Optical properties of β-$FeSi_2$ under pressure

K. Takarabe,* R. Teranishi, J. Oinuma, and Y. Mori
Okayama University of Science, Ridai, Okayama 700-0005, Japan

T. Suemasu, S. Chichibu, and F. Hasegawa
Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
(Received 21 July 2001; revised manuscript received 26 November 2001; published 15 April 2002)

We have investigated the high-pressure optical absorption of Iron disilicide, β-$FeSi_2$, thin films(90 nm in thickness) prepared from Si/Fe multilayers on Si (001) with template and SiO_2 capping. It is found that the experimental absorption coefficient in the range of photon energy of about 0.3 eV beyond the band gap is a few orders of magnitude larger than the first-principles calculated absorption coefficient. A possible explanation for this large absorption coefficient is the saddle-point exciton effect by the calculated band structure. No critical points with negative hydrostatic pressure coefficients such as those of Si and GaAs are observed in β-$FeSi_2$ near the band gap. The pressure coefficient for the direct band gap of β-$FeSi_2$ is determined to be 15.9 meV/GPa. This small coefficient is due to the negative deformation potential of the valence-band maximum, and the large bulk modulus of β-$FeSi_2$.

DOI: 10.1103/PhysRevB.65.165215 PACS number(s): 78.20.Bh

I. INTRODUCTION

Iron disilicide, β-$FeSi_2$, has attracted much attention as a promising material for optoelectronic applications.[1,2] β-$FeSi_2$ emits light of 1.55 μm (0.8 eV) suitable for SiO_2 optical fiber communications and can be grown epitaxially on Si. β-$FeSi_2$ is also known to be a Kankyo semiconductor (ecologically friendly semiconductor).[3] A well annealed thin-film sample shows a highest hole mobility of 13 000cm^2/Vs at 50 K, which exceeds the electron mobility.[4] Room-temperature electroluminescence action has been already reported.[5]

There are a growing number of studies on the basic properties of β-$FeSi_2$. For example, Filonov *et al.* calculated the dielectric functions in a wide range of photon energies up to 5 eV, and compared these with the ellipsometric experiments.[6] However, the nature of the band gap is still in dispute. Photoluminescence studies suggest that β-$FeSi_2$ is direct (for example, Ref. 1), but absorption studies suggest that it is indirect (for example, Ref. 2). Theoretical studies predict that the nature of the gap critically depends on the lattice strain of β-$FeSi_2$.[7–9]

Here, we performed a first-principles calculation of the optical properties of β-$FeSi_2$ focusing on the near-edge absorption coefficient, and report on the high-pressure measurement of its absorption spectra up to 5 GPa. Note that a part of the experimental work has been reported elsewhere.[10]

II. EXPERIMENTS

The samples used in the present experiment were continuous and highly [100]-oriented β-$FeSi_2$ films (90 nm thickness) prepared from Si/Fe multilayers on Si(001) with template and SiO_2 capping. The films were grown as follows: First, a 20-nm-thick β-$FeSi_2$ epitaxial layer was grown by reactive deposition epitaxy (Fe deposition on heated Si) at 470 °C as a template to control the crystal orientation of β-$FeSi_2$. Then, 45 layers of the Si(1.6 nm)/Fe(0.5 nm), corresponding to a β-$FeSi_2$ film of about 90 nm thickness, including the template, were deposited at room temperature. The Si and Fe were deposited by electron-beam (EB) evaporation, and the deposition rates of Fe and Si were controlled at 0.02 nm/s and 0.1 nm/s, respectively, by an electron-impact emission spectroscopy sensor. After capping the Si/Fe multilayers with an EB-evaporated 100-nm-thick SiO_2 layer to prevent aggregation, the films were annealed at 900 °C for 14 hrs in Ar to form β-$FeSi_2$ films.[11] The grown films were fully relaxed and the lattice constants were shown to be equal to the values of bulk β-$FeSi_2$ by x-ray measurement. The lattice constants were $a=0.986$ nm, $b=0.779$ nm, and $c=0.783$ nm, respectively. The a axis of the grown film was perpendicular to Si(001).

High-pressure optical spectra were measured by using a diamond anvil cell in conjunction with a short focal-length spectrometer attached with a 200-W tungsten lamp. Both the sample consisting of $Si_{sub}(50\ \mu m)/\beta$-$FeSi_2(0.09\ \mu m)/SiO_2(0.1\ \mu m)$ and the reference consisting of $Si_{sub}(50\ \mu m)/SiO_2(0.1\ \mu m)$ were shaped into (200×200-μm^2 areas and put into a metal gasket with a 4:1 methanol-ethanol mixture as a pressure transmitting medium. The Si substrate was thinned to 50 μm in thickness. The transmission measurements were performed for both the sample and the reference at various pressures, with the temperature held constant at room temperature. The direction of the incident light was parallel to the a axis but not polarized.

The absorption coefficients were calculated by the ratio of transmission light intensities between the sample and the reference. In these experiments, no reflectivity correction was made due to the difficulties in measuring the reflectivity. However, we employed an empirical method by taking the baseline of the interference fringe below the absorption edge as the zero value of the absorption coefficient. The absorption edge of the Si substrate is around 1.1 eV and the absorption coefficient increases with increasing photon energy but

 ©2002 The American Physical Society

it is only about 200 cm^{-1} at 1.3 eV. This absorption coefficient is fairly small compared with that of β-$FeSi_2$ in the range of photon energy investigated, and the SiO_2 cap is more transparent than Si. Consequently, the determined absorption coefficient of β-$FeSi_2$ under pressure is reasonably accurate.

III. COMPUTATIONAL DETAIL

A full-potential linearized augmented plane-wave (FLAPW) method implemented in WIEN97 code was employed to calculate the electronic and optical properties of β-$FeSi_2$.[12] The calculation was based on the density-functional theory (DFT) and used a generalized gradient approximation. The base set was expanded to about 2×10^3 plane waves outside the core region. A dense sampling up to 346 k points in the irreducible Brillouin zone (BZ) was conducted for the self-consistent cycle (SCF), and the total energy was converged within 0.1 mRy. The BZ integration was computed with the modified tetrahedron method[13] and a constant matrix element in the tetrahedron was assumed for the calculation of optical properties.

The crystal structure was base-centered orthorhombic ($Cmca$) and the primitive unit cell consisted of eight Fe atoms and 16 Si atoms. The bulk lattice constants and internal positions for each atom were attained from previous experiments.[14] Geometry optimization was performed for only several structures with different internal free parameters. This limitation was due to the time-consuming (SCF) results cycle, i.e., three days for one cycle with a large number of electrons in the primitive unit cell of β-$FeSi_2$. All the investigated structures, however, were higher in the total energy than that for the experimental structure.

IV. RESULTS AND DISCUSSION

A. Band structure under pressure

The calculated band structure is shown in Fig. 1. The valence-band maximum (VBM) is at $Y,(2\pi/a,0,0)$, and is more than 0.1 eV higher than the local maximum along the $Z\Gamma$ (Λ) direction. The conduction-band minimum is along the $Z\Gamma$ (Λ) direction. Thus, the Y-Λ indirect gap is 0.67 eV and the direct gap at the Y point is 0.73 eV. The next direct band gap along the $Z\Gamma$ (Λ) direction is 0.81 eV. On the other hand, the experimental direct band gap is 0.873 eV at room temperature as discussed later. The theoretical band gap is 0.143 eV lower than the experimental result. It is well known that the DFT theory underestimates the band gap. Comparing this with various different first-principles calculations,[7–9,15,16] the topology near the gap is the same except for the quantitative difference in energy. This topology is in contrast to that of Filonov *et al.*[6] who reported that the VBM was along the Λ direction and the Y point was lower than the VBM. It is also in contrast with the result of Christensen, who suggested that the VBM was at the Γ point.[17] The scalar-relativistic linear muffin-tin orbital (LMTO) method was used for both of these calculations. The LMTO method assumes the potential to be spherically symmetric in an atomic sphere, while the FLAPW method makes no shape approximation in the form of the potential. The FLAPW method accordingly becomes more accurate in all nonisotropic systems.

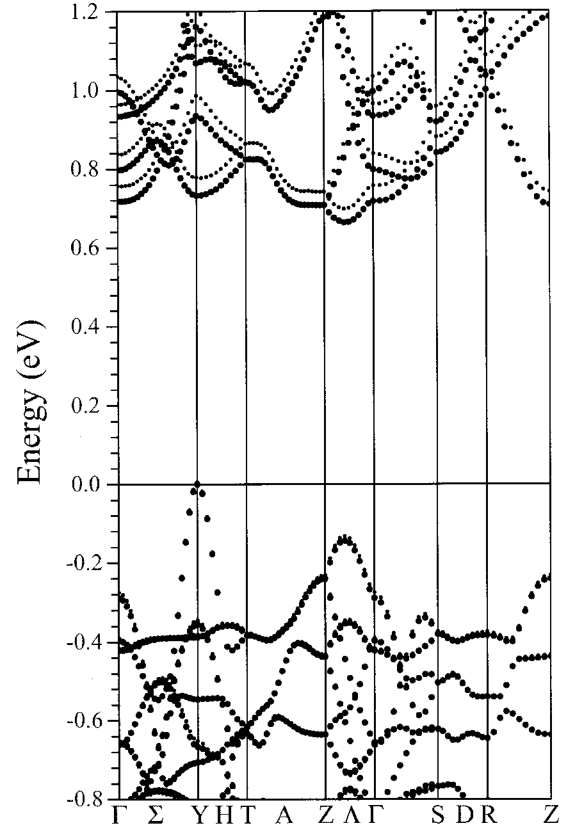

FIG. 1. Band structures at $V/V_0=1(\bullet)$ and $0.983(\cdot)$ along high symmetry axes. The valence-band maximum at the Y point is taken as the reference energy.

Figure 1 shows the band structure under compression with $V/V_0=0.983$ together with that at an ambient pressure. The VBM is taken as the reference, so the relative change of the band gap can be seen. There is no obvious change in the dispersion of the valence band and the conduction band except for the uniformly upward shift in energy. This contrasts sharply with the band-gap pressure coefficients in common semiconductors such as Si and GaAs; in particular, the Γ and X conduction-band edges are opposite in sign in Si and GaAs.

It is worth noting that the unit cell of β-$FeSi_2$ is large compared with common semiconductors consisting of only two atoms in the primitive unit cell. Consequently, the BZ of β-$FeSi_2$ is much smaller, and many critical points appear at the BZ edges, which result in the critical-point exciton.[18]

B. High-pressure absorption experiment

The absorption spectra at various pressures are shown in Fig. 2. The absorption edge is known to be around 0.8 eV, and the change in the slopes is seen at around 0.9 eV at an ambient pressure. From the calculated band structure in Fig. 1, the first absorption edge is indirect and the second is direct. To conclude that the first edge is indirect, it is necessary

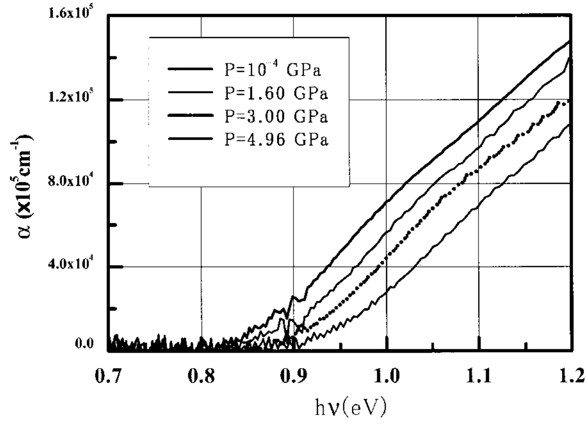

FIG. 2. Experimental absorption spectra at various pressures.

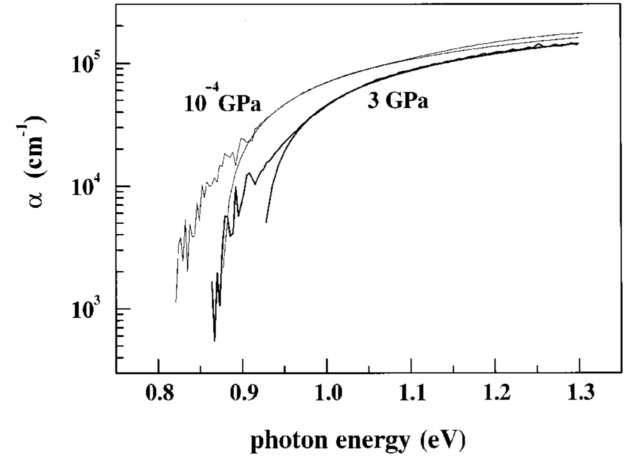

FIG. 3. Experimental absorption spectra at two pressures with the best-fit curves.

to observe a phonon replica of the absorption spectra in a similar way to common semiconductors. However, the sample here was too thin to observe the absorption coefficient below the indirect gap, where the interference fringes mask the detail of the absorption spectra. On the other hand, a very similar result was reported by Henrion *et al.* for the molecular beam epitaxy grown film of 750 nm thickness on Si.[19] This is about eight times thicker than our sample. Henrion *et al.* claimed that they observed one phonon emission and absorption spectrum, and reported that the indirect edge was at 0.75 eV and the direct edge was at 0.87 eV. Although the measurement was limited to the photon energy up to 0.95 eV, the result of Henrion *et al.* shows the energy difference between the indirect and direct edges is about 0.12 eV. This separation deviates about 0.06 eV from the calculated band structure. By increasing pressure, the absorption spectra move in parallel to higher energies up to 5 GPa. There is no observable change in the spectral shape such as that seen in GaAs when crossing from the direct to the indirect gap. To estimate the direct band gap at various pressures, an empirical fit has been employed, as discussed below.

The absorption spectrum is usually analyzed by Eq. (4.1), where a single pair of valence and conduction bands are assumed to participate in the photon absorption.

$$\alpha=\frac{A}{\hbar\omega}(\hbar\omega-Eg)^{\beta}. \tag{4.1}$$

Here A is the constant including the square of the photon-energy independent optical dipole matrix element, $\hbar\omega$ is the photon energy, Eg is the band gap, and β is the parameter for the joint density of states.[20]

From the band structure in Fig. 1, it is known that in β-$FeSi_2$ the physical picture of a single pair of valence and conduction bands for the optical absorption is correct only for an indirect absorption at a very narrow range of energies. Taking the parameter β as a free parameter, the above equation was employed to fit the experimental spectra of the direct absorption regime. The best-fit curves were obtained with $\beta=0.90$ and the parameter values used are compiled in Table I. The best fit curves for 10^{-5} GPa and 3 GPa are shown in Fig. 3, where only the direct band-gap energy Eg was adjusted. The direct band-gap energy of 0.875 eV at an ambient pressure is in good agreement with the result of Henrion *et al.*[19] The disagreement between the best-fit curve and the absorption spectrum at lower energy is due to the indirect absorption edge.

Based on the best-fit curves, the direct band-gap energy was evaluated at various pressures. The evaluated direct band-gap energies are plotted up to 5 GPa in Fig. 4. We also employed an alternative simple method to evaluate the pressure coefficient using the plot of the energy versus pressure. For example, we used a plot at the absorption coefficient of 3×10^{4} cm^{-1}. These two methods give almost the same pressure coefficient within the error from the experimental scatter. This result shows again that the spectra shifts monotonically with pressure.

TABLE I. Parameter values used to calculate the best fit curves by Eq. (4.1) (see the text).

P(GPa)	A(10^6 eV$^{1-\beta}$cm^{-1})	β	Eg(eV)
$1x10^{-5}$	4.5	0.90	0.875
3.0	4.5	0.90	0.922

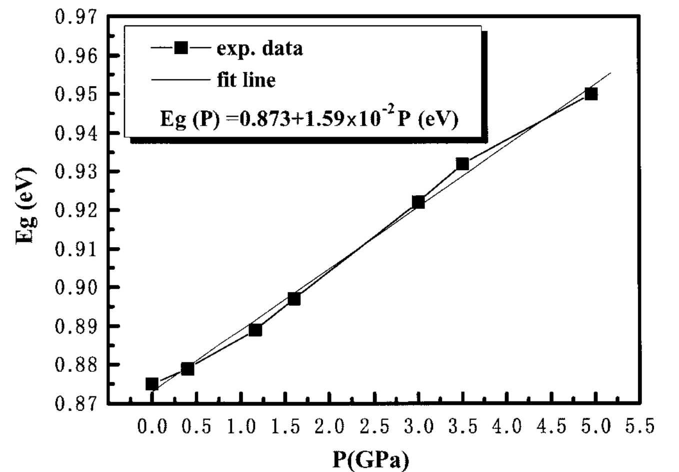

FIG. 4. Direct band gap vs pressure. The slope of the linear fit line is 15.9 meV/GPa.

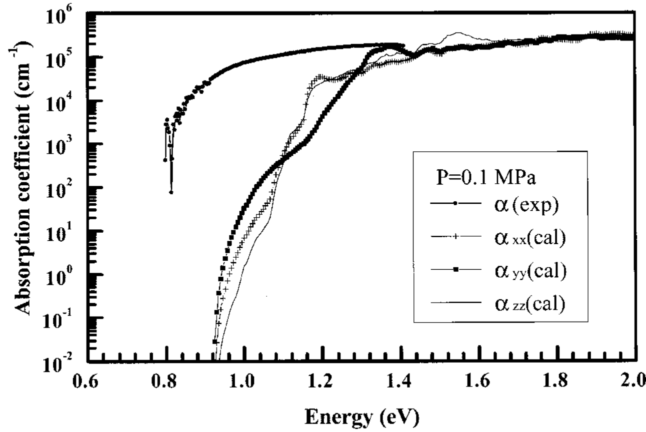

FIG. 5. Experimental absorption spectrum at ambient pressure and the calculated absorption spectra for three polarizations. The calculated spectra are shifted up by 0.143 eV.

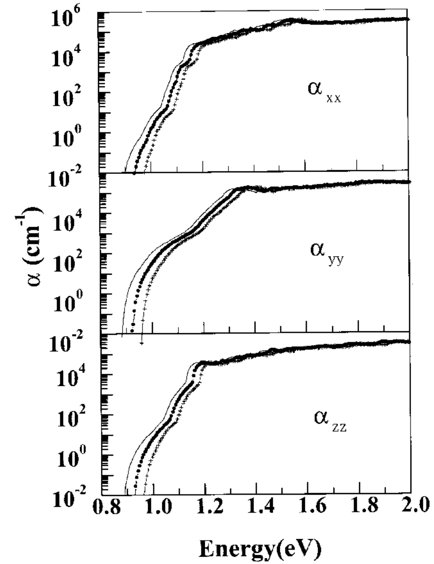

FIG. 6. Calculated absorption spectra at three values of V/V_0:1,0.983, and 0.967.

The evaluated linear pressure coefficient of the direct band gap is 15.9 meV/GPa. The pressure coefficient of the Γ direct gap is, for example, 108 meV/GPa for GaAs.[21] Consequently, that of β-$FeSi_2$ is 6.8 times smaller than that of GaAs. The bulk modulus of β-$FeSi_2$ is 180–200 GPa, being 2.4–2.7 times larger than the value 75 GPa for GaAs.[16,17,22] This inherent hardness of β-$FeSi_2$ can account for only about 40% of the ratio of the pressure coefficient of the direct band gap compared to GaAs. On the other hand, the band-gap deformation potential of β-$FeSi_2$ at the Y point is calculated to be -2.4 eV from three different volumes of $V/V_0 = 1.0, 0.983$, and 0.967. The magnitude of this theoretical deformation potential is again 2.4 times smaller than the value -8.33 eV for GaAs.[23] The main reason for this difference is that the deformation potential of the VBM in β-$FeSi_2$ is negative from our calculation, which shows that the VBM shifts to higher energy with increasing pressure. This behavior is in contrast to that for GaAs and other common semiconductors, for which the deformation potential is opposite in sign, and therefore, the VBM is lowered in energy. The chemical picture for this behavior in common semiconductors is that the VBM is the bonding state.

C. Comparison of experimental and calculated absorption spectra

The absorption spectra for direct transitions when an electric dipole is allowed were calculated along three principal polarizations. It is known that the calculated band gap within the DFT is smaller than the experimental band gap, simply because the DFT is a ground-state theory. Subsequently, a scissor method is often applied, namely, the calculated absorption spectra are shifted up by a suitable amount of energy. In the present case, the calculated spectra are shifted up by 0.143 eV, and shown in Fig. 5 along with the experimental absorption curve at an ambient pressure. The experimental spectra were measured for $y(b)$ and $z(c)$ polarizations.

The calculated direct absorption coefficient increases in two stages. For example, the y component reaches 10^{-3} cm^{-1} at around 1.1 eV, and then reaches 10^5 cm^{-1} at around 1.25 eV. This two-stage increase also appears for the other two polarizations. Similarly, no qualitative and quantitative differences appear in the absorption coefficient for the three polarizations when the energy exceeds about 1.5 eV. The difference is only prominent near the band gap.

The experimental absorption coefficient reaches about 10^5 cm^{-1} at about 1.4 eV and is in good agreement with the calculated result. From this we can see that the direct absorption process dominates in the higher-energy region. On the other hand, the experimental absorption coefficient exceeds the calculated coefficient by more than two to three orders of magnitude in the range of a half electron volt from the absorption edge to the energy where both coefficients coincide. The indirect absorption is not included in this calculation, although the contribution from this is expected to be smaller than the direct absorption at higher energy.

A possible cause for this strong direct absorption is the saddle-point exciton.[18] As known from the calculated band structure in Fig. 1, many BZ edges appear, which are due to the low symmetry and the relatively large unit cell, in other words, a small BZ. The BZ edges form various saddle points. On the other hand, the higher-energy saddle-point exciton is not resolved into each structure due to a relatively short lifetime, and results in a broadening of spectrum.[18] This Coulombic excitonic effect increases the absorption coefficient in the lower-energy region. However, the increase is characteristic depending on the ratio of the exciton binding energy (E_B) to the measure of the bandwidth energy(E_0).[18] For example, $E_B = 4.2$ and 14.3 meV for GaAs and Si, respectively, and $E_0 \approx 1$ eV for both.[24] For this case, the ratio is only 0.042 to 0.014 and so the absorption enhancement is weak in the continuous spectral region except for the discrete or quasicontinuous region below the band gap. In β-$FeSi_2$, the exciton binding energy was reported to be 16 meV by analyzing the Rydberg series.[25] For this case, the dispersion of the electronic band is weak due to the localized d electrons in the electronic band and $E_0 \approx 0.1$ eV from the calculated band

structure in Fig. 1. Then the ratio increases to 0.16. This value is ten times larger than that of GaAs and Si and is sufficient for the enhancement of the absorption in the continuous spectral region beyond the band gap. Thus a large absorption coefficient beyond the band gap is characteristic in β-$FeSi_2$.

The absorption spectra under compression were calculated for three principal polarizations. The resulting spectra are shown in Fig. 6. It is seen that under pressure the spectra shift in parallel to higher energies, which reproduces the characteristic behavior of the experimental spectra.

V. CONCLUSIONS

A high-pressure optical absorption experiment on epitaxially grown β-$FeSi_2$ on Si (001) substrate and the first-principles FLAPW calculations of band structure and optical absorption coefficients have been reported. From the theoretical band structure, the band gap of relaxed epitaxially grown β-$FeSi_2$ on Si (001) substrate is shown to be indirect with a direct gap lying several tenths of a mev higher. The indirect transition occurs along the $Z\Gamma$ (Λ) direction and the direct transition occurs at the Y point. The experimental absorption coefficient exceeds the calculated absorption coefficients by more than two orders of magniude particularly in the range of 0.3–0.4 eV beyond the direct band gap. We propose that a possible cause for this is the saddle-point excitons. Based on the empirical expression, the pressure coefficient of the direct band gap is determined to be 15.9 meV/GPa. Two possible reasons for this small pressure coefficient compared with common semiconductors are the negative deformation potential of the valence-band maximum and the large bulk modulus in β-$FeSi_2$.

ACKNOWLEDGMENT

One of the authors (K.T.) wishes to thank L. Anthony of Okayama University of Science for a detailed reading of the final manuscript.

*Corresponding author. Email address: takarabe@das.ous.ac.jp

[1] D. Leong, M. Harry, K.J. Reeson, and K.P. Homewood, Nature (London) **387**, 686 (1997).
[2] V.L. Shaposhinov *et al.*, in *Semiconducting Silicides*, edited by V.E. Borisenko (Springer, Berlin, 1999), Chap. 4.
[3] Y. Makita, in *Proceedings of the Japan-UK Joint Workshop on Kankyo-Semiconductors (Ecologically Friendly Semiconductors)*, edited by Y. Makita (Society of Kankyo Semiconductors in Japan, Japan, 1999), p. 1.
[4] K. Takakura, T. Suemasu, Y. Ikura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L789 (2000).
[5] T. Suemasu, Y. Negishi, K. Takakuraa, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L1013 (2000).
[6] 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. **83**, 4410 (1998).
[7] L. Miglio, V. Mergalli, and O. Jepsen, Appl. Phys. Lett. **75**, 385 (1999).
[8] K. Yamaguchi, K. Mizushima, and K. Sassa, Mater. Res. Soc. Symp. Proc. **579**, 215 (2000).
[9] K. Yamaguchi and K. Mizushima, Phys. Status Solidi B **223**, 253 (2001).
[10] K. Takarabe, R. Teranisi, J. Oinuma, Y. Mori, T. Suemasu, S. Chichibu, and F. Hasegawa, Phys. Status Solidi B **223**, 259 (2001).
[11] M. Tanaka, Y. Kumagai, T. Suemasu and F. Hasegawa, Jpn. J. Appl. Phys., Part 1 **36**, 3620 (1997); T. Suemasu, N. Hiroi, T. Fujii, K. Takakura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **38**, L878 (1999); K. Takakura, T. Suemasu, N. Hiroi, and F. Hasegawa, *ibid.* **39**, L233 (2000).
[12] P. Blaha, K. Schwartz, and J. Luitz, computer code WIEN97, A FLAPW Package, 1999, ISBN-3-9501013-04.
[13] P.E. Blöchl, O. Jepson, and O.K. Anderson, Phys. Rev. B **49**, 16 223 (1994).
[14] P.Y. Dusausoy, J. Protas, R. Wandji, and B. Roques, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **B27**, 1209 (1971).
[15] S.J. Clark, H.M. Al-Allak, S. Brand, and R.A. Abram, Phys. Rev. B **58**, 10 389 (1998).
[16] E.G. Moroni, W. Wolf, J. Hafner, and R. Podloucky, Phys. Rev. B **59**, 12 860 (1999).
[17] N.E. Christensen, Phys. Rev. B **42**, 7148 (1990).
[18] H. Chu and Yia-Chung Chang, Phys. Rev. B **36**, 2946 (1987).
[19] W. Henrion, St. Brehme, I. Siebeer, H. von Känel, Y. Tomm, and H. Lange, Solid State Phenom. **51-51**, 341 (1996).
[20] F. Wooten, *Optical Properties of Solids* (Academic Press, New York, 1972), p. 115.
[21] A.R. Gõni, K. Strössner, K. Syassen, and M. Cardona, Phys. Rev. B **36**, 1581 (1987).
[22] M. L. Cohen, *Elementary Excitations in Solids*, edited by J.L. Birma, C. Sebene, and R.F. Wallis (North-Holland, Amsterdam, 1992), p. 15.
[23] Chris G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
[24] C.F. Klingshirn, *Semiconductor Optics* (Springer-Verlag, Berlin, 1995), p. 166.
[25] M. Rebien, W. Henrion, U. Müller, and S. Gramlich, Appl. Phys. Lett. **74**, 970 (1999).