhombic Brillouin zone at the experimentally determined lattice constants. For osmium disilicide the dashed and solid lines indicate the cases with and without the atomic position relaxation, respectively. Zero of the energy scale corresponds to the Fermi energy.

TABLE I. Orbital character and the corresponding occupancy of the states (Ref. 27) (in %), at the *Y* point.

		β-FeSi$_2$		OsSi$_2$	
Site/Band		Valence	Conduction	Valence	Conduction
Fe-1/Os-1	s		(1)	(1)	
	p	$x(12)$	$x(1)$	$x(14)$	
	d	$yz(4)$	$x^2-y^2(14)$	$yz(1)$	$xy(14)$
			$yz(9)$		$xz(2)$
Fe-2/Os-2	s	(2)		(2)	
	p	$y(7)$		$y(10)$	
		$z(9)$		$z(8)$	
	d	$x^2-y^2(5)$	$xy(48)$	$x^2-y^2(2)$	$xy(6)$
		$yz(2)$	$xz(14)$	$yz(2)$	$xz(5)$
Si-1	s		(1)		(17)
		$x(13)$	$x(2)$	$x(13)$	$x(2)$
	p	$y(4)$	$z(1)$	$y(4)$	$y(2)$
		$z(2)$		$z(1)$	
		$3z^2-r^2(4)$		$3z^2-r^2(6)$	$3z^2-r^2(2)$
		$x^2-y^2(5)$		$x^2-y^2(4)$	$x^2-y^2(1)$
	d	$xy(1)$		$xy(1)$	$xy(3)$
		$xz(1)$		$xz(1)$	$xz(1)$
		$yz(1)$		$yz(1)$	$yz(4)$
Si-2	s		(5)		(19)
		$y(4)$	$z(2)$	$y(3)$	$x(2)$
	p	$z(13)$		$z(16)$	$y(10)$
					$z(4)$
		$x^2-y^2(8)$	$x^2-y^2(2)$	$x^2-y^2(8)$	$3z^2-r^2(1)$
		$xy(3)$		$xy(2)$	$x^2-y^2(2)$
	d				$xz(1)$
					$yz(2)$

Λ^*). The first direct transition at the *Y* point was estimated to be 0.73 eV. The first conduction band at the Λ^* point has a small dispersion and an actual position of the CBM is shifted towards the *H* point (see for details Ref. 9). We found the value of the transition at Λ^* (still indirect) to be about 0.77 eV. Such a result is fully consistent with other full-potential[12] and pseudopotential[10–12] calculations. The atomic position relaxation did not lead to any sizable variation of the band shape and the position of the CBM: only a slight reduction (less than 0.02 eV) of the band-gap energies was observed.

Taking into account the experimental lattice constants and atomic positions of OsSi$_2$ (see Ref. 15) we have obtained a band structure presented in Fig. 2 (solid line), which displays an indirect band gap of 0.92 eV between the VBM and the CBM located at Λ^* and at *Y*, respectively. There are two well-pronounced extrema both in the valence (the Λ^* and *Y* points) and the conduction (the Γ and *Y* points) bands, and the direct transition at *Y* has a value of 0.99 eV. This result agrees to the calculation performed by Filonov *et al.*,[19] while the prediction of van Ek *et al.*[20] is too small. By performing the relaxation of the atomic positions we found the latter to be very close to the experimental ones (the difference in fractional coordinates is only in the third or fourth significant digit) and the variation of the Os-Si, Si-Si, and Os-Os distances to be negligible (the maximum deviation is less than 0.02 Å). Still some changes in the electronic structure can be found (see Fig. 2, dashed line): the CBM now is at the Γ point due to the raising of the first conduction band at *Y* and the indirect gap is 1.01 eV, whereas the direct transition at *Y* corresponds to 1.13 eV. This issue shows that the bands near the energy gap, especially at the *Y* point, are highly sensitive to small variations in the positions of the atoms.

It is also clearly seen that the shape of the last valence band for both isostructural compounds is almost the same, except for the position of the VBM. Still, some changes are present in the first conduction band. In particular, one of the conduction band minima in OsSi$_2$ is shifted from Λ^* to Γ with respect to β-FeSi$_2$. In order to explain these features we analyzed the orbital contributions in the two bands. It is found that both disilicides qualitatively display the same angular character of the orbitals at any *k* point only for the last valence band (it is particularly evident in the *Y* point; see Table I). The reason for a variation in the orbital angular character for the first conduction band is probably the larger

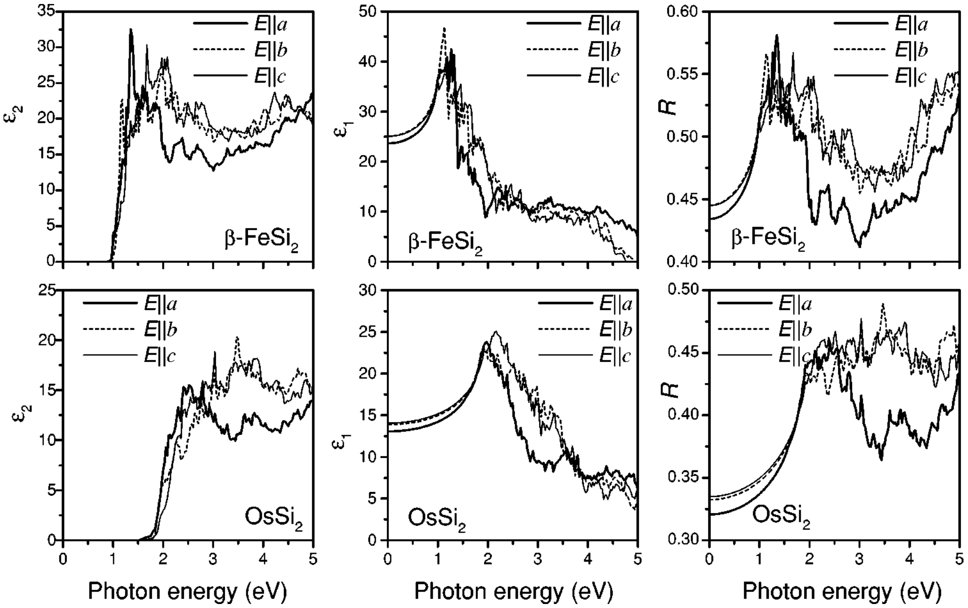

FIG. 3. Calculated imaginary (ε_2) and real (ε_1) parts of the dielectric function and reflectivity (R) versus photon energy of β-FeSi$_2$ and OsSi$_2$ for the different light polarizations.

extent of the osmium 5d orbitals, compared to the iron 3d ones, and their overlap with Si-p states. This feature, in turn, originates a larger bonding-antibonding gap and a bigger dispersion for the valence and conduction bands near the gap for OsSi$_2$. It can also be responsible for the high sensitivity of the bands near the energy gap to slight deviations in the atomic positions.

In summary, our calculations predict an indirect nature of isostructural iron and osmium disilicides and the gap value for OsSi$_2$ turns out to be larger than the one for β-FeSi$_2$. For what concerns the size of the fundamental gaps, at variance to the fact that the density functional method is usually expected to underestimate by some 30% experimental data, an opposite behavior is found by comparing the calculated and the measured optical spectra, as described below.

B. Optical properties

The calculated imaginary part of the dielectric function for the isostructural disilicides in the energy range from 0 to 5 eV is presented in Fig. 3. Both compounds are characterized by having almost the same shape of the ε_2 curves for the b and c light polarizations, whereas some differences can be found in case of $E\|a$: the main maximum is displaced to lower energies with a sizable drop in ε_2 values for higher energies. Some peculiarities are also present for the other optical functions reported in Fig. 3, namely, the real part of the dielectric function (ε_1) and the reflectivity (R). Anisotropy effects are evident in the optical properties of β-FeSi$_2$ and OsSi$_2$ in the energy range here analyzed. This is due to the fact that in the CaF$_2$ structure, the form which originates the orthorhombic β-FeSi$_2$ by a Jahn-Teller distortion,[28] the (001) and (110) planes correspond to the (100) and (010)/(001) planes of iron disilicide, respectively. Some differences in optical spectra for the b and c light polarizations can be observed due to the local distortion.[24] However, in Fig. 4 the real and imaginary parts of the dielectric function measured on single crystals show that the optical spectra for $E\|b$ and $E\|c$ are very similar. Concerning the spectra obtained for $E\|a$, the difficulty in measuring the small needles and the incertitude in their orientation prevents a quantitative comparison of the data. However, there is a clear indication of a lower ε_1 and ε_2 for the a-axis component with respect to b and c, particularly at energies below 2 eV.[29] Anyway, there is additional experimental evidence of the optical anisotropy in iron disilicide,[24] and previous theoretical calculations[23,30] also confirm this effect.

In order to assess the qualitative prediction of our calculations we have compared theoretical data to the results of the ellipsometry and reflectivity measurements on iron disilicide thin films and osmium disilicide polycrystals (shown

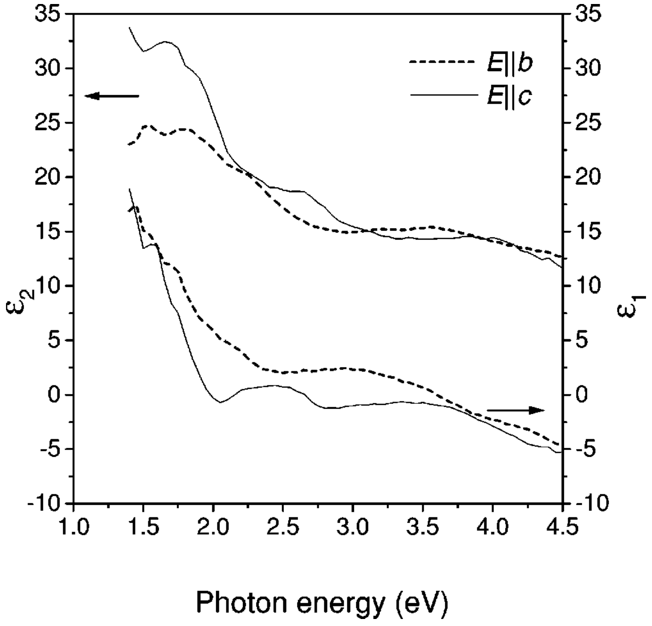

FIG. 4. Experimentally measured dielectric function (ε_2,ε_1) versus photon energy for $E\|b$ and $E\|c$ of single crystals of iron disilicide.

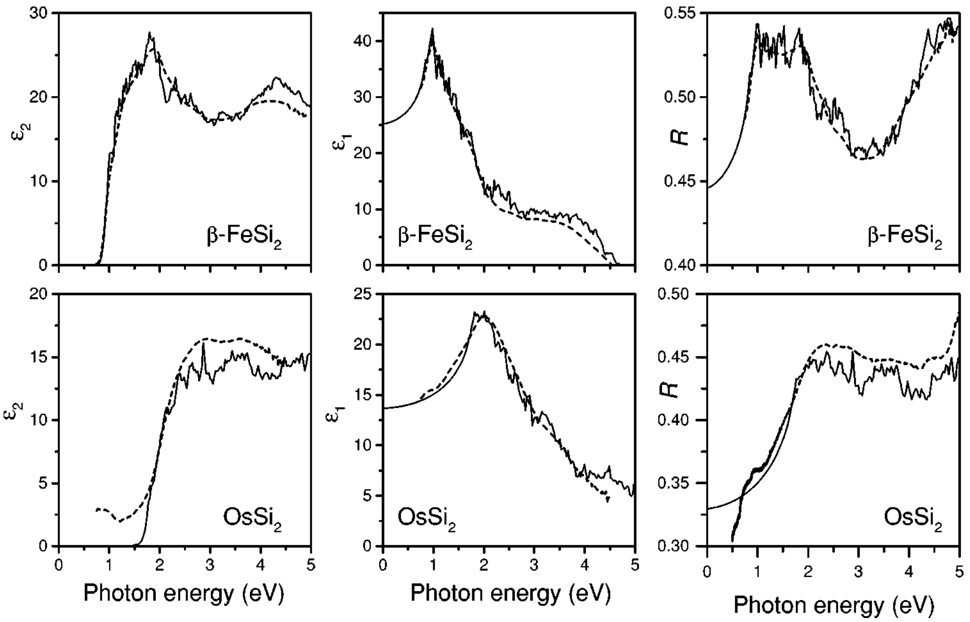

FIG. 5. Comparison between theoretically calculated (solid line) and experimentally measured (dashed line) dielectric function $(\varepsilon_2,\varepsilon_1)$ and reflectivity (R) of iron and osmium disilicides versus photon energy.

in Fig. 5). In the case of β-FeSi$_2$ we have found an excellent agreement for the calculated $E\perp a$ polarization. Since only polycrystalline OsSi$_2$ has been investigated we compared the experimental optical spectra to an average of computed spectra for the a, b, and c light polarizations. A very good correlation is clearly seen between experimental and theoretical curves (see Fig. 5) except for broad tails below 1.8 eV in the experimental data, which is ascribed to the presence of aluminum impurities in the samples.

Oddly enough, all computed curves (for both β-FeSi$_2$ and OsSi$_2$) have been displaced by some 0.15 eV to lower energies at variance with respect to what is expected on the basis of the common gap underestimation provided by the density functional method. Qualitatively, this negative displacement can be attributed to the temperature shift of the gap[6] between the experimental measurements taken at room temperature and the *ab initio* calculations performed at zero temperature. In addition to that, we did not take into account an actual electron-hole excitation,[31] resulting in a negative shift of optical spectra without the analogous shift of the transition energies. Still, the latter effect cannot be sizable because of the dielectric screening. It is more likely the quantitative inconsistency to be originated from the fact that the gap size is crucially determined by the Jahn-Teller distortion from the metallic CaF$_2$ structure.[28] Actually, it is probable that the *ab initio* methods do not reproduce correctly the delicate balance between local atomic dispersions around Fe or Os sites and the strong variations in the electronic structure.

The energy dependence of the imaginary part of the dielectric function can be interpreted in terms of interband transitions (see Figs. 2 and 3), indicating that for iron and osmium disilicides the first direct transition at the Y point (0.73 eV and 1.01, respectively) has a low value of oscillator strength, and the region of the strong increase of ε_2 (from 0.97 eV for β-FeSi$_2$ and 1.85 eV for OsSi$_2$) can be associated with the joint density of the interband states. In the case of β-FeSi$_2$ this fact has already been reported and ascribed to the mainly d character of the states at the top of the valence bands and the bottom of the conduction bands (see Refs. 13 and 23). However, the maximum of the valence band in the Y point for both compounds is found to have a sizable admixture of the metal and silicon p states.[9,12,19] In order to disclose this contradiction we have analyzed more in detail the corresponding orbital configurations and projected occupancies of the states at the Y point, which are summarized in Table I. Here, one should consider that the probability of two-site transitions during excitation (for example from Si-p to Fe-d or Os-d states) is significantly lower than one-site transitions. It is also clearly seen that in the valence band the projected occupancies for the metal-p states are relatively small: the biggest one is only about 15% (see Table I). For OsSi$_2$ we have found that the main contributions to the transition are negligible, which are coming from the following matrix elements: $\langle x|y|xy\rangle$ from the Os-1 site, $\langle y|x|xy\rangle$ and $\langle z|x|xz\rangle$ from the Os-2 site, $\langle x|x|s\rangle$ from the Si-1 site, $\langle z|z|s\rangle$ and $\langle x^2\text{-}y^2|y|y\rangle$ from the Si-2 site. Similar estimations for β-FeSi$_2$ showed that the corresponding contributions were even smaller with respect to OsSi$_2$ due to the lack of the silicon s and d states in the conduction band. Moreover, numerical estimates of the dipole matrix elements corresponding to the direct transitions at the Λ^* and Γ points predict also a very small value of oscillator strength.

To this end, our findings have to be carefully considered in comparison between theory and experiment in the gap size and nature. Actually, by taking into account the gap estimations in β-FeSi$_2$ [0.80–0.89 eV (Ref. 5)] and the fact that linear extrapolation of the $\varepsilon_2{}^2(E)$ values for OsSi$_2$ to $\varepsilon_2{}^2=0$ (see Ref. 32) yields a direct allowed transition at 1.835 ± 0.005 eV (which is very close to the previously reported values[17]), as shown in Fig. 6, we note that they are far beyond the calculated values of the fundamental gap.

V. CONCLUSIONS

The performed investigation of electronic and optical properties of isostructural β-FeSi$_2$ and OsSi$_2$ shows that the

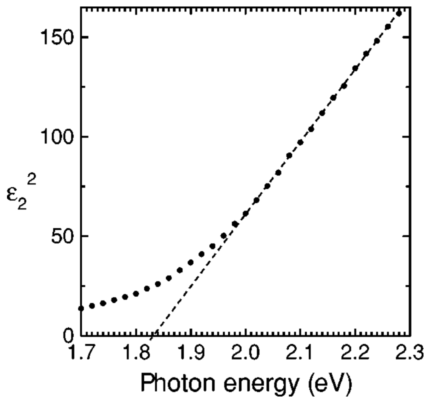

FIG. 6. Squared imaginary part of the dielectric function of an osmium disilicide polycrystal measured by ellipsometry. The dashed lines indicate direct allowed transitions.

band structures of these compounds are characterized by an indirect nature of the band gap. For osmium disilicide the calculations predict the size of the gap to be bigger than the one of iron disilicide and highly sensitive to a slight variation of the atomic positions. For both compounds calculated optical spectra indicate anisotropy effects for the $E\|a$ and $E\perp a$ light polarizations. Actually, comparison between theoretically computed and experimentally measured optical functions of β-FeSi$_2$ and OsSi$_2$ displays very good agreement in shape, while an anomalous underestimation of the gap size is apparent. The low value of the oscillator strength of the first direct transition is found to be the intrinsic feature for both isostructural materials. This indicates that the rise in the ε_2 spectra can mainly be attributed to a corresponding increase in the joint density of the interband states. Our study also shows that polycrystalline samples of OsSi$_2$ with relatively good crystal quality can be obtained by mechanical alloying.

ACKNOWLEDGMENTS

The authors are grateful to A. G. Birdwell for AFM measurements. The work was partially supported by Confinaziamento 40% 1998 of the Italian Ministry of University and Research (Grant No. 9802154837) and Grant No. F99R-115 of Belarusian Basic Research Foundation.

---

[1] *Semiconducting Silicides*, edited by V. E. Borisenko (Springer, Berlin, 2000).

[2] D. Leong, M. Harry, K. J. Reeson, and K. P. Homewood, Nature (London) **387**, 686 (1997).

[3] T. Suemasu, Y. Negishi, K. Takakura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L1013 (2000).

[4] H. Lange, Phys. Status Solidi B **201**, 3 (1997).

[5] M. C. Bost and J. E. Mahan, J. Appl. Phys. **58**, 2696 (1985); C. A. Dimitriadis, J. H. Werner, S. Logothetidis, M. Stutzmann, J. Weber, and R. Nesper, *ibid.* **68**, 1726 (1990); D. J. Oostra, C. W. T. Bulle-Lieuwma, D. E. W. Vanderhoudt, F. Felten, and J. C. Jans, *ibid.* **74**, 4347 (1993); K. Lefki, P. Muret, N. Cherief, and R. C. Cinti, *ibid.* **69**, 352 (1991); M. Rebien, W. Henrion, U. Müller, and S. Gramlich, Appl. Phys. Lett. **74**, 970 (1999); V. Darakchieva, M. Baleva, M. Surtchev, and E. Goranova, Phys. Rev. B **62**, 13 057 (2000).

[6] M. Ozvold, V. Gasparik, and M. Dubnicka, Thin Solid Films **295**, 147 (1997); Z. Yang, K. P. Homewood, M. S. Finney, M. A. Harry, and K. J. Reeson, J. Appl. Phys. **78**, 1958 (1995); C. Giannini, S. Lagomarsino, F. Scarinci, and P. Castrucci, Phys. Rev. B **45**, 8822 (1992); E. Arushanov, E. Bucher, C. Kloc, O. Kulikova, L. Kulyuk, and A. Siminel, *ibid.* **52**, 20 (1995); M. Rebien, W. Henrion, U. Müller, and S. Gramlich, Appl. Phys. Lett. **74**, 970 (1999).

[7] C. Giannini, S. Lagomarsino, F. Scarinci, and P. Castrucci, Phys. Rev. B **45**, 8822 (1992); K. Radermacher, R. Carius, and S. Mantl, Nucl. Instrum. Methods Phys. Res. B **84**, 163 (1994); H. Lange, W. Henrion, B. Selle, G.-U. Reinsperger, G. Örtel, and H. von Känel, Appl. Surf. Sci. **102**, 169 (1996).

[8] C. Spinella, S. Coffa, C. Bongiorno, S. Pannitteri, and M. G. Grimaldi, Appl. Phys. Lett. **76**, 173 (2000).

[9] A. B. Filonov, D. B. Migas, V. L. Shaposhnikov, N. N. Dorozhkin, G. V. Petrov, V. E. Borisenko, W. Henrion, and H. Lange, J. Appl. Phys. **79**, 7708 (1996).

[10] S. J. Clark, H. M. Al-Allak, S. Brand, and R. A. Abram, Phys. Rev. B **58**, 10 389 (1998).

[11] D. B. Migas and Leo Miglio, Phys. Rev. B **62**, 11 063 (2000).

[12] E. G. Moroni, W. Wolf, J. Hafner, and R. Podloucky, Phys. Rev. B **59**, 12 860 (1999).

[13] R. Eppenga, J. Appl. Phys. **68**, 3027 (1990).

[14] P. Y. Dusausoy, J. Protas, R. Wandji, and B. Roques, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **27**, 1209 (1971).

[15] I. Engström, Acta Chem. Scand. **24**, 2117 (1970).

[16] S. H. Han and B. A. Cook, in the *Thirteenth International Conference on Thermoelectrics*, edited by B. Matheprakasam and P. Heenay, AIP Conf. Proc. No. **316** (AIP, New York, 1995), p. 66; Y. S. Chang and M. L. Chou, J. Appl. Phys. **66**, 3011 (1989).

[17] K. Mason and G. Müller-Vogt, J. Appl. Phys. **63**, 34 (1983).

[18] L. Schellenberg, H. F. Braun, and J. Müller, J. Less-Common Met. **144**, 341 (1988).

[19] A. B. Filonov, D. B. Migas, V. L. Shaposhnikov, N. N. Dorozhkin, V. E. Borisenko, and H. Lange, Appl. Phys. Lett. **70**, 976 (1997).

[20] J. van Ek, P. E. A. Turchi, and P. A. Sterne, Phys. Rev. B **54**, 7897 (1996).

[21] H. Jiang, C. S. Petersson, and M.-A. Nicolet, Thin Solid Films **140**, 115 (1986); for β-FeSi$_2$ oxidation see M. Rebien, W. Henrion, H. Angermann, and A. Röseler, Surf. Sci. **462**, 143 (2000).

[22] D. Brixner, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic Press, New York, 1985), p. 759.

[23] V. N. Antonov, O. Jepsen, W. Henrion, M. Rebien, P. Stauss, and H. Lange, Phys. Rev. B **57**, 8934 (1998).

[24] G. Guizzetti, F. Marabelli, P. Pellegrino, B. Pivac, L. Miglio, V. Meregalli, H. Lange, W. Henrion, and V. Tomm, Phys. Rev. B **55**, 14 290 (1997).

[25] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of

Technology, 1997 [improved and updated Unix version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990)].

[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[27] Some 30% of the electronic charge, obtained by our calculation at the *Y* point, is outside the muffin-tin spheres. However the site and orbital distributions nicely agree to those in Refs. 9 and 19. The latter, still not a full-potential calculation, takes into account 100% of the electronic charge at *Y*.

[28] F. Tavazza, V. Meregalli, L. Miglio, and M. Celino, Phys. Rev. B **59**, 3480 (1999).

[29] S. Bocelli, G. Guizzetti, F. Marabelli, G. B. Parravicini, M. Patrini, W. Henrion, H. Lange, and Y. Tomm, in *Silicide Thin Films, Fabrication, Properties, and Applications*, edited by R. T. Tung, K. Maex, P. W. Pellegrini, and L. H. Allen, MRS Symposia Proceedings No. **402** (Materials Research Society, Pittsburgh, 1996), p. 349.

[30] A. B. Filonov, D. B. Migas, V. L. Shaposhnikov, V. E. Borisenko, W. Henrion, M. Rebien, P. Stauss, H. Lange, and G. Behr, J. Appl. Phys. **79**, 7708 (1998).

[31] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **81**, 2312 (1998); Phys. Rev. B **62**, 4927 (2000).

[32] S. Adachi, *Optical Properties of Crystalline and Amorphous Semiconductors* (Kluwer, Boston, 1999), p. 72.