Structural, electronic, and optical properties of β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$

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Optimized crystal structure, electronic bands, and density of states near the band gap, and the dielectric function of β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$ with x equal to 0.0625 and 0.125 were obtained by means of total energy ultrasoft pseudopotential and full-potential linearized augmented plane-wave calculations. We address a preferential occupation of the Fe-1 and Fe-2 sites by the Co atoms at different concentrations indicating the Fe-2 site to be energetically favorable. We also discuss a variation in the energy gap and in the position of the donor level in β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$ with increasing Co content. Calculated imaginary and real parts of the dielectric function show a good agreement with results of ellipsometric measurements of samples grown by molecular-beam epitaxy.

I. INTRODUCTION

The semiconducting β phase of iron disilicide (β-FeSi_2), compatible with silicon technology and environment friendly, has attracted much attention because of its perspectives in optoelectronic and thermoelectric applications.[1] Very recently a number of physical limitations were reported which prevent an efficient light emission from the disilicide.[2,3] Nevertheless, doped by Co or Mn, this material can be used for manufacturing thermoelectric power generation systems.[4] A variety of techniques, such as solid-state epitaxy,[5] reactive deposition epitaxy,[5] molecular-beam epitaxy,[5,6] ion-beam synthesis,[7,8] chemical vapor transport,[9] and pulsed laser deposition[10] have been used to obtain both thin films and bulk crystals of β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$. The solubility limit of Co is reported to be about 20%.[11] Conversion electron Mössbauer spectroscopy (CEMS) (Refs. 8 and 10) and electron paramagnetic resonance spectroscopy (EPR) (Ref. 9) experiments demonstrate that Co is a substitutional impurity mainly on the Fe-2 site in the disilicide crystal structure (for details of the β-FeSi_2 crystal structure see Ref. 12). However, some indications of a partial occupation of the Fe-1 site also exist.[8,10] From Hall effect and electrical resistivity measurements[13–17] the activation energy of the Co donor is found to be scattered between 13.5 and 97 meV. Optical experiments[7,10] just report a qualitative trend in decrease of the energy gap value with increasing Co content. To our knowledge there is one theoretical prediction on β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$ addressing the preferential Fe-2 site to be

occupied by Co and reporting the corresponding density of states.[18] These calculations have been carried out just in the case of one Co concentration, so that it is not possible to trace a variation in the position of the donor level and in the gap value with the Co content. For such reasons it is useful to perform an extended theoretical study on β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$ in close comparison with experimental results.

In this paper we apply an *ab initio* total energy ultrasoft pseudopotential method (code VASP)[19–21] perfectly suitable for a full structural optimization, and a full-potential linearized augmented plane wave method (code WIEN97) (Ref. 22) for electronic and optical property calculations. Therefore we trace the variations in the lattice parameters, band diagrams, density of states, and optical functions of β-$(\mathrm{Fe}_{1-x}\mathrm{Co}_x)\mathrm{Si}_2$ with different Co concentrations, comparable to the experimental ones. We also present ellipsometric measurements on high-quality samples of iron disilicide doped by Co in comparison with theoretical predictions.

II. EXPERIMENT

Epitaxial β-$(\mathrm{Fe,Co})\mathrm{Si}_2$ films were grown in an ultrahigh-vacuum molecular-beam-epitaxy growth chamber on Si(100) substrates using a template technique.[23] The purity of the separately controlled Fe, Si, and Co sources was $5N$. In a first step Fe and Si were coevaporated with a small Fe excess onto the unheated substrate and subsequently annealed at $420°\mathrm{C}$ for 3 min. The thickness of this first layer was around

0.9 nm. Reflection high-energy electron-diffraction observations showed only the known β-FeSi$_2$ pattern for the epitaxial relationship β-FeSi$_2(100)/$Si(100), with mostly type-A orientation.[24] After cooling down Fe, Si and Co were co-evaporated in stoichiometric metal/2Si proportion onto the unheated substrate and annealed at 660°C for 3 min to increase the template layer thickness. The total layer thickness became around 4.5 nm. During further epitaxial growth to the desired film thickness of approximately 250 nm the substrate temperature was kept close to 660°C. The epitaxial β-FeSi$_2$ films on the highly symmetrical Si(100) surface are known to develop rotational domains, and hence, are not truly single crystalline. However, only grains with the *a* axis perpendicular to the substrate surface can be found,[25] as verified by reflection high-energy electron diffraction. The Co concentration in the films was determined by elastic recoil detection as well as Rutherford backscattering.[26] We select for our study the samples of β-(Fe$_{1-x}$Co$_x$)Si$_2$ having *x* equal to 0.009, 0.066, and 0.14 which correspond to 0.3, 2.2, and 4.6 Co at. %, respectively.

X-ray diffraction spectra were collected using a Philips diffractometer in Bragg-Brentano geometry equipped with incident soller slits, theta-compensating slits, a 0.2-mm receiving slit, a graphite monochromator, and a scintillation detector. The measurements were performed at ambient temperatures using Cu $K\alpha$ radiation with a 0.02° 2Θ step size, and a 3 sec count turn. The observed 2Θ peak positions were corrected using Standard Reference Material 660 (LaB$_6$ compound) as an external calibrant. The uncertainty of the lattice parameter measurements is ± 0.0002 Å.

Spectroscopic ellipsometry measurements at room temperature were carried out on a J.A. Woollam Co. VASE ellipsometer over the photon energy range 0.75–4.5 eV at an angle of incidence of 77.00°± 0.02°. In order to extract the bulk dielectric function values from the extremely surface sensitive ellipsometric spectra, a layer model was established taking into account the native oxide overlayer as described in Ref. 27.

III. STRUCTURAL MODELS OF β-(Fe$_{1-x}$Co$_x$)Si$_2$

β-FeSi$_2$ has a base-centered orthorhombic structure (space group $Cmca$, 24 atoms, $a=9.863$ Å, $b=7.791$ Å, and $c=7.833$ Å) (Ref. 12) with four inequivalent sites Fe-1, Fe-2, Si-1, and Si-2. In our study it is convenient to use a simple orthorhombic structure with 48 atoms, which is shown in Fig. 1, in order to compare results with different Co concentrations in β-(Fe$_{1-x}$Co$_x$)Si$_2$. Thus, by substituting one or two Fe with Co, *x* is equal to 0.0625 or 0.125, respectively, which is in the range of the experimentally achieved concentrations. In the former case one Co atom can occupy only the Fe-1 or Fe-2 site, whereas in the latter case several possibilities exist and different configurations of the impurity atom positions should be taken into account as well. Here we investigate the following variants: β-(Fe$_{0.9375}$Co$_{0.0625}$)Si$_2$, one Co either in Fe-1 or in Fe-2; β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$, two Co in Fe-2 [namely, configurations (8,1), . . . ,(8,7) according to Fig. 1], and one Co in Fe-1 and another Co in Fe-2.
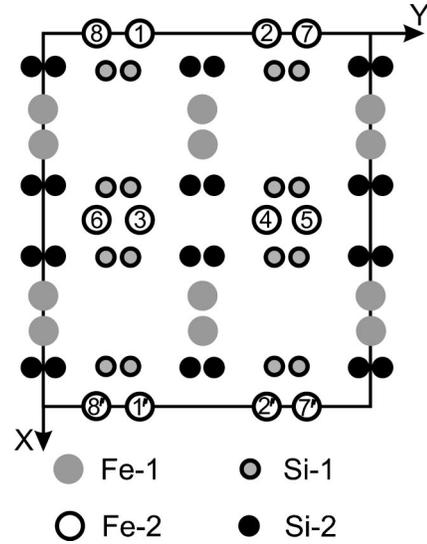
FIG. 1. Simple orthorhombic unit cell of β-FeSi$_2$ in the (001) projection. The numeration of the Fe-2 atoms is given according to Ref. 12.

IV. COMPUTATIONAL DETAILS

Total energy calculations and full structural optimization have been performed by the first-principles code VASP (Vienna *ab initio* simulation package) with a plane-wave basis-set and ultrasoft pseudopotentials (USPP).[19–21] We used the generalized gradient approximation of Perdew and Wang.[28] The ultrasoft Vanderbilt-type pseudopotentials have been employed for the $3d^74s^1$, $3d^84s^1$, and $3s^23p^2$ atomic configurations of Fe, Co, and Si, respectively. Nonlocal contributions were evaluated using the real space projection scheme. We applied the smearing method of Methfessel and Paxton in the Brillouin-zone integration. Total energy minimization, via a lattice parameter optimization and an atomic position relaxation in a conjugate gradient routine, has been obtained by calculating the Hellmann-Feynman forces and the stress tensor. The Pulay correction was included in order to compensate for changes in the basis set due to variation in the shape of the unit cell. It has been found that the convergence in the total energy is better than 1 meV/atom using an energy cutoff of 360 eV and a $4\times4\times4$ grid of Monkhorst-Pack points.

We have also applied a full-potential linearized augmented plane wave (FLAPW) method, package WIEN97 described in detail elsewhere,[22] for electronic and optical property calculations, using the fully optimized crystal structure obtained by USPP. The exchange and correlation potentials were included, as in the case of USPP, by the generalized gradient approximation of Perdew and Wang.[28] The corresponding plane-wave cutoff of $R^*_{mt}K_{max}$ was equal to 8. A self-consistent procedure has been carried out on grids of 38 and 62 **k** points uniformly distributed in the irreducible part of the Brillouin zone (BZ) in order to check convergence in the total energy and in the position of the Fermi level. For the band-structure representation we choose up to 30 **k** points for any high-symmetry directions. The modified tetrahedron method with Blöchl corrections was employed to cal-
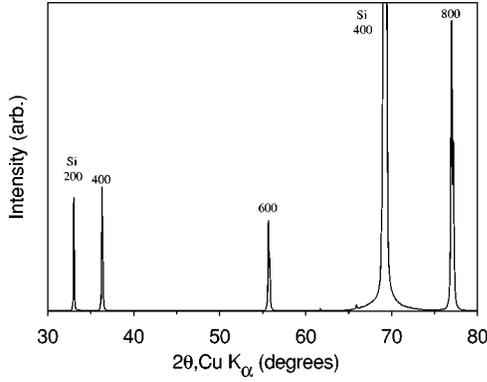
FIG. 2. XRD spectrum of β-$(Fe_{0.86}Co_{0.14})Si_2$. Substrate peaks are marked by Si.

culate the density of states (DOS). The dipole matrix elements were computed on a dense mesh of 400 **k** points. 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).

V. RESULTS AND DISCUSSION

A. Structural properties

Our x-ray diffraction (XRD) analysis of β-$(Fe_{1-x}Co_x)Si_2$ samples clearly shows only β-$FeSi_2$(100)-type reflections (Fig. 2), independently of azimuthal sample orientation and of Co concentration, demonstrating an epitaxial nature of the silicide film. No traces of stress in the film were observed, even though the theoretically forbidden Si (200) reflection could indicate it. This reflection is usually present for Si single crystal wafer both prior and after film deposition. We have also noticed a systematic shift of β-(Fe,Co)Si_2 (100) reflections to lower 2Θ angles with increasing Co content. This suggests that the β-$FeSi_2$ lattice expands when adding Co atoms. In fact, we found only the a side to enlarge with Co concentration, as demonstrated in Fig. 3, while the b and c ones remain almost unchanged, in agreement with data reported in Refs. 10 and 29.

The same trend has been observed for the lattice constants of β-$(Fe_{1-x}Co_x)Si_2$ optimized by USPP: substitution of Co for Fe, independently of the site, leads only to an increase of the a side with Co content whereas b and c are almost invariable (Table I). This issue also correlates well with very recent first-principles calculations.[18] Nevertheless, this is at variance to the prediction of Motta and Christensen[30] for $(Fe_{1-x}Co_x)Si_2$ in the CaF_2 structure (γ phase), showing that in our case the expansion in a is due to the electronic effects related to the Jahn-Teller distortion, rather than to an atomic site effect. Moreover, after relaxation of β-$FeSi_2$, where we artificially added one electron per unit cell, the extension of the a side turned out to be bigger with respect to the one for b and c. Thus, by adding Co the orthorhombic β-$FeSi_2$ starts transforming towards the cubic γ-$FeSi_2$. It can be understood by considering that the (100) planes in β and γ phases coincide, while the (110) plane in the γ phase corresponds to
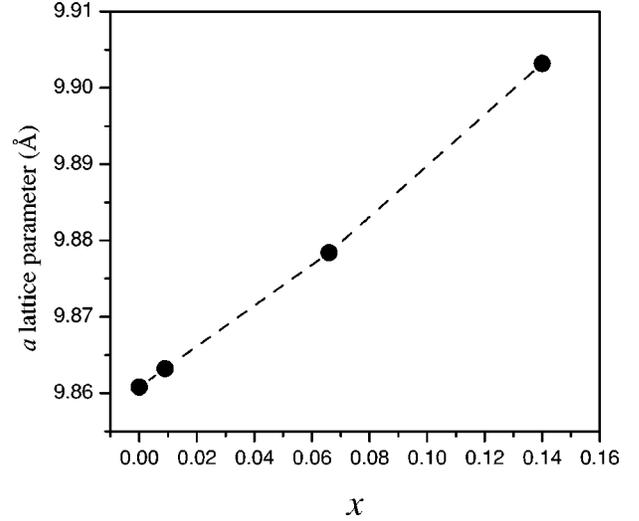
FIG. 3. Variation in the a lattice parameter in β-(Fe,Co)Si_2. The dashed line is a guide to the eye.

(010) and (001) in the β phase, and the a side in the orthorhombic structure is shorter than double a of the cubic structure.[31]

In agreement with CEMS and EPR investigations[8–10] we have found the cobalt occupation of the Fe-2 site to be energetically preferable. In particular, for β-$(Fe_{0.9375}Co_{0.0625})Si_2$ a total energy difference of about 1 meV/atom is estimated. For comparison a value of 2 meV/atom has been obtained for β-$(Fe_{0.875}Co_{0.125})Si_2$ by Tani and Kido.[18] In the case of β-$(Fe_{0.875}Co_{0.125})Si_2$ with two Co in Fe-2 we note that a variation in the total energy for all possible configurations $[(8,1), \ldots, (8,7)]$ is negligible (about 0.02 meV/atom). Surprisingly, it makes no difference in energy if one of the two Co atoms is in Fe-1. This point indicates a possible random Co occupation of both the Fe-1 and Fe-2 sites at x more than 7%, fully corresponding to the CEMS data presented in Ref. 10.

B. Band structure and density of states

The band structures of β-$FeSi_2$, β-$(Fe_{0.9375}Co_{0.0625})Si_2$, and β-$(Fe_{0.875}Co_{0.125})Si_2$ along some high-symmetry directions of the simple orthorhombic BZ are shown in Fig. 4. In

TABLE I. Theoretical predictions on the lattice constants (Å) of β-$(Fe_{1-x}Co_x)Si_2$ at different concentrations of the Co atoms. The variation in the lattice parameters of β-$(Fe_{0.875}Co_{0.125})Si_2$, where the Co atoms occupy the Fe-2 site but are in different positions, is less than 0.03%.

| | β-$FeSi_2$[a] | β-$(Fe_{0.9375}Co_{0.0625})Si_2$ | | β-$(Fe_{0.875}Co_{0.125})Si_2$ | |
		One Co in Fe-1	One Co in Fe-2	Co both in Fe-1 and Fe-2	Two Co in Fe-2
a	9.899	9.918	9.932	9.961	9.966
b	7.782	7.781	7.779	7.781	7.777
c	7.836	7.841	7.840	7.845	7.842

[a]From Ref. 32.
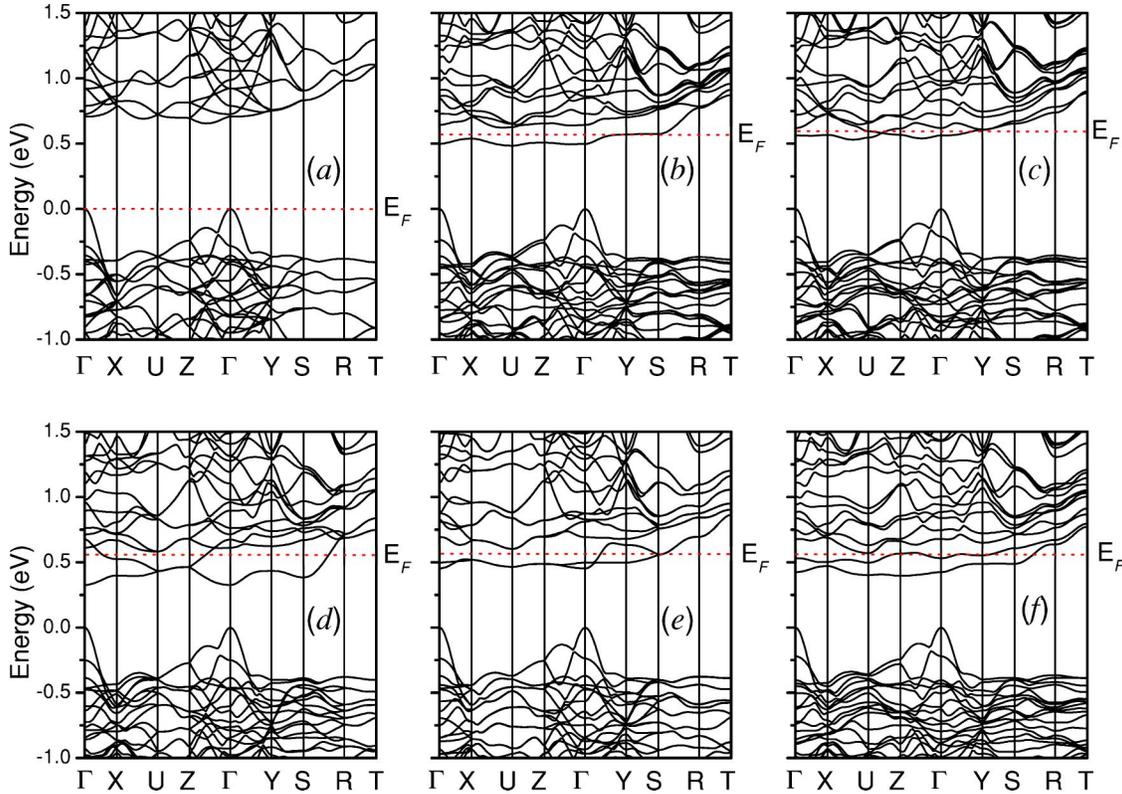
FIG. 4. (Color online) Band diagrams, calculated by FLAPW, of (a) β-FeSi$_2$; (b) β-(Fe$_{0.9375}$Co$_{0.0625}$)Si$_2$, Co in Fe-2; (c) β-(Fe$_{0.9375}$Co$_{0.0625}$)Si$_2$, Co in Fe-1; (d) β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$, the (8,1) variant; (e) β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$, the (8,5) variant; (f) β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$ with one Co in Fe-1 and another Co in Fe-2. Zero of the energy scale corresponds to the top of the 128th band and the dashed line indicates the position of the Fermi level (E_F).

the case of β-FeSi$_2$ [Fig. 4(a)] the gap is formed between the 128th and 129th bands (the number of valence electrons in the unit cell is 256) and the band structure is characterized by an indirect transition of 0.67 eV: the valence band maximum is at the Γ point and the conduction band minimum is at the Λ^* point (approximately $0.6\times\Gamma$-Z). This is in good agreement with our previous calculations,[32,33] taking into account that the Y point in the base-centered orthorhombic BZ is folded into the Γ point in the simple orthorhombic BZ. In the case of β-(Fe$_{1-x}$Co$_x$)Si$_2$ [see Figs. 4(b)–4(f)] there is a gap between the 128th and 129th bands and it is evident that the shape of the former band is similar to the one of β-FeSi$_2$. This is also true for the other configurations of β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$, which are not shown in the band diagram plots.

The Fermi level in β-(Fe$_{1-x}$Co$_x$)Si$_2$ is shifted up into the conduction band (Fig. 4) due to the fact that the number of the valence electrons is increased in the unit cell to 257 and 258 for β-(Fe$_{0.9375}$Co$_{0.0625}$)Si$_2$ and β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$, respectively. Strictly speaking, this issue points out β-(Fe$_{1-x}$Co$_x$)Si$_2$ to be a metal while optical and transport measurements carried out on cobalt doped iron disilicide samples demonstrate semiconducting properties. This contradiction can be interpreted by considering that the electrons in the half-filled 129th and 130th bands are probably thermally activated even at low temperatures, whereas the electron transfer from the valence band (the 128th and lower bands)

to the Fermi level across the energy gap is responsible for the semiconducting character. Therefore, β-(Fe$_{1-x}$Co$_x$)Si$_2$ should be treated as a doped semiconductor. The resistivity measurements[17] support this statement, demonstrating normal transport in the conduction band only at temperatures above 100 K, while a dominating transport path in the defect band due to the Co donor level is detected in the low-temperature range.

We have also estimated a position of the donor level in β-(Fe$_{1-x}$Co$_x$)Si$_2$ by analyzing in detail the corresponding DOS close to the Fermi level (Fig. 5). The peak below the Fermi level (E_F), which can be associated with a donor level (E_d), is evident both for β-(Fe$_{0.9375}$Co$_{0.0625}$)Si$_2$ and β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$. The difference between the Fermi and donor levels (E_F-E_d) turns out to be 0.065 and 0.058 eV for $x=0.0625$ and $x=0.125$, respectively, in perfect agreement with the measured activation energy value (0.053 eV) for the Co donor in β-FeSi$_2$ crystals.[17]

As we have already demonstrated above, in β-(Fe$_{1-x}$Co$_x$)Si$_2$ the a side increases with x (while b and c remain unchanged) acting as a uniaxial strain on the iron disilicide crystal structure. The latter point has been investigated in Ref. 32 displaying a gap reduction with increasing of the a side. For comparison, in β-FeSi$_2$ the gap value of $\sim$0.60 eV is predicted at $a=9.97$ Å (see Fig. 5 in Ref. 32), which is very close to the case of β-(Fe$_{0.875}$Co$_{0.125}$)Si$_2$. Thus, the uniaxial extension of the a side in
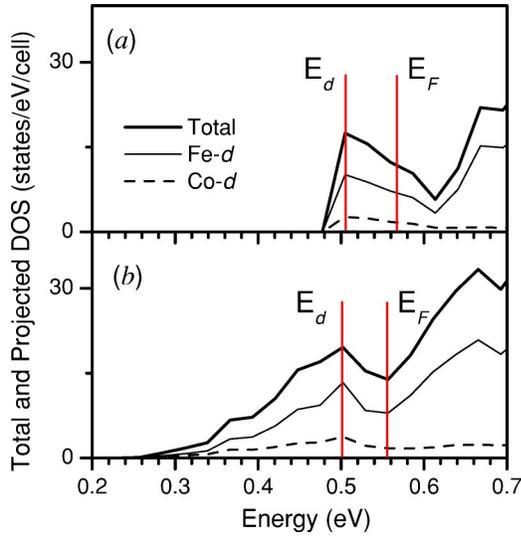
FIG. 5. (Color online) Total and projected (summed over the atomic types) density of states near the Fermi level of (a) β-$(Fe_{0.9375}Co_{0.0625})Si_2$, Co in Fe-2; (b) the average of all β-$(Fe_{0.875}Co_{0.125})Si_2$ cases. Zero of the energy scale corresponds to the top of the 128th band. The positions of the Fermi level (E_F) and the donor level (E_d) are indicated by the solid vertical lines.

FIG. 6. (Color online) Measured imaginary and real parts of the dielectric function (ε_2, ε_1) of β-$(Fe_{1-x}Co_x)Si_2$ vs photon energy. The thicker lines correspond to the case of ε_1.

β-$(Fe_{1-x}Co_x)Si_2$ is responsible for the band-gap shrinkage. This statement can also be confirmed by considering the fact that in β-$(Fe_{1-x}Mn_x)Si_2$ at $x \lesssim 0.2$ neither variation in the a side nor in the value of the gap has been observed.[10] In addition, moderate changes in the b and c sides do not sizably affect band-gap values as predicted in Ref. 32.

Another feature, which is worth discussing, is a small contribution of the Co-d states at the donor level, as can be seen in Fig. 5. In fact, the Fe-d states are dominant there like in the bottom of the conduction band in β-$FeSi_2$.[33] This effect can be ascribed to the fact that Fe and Co are chemically very similar in β phase of iron disilicide and the substitution of Co for Fe at the concentrations considered does not sizably affect the metal-silicon bonding, preventing a localization of the Co-d states at the donor level.

C. Dielectric function

The imaginary and real parts of the dielectric function of β-$FeSi_2$ films with and without Co addition measured by ellipsometry are presented in Fig. 6. Unlike β-$(Fe,Cr)Si_2$, where a relatively small concentration of Cr sizably modifies the shape of the spectra,[25] just small changes can be found for β-$(Fe_{0.94}Co_{0.06})Si_2$ and β-$(Fe_{0.86}Co_{0.14})Si_2$ with respect to β-$FeSi_2$. Thus, the magnitude of the main peak of ε_2 and ε_1 decreases negligibly and these spectra are shifted slightly towards lower energies with increasing Co content. The same trends we traced in the theoretical ε_2 and ε_1 curves which are very close in shape to those of β-$FeSi_2$ (see Fig. 3 of Ref. 33). A comparison of theoretical and experimental spectra for different Co concentrations in β-$(Fe_{1-x}Co_x)Si_2$, which is shown in Fig. 7, reveals a very good agreement. Here calculated optical functions are plotted for $E \perp a$ and displaced to lower energies by some 0.1 eV (see for discussion Ref. 33).
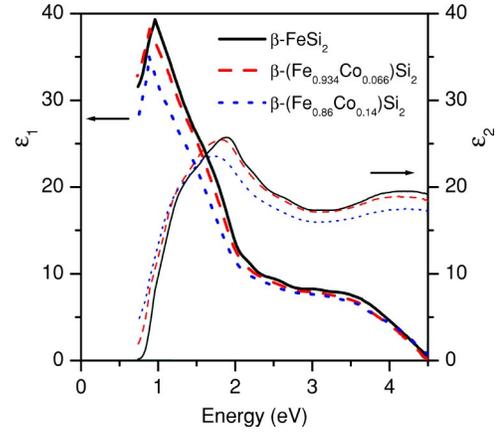
In Fig. 8 we demonstrate a variation of the gap in β-$(Fe_{1-x}Co_x)Si_2$ with the Co content as predicted by the *ab initio* calculations along with our ellipsometric measurements and available literature data. The direct energy gap was determined by extrapolating the measured $\varepsilon_2^2(\hbar\omega)^4$
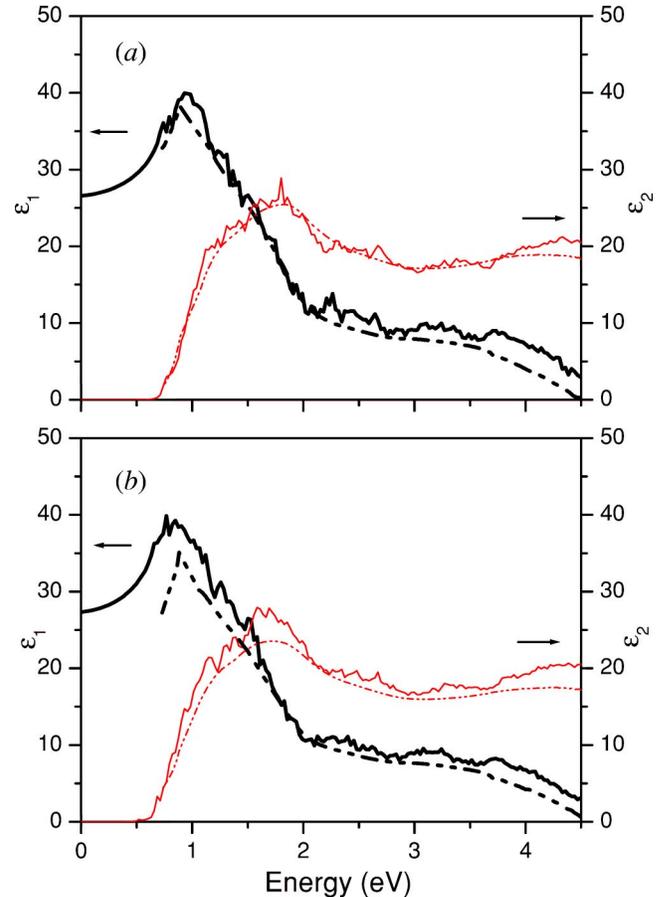
FIG. 7. (Color online) Comparison between calculated (solid line) and measured (dashed line) dielectric function (ε_2, ε_1) of β-$(Fe_{1-x}Co_x)Si_2$ (a) at $x \sim 6\%$; (b) at $x \sim 14\%$ vs photon energy. The thicker lines correspond to the case of ε_1.
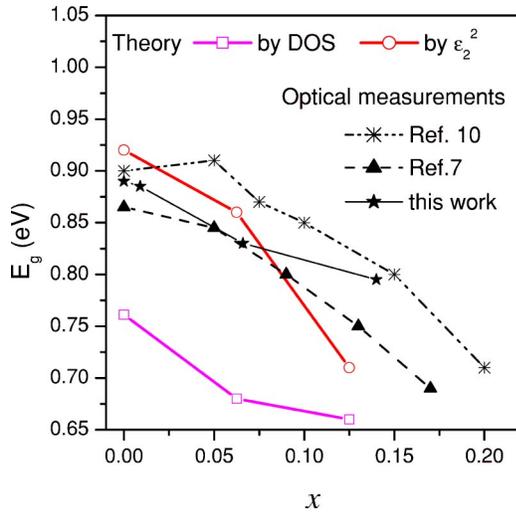
FIG. 8. (Color online) Dependence of the gap value in β-$(Fe_{1-x}Co_x)Si_2$ on the Co content. The theoretical values are obtained from DOS (the difference between the Fermi energy and the top of the 128th band) and from imaginary part of the dielectric function (the linear extrapolation of ε_2^2 to zero).

spectra to zero.[34] Although exciton absorption was observed for undoped β-$FeSi_2$ at low temperatures,[35] the single-particle gap was evaluated, as Coulomb enhancement effects should be negligible for strongly doped material at room temperature. One of the theoretical curves in the figure is the difference between the Fermi level and the top of the 128th band and this curve is shifted up in energy by 0.1 eV due to the band gap underestimation by DFT methods.[32] Another theoretical curve is obtained by a linear extrapolation of ε_2^2 to zero. We do not want to lay stress on a quantitative prediction of the gap value in β-$(Fe_{1-x}Co_x)Si_2$ with respect to Co concentration because even in the case of pure β-$FeSi_2$ the experimental gap estimates vary from 0.77 to 0.89 eV (Ref. 3) and a combined investigation with different optical

techniques on high-quality samples is really necessary.[3] From the other side, calculations show very low values of oscillator strength of the low-energy transitions,[33] which can explain so different theoretical results and some variation in experimental data on band-gap energies presented in Fig. 8. We would like to point out here that both theoretical and experimental curves (Fig. 8) display a different slope. In fact, our ellipsometric measurements on samples grown by molecular-beam epitaxy provide a similar slope only to the theoretically predicted one on the basis of the difference between the Fermi level and the top of the 128th band.

VI. CONCLUSIONS

The influence of Co addition on the properties of β-$FeSi_2$ has been investigated both theoretically and experimentally. Our estimates of the variation in the lattice parameters of β-$(Fe_{1-x}Co_x)Si_2$ demonstrate only an increase in the a side with the Co content while the b and c ones remain almost invariable. We predict the Fe-2 site to be preferentially occupied by Co, still at x more than 7% substitution of Fe atoms in the Fe-1 site is also possible. The position of the donor level of ~ 0.06 eV in β-$(Fe_{1-x}Co_x)Si_2$ is found to be almost independent of the Co concentration in the range of $0.0625 \leqslant x \leqslant 0.125$ and this donor level is not characterized by localized Co-d states. Both theory and experiment agree in indicating that doping of β-$FeSi_2$ by Co does not sizably affect optical properties. We also point out that the gap reduction in β-$(Fe_{1-x}Co_x)Si_2$ with the Co content occurs due to the increase of a side; however, its qualitative and quantitative predictions both by optical and transport measurements can be different.

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