Ge quantum dots structural peculiarities depending on the preparation conditions†

Simon Erenburg,[a]* Nikolai Bausk,[a] Lev Mazalov,[a] Alexandr Nikiforov[b] and Andrei Yakimov[b]

[a]Institute of Inorganic Chemistry SB RAS, Lavrentiev Avenue 3, Novosibirsk 630090, Russia, and [b]Institute of Semiconductor Physics SB RAS, Lavrentiev Avenue 13, Novosibirsk 630090, Russia. E-mail: simon@che.nsk.su

Two-dimensional pseudomorphous Ge films have been grown to a critical thickness of 4 monolayers (ML) on Si(001). As a result of continuing deposition, pyramid-like Ge islands were grown in Stranski–Krastanov mode. The pyramid-like Ge islands deposited on Si(001) substrate using molecular beam epitaxy at 573 K reveal quantum dots (QDs) properties. The local microstructure parameters determined by EXAFS spectroscopy are linked to nanostructure morphology and adequate models are suggested and discussed. The pure Ge nanoclusters are covered by a 1–2 ML film with about 50% Si atom impurity caused by interface diffusion at 773 K. The influence of the effective thickness of the Ge film, Ge nanocluster sizes and Ge, Si deposition temperature on the QDs microstructure parameters is revealed. The first attempt to extract information about the energy structure of the free states of the quantum dot from X-ray absorption spectra (XANES spectra) was made. It was established that the maximum in the XANES spectra of a sample doped with boron is due to the appearance of free levels in the quantum dots at a depth of the order of 1.1 eV from the bottom of the Ge conduction band.

Keywords: EXAFS; XANES; quantum dots; molecular beam epitaxy.

1. Introduction

The development of a technique to determine the spatial and electronic structure parameters on the surface of materials will allow the controllable fabrication of structures containing nanoclusters with discrete electronic spectra. The fabrication of such systems will allow the traditional trend towards miniaturization and in element engineering for quantum computers (Shchukin & Bimberg, 1998; Barenco *et al.*, 1995) to be achieved.

Along with the traditional surface-sensitive methods, such as Auger spectroscopy and low-energy electron diffraction, attempts have been made to use the traditional physical methods which were earlier considered to be unsuitable for solving such tasks. Here we report the use of EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) spectroscopy methods to study the spatial and electronic structure of Ge/Si heterostructures. Measurements of X-ray absorption fine structure at the germanium *K*-edge (Ge*K* XAFS measurements) have been performed using surface-sensitive total electron yield and fluorescent detection mode.

The phenomenon of self-organization in the process of heteroepitaxial semiconductor system growth allows the fabrication of dense, extended, well ordered structures containing islands of uniform shape and size. Such structures are especially important for high-technology applications. In semiconductor nanostructures with spontaneously ordered inclusions of a narrower bandgap material within a broader bandgap matrix, the limiting case of the dimensional quantization is realised. Zero-dimensional quantization exists within a certain interval of microinclusion sizes with the formation of so-called quantum dots (QDs) characterized by discrete electronic spectra.

In a heteroepitaxial system with a mismatch between the lattice constants, the initial growth may occur in layers. The formation of thicker layers leads to a tendency towards elastic strain relaxation and elastic energy decrease by disturbing the two-dimensional growth and forming isolated islands, the so-called Stranski–Krastanov growth.

In a series of comparatively recent studies it was shown by different experimental methods [capacitance spectroscopy (Yakimov *et al.*, 1998), hopping transport (Yakimov, Dvurechenskii *et al.*, 1999), admittance spectroscopy (Yakimov, Adkins *et al.*, 1999) and optical spectroscopy (Yakimov *et al.*, 2000)] that at a certain thickness of the epitaxic Ge film on Si(001) in the electronic spectra of the heterostructures there appear features associated with the zero-dimensional density of states. These features are due to the dimensional quantization of the hole spectrum in the Ge islands appearing during disturbed two-dimensional growth.

The spectrum of states in the self-organizing nanoclusters may be largely influenced by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters of the nanocluster and substrate. In the Ge/Si system the lattice mismatch amounts to 4.2%. This will cause changes in the local structure: local distortions of the symmetry, changes in the valence angles and inter\-forcelb]atomic distances. Such structural changes may change the energy spectrum by a magnitude of the order of 0.1 eV (Rieger & Vogl, 1993), which is comparable with the dimensional quantization energy in a QD.

The local structural changes in the thin layers and nanoclusters are not detectable by traditional X-ray structural analysis or electron diffraction because such systems have no long-range ordering. EXAFS and XANES spectroscopy provide a unique possibility for solving such problems (Koninsberger & Prins, 1988). These methods allow the determination of the parameters of the local environment of the atoms and electronic parameters of the nanoclusters. Thus, Kakar *et al.* (1998), using XANES spectroscopy, found a broadening of the forbidden gap with decreasing size of the CVD-grown germanium nanoclusters in silicon. Oyanagi *et al.* (1997) and Wei *et al.* (1999), using EXAFS spectroscopy, studied the local environment of Ge adatoms on Si(001), the structure of thin Ge layers on Si(001), and a superlattice with strained $(Ge_4/Si_4)_5$ layers. Erenburg *et al.* (2000), Erenburg, Bausk, Mazalov *et al.* (2001) and Erenburg, Bausk, Stepina *et al.* (2001), using total electron yield and fluorescent detection mode Ge*K* XAFS measurements, revealed that Ge QDs are characterized by interatomic Ge—Ge distances of 2.41 Å, which is 0.04 Å less than in bulk Ge.

The growth of self-organizing Ge islands and later of the blocking Si layer is evidently accompanied by the temperature-dependent surface diffusion of Si and Ge atoms, affecting the composition of the wetting layer and the composition and width of the intermediate layer at the Si–Ge interface. These characteristics of the transitional layers should have a substantial influence on the features in the QD energy spectrum. Therefore, energy spectrum calculations for QDs and interpretation peculiarities of their experimental energy spectra as well as the design of elements with given electronic properties must take into account the variation of the QD local structure.

† Presented at the 'XIV Russian Synchrotron Radiation Conference SR2002', held at Novosibirsk, Russia, on 15–19 July 2002.

In this work, surface-sensitive EXAFS measurements based on total electron yield and fluorescent detection have been used to study the peculiarities of Ge/Si structures.

2. Experimental

Two structures prepared by molecular beam epitaxy (MBE) on two halves of an Si(001) substrate were studied experimentally. Both structures contained layers of Ge separated by 10 nm-thick blocking layers of Si and differed from each other only in the thickness of their Ge layers. In one structure each Ge layer had a thickness of 4 monolayers (ML); in the other structure this thickness was equal to 6, 8 and 10 ML. It was suggested that in the structure of the first type a pseudomorphous film of Ge would be formed; in the second type of structure, disturbances of the two-dimensional growth after a thickness of 4 ML will occur with the formation of pyramidal Ge nanoclusters. 10 ML clusters have lateral dimensions of $\sim$15 nm, a height of $\sim$1.5 nm and a separation between the islands of $\sim$5 nm. The wetting-layer thickness and the size of the Ge nanoclusters on Si grown under disturbed growth conditions were determined by electron diffraction, high-resolution electron microscopy and scanning tunnelling electron microscopy (Yakimov, Dvurechenskii *et al.*, 1999). The Ge film growth temperature was equal to 573 K, the growth rate was 0.035 nm s^{-1} and the deposition temperature of the blocking layer was 773 K and 573 K. For use as reference compounds, thick films (300 nm) of solid solutions of a different composition (30% Ge, 50% Ge and 75% Ge) were prepared by MBE under the same conditions.

The Ge*K* EXAFS and XANES spectra in the Ge/Si(100) heterostructures were measured using synchrotron radiation of the VEPP-3 storage ring at the Budker Institute of Nuclear Physics, Novosibirsk, Russia. The X-ray energy was defined by a double-crystal monochromator with a channel-cut Si(111) single crystal. The spectra were recorded using the surface-sensitive EXAFS technique based on the measurements of the flux of electrons of the whole energy spectrum (total electron yield technique) and of the flux of fluorescent X-rays (fluorescent detection mode). For an anisotropy study of the Ge atom environment in heterostructures, the Ge*K* spectra have been measured at the parallel ($\|$) and perpendicular ($\perp$) Si(001) orientations relative to the electric field vector **E** of the linearly polarized synchrotron radiation beam.

The obtained data were processed using the *EXCURV92* software package (Binsted *et al.*, 1991). During the data processing, the phase and amplitude characteristics were calculated in the X_α-DW approximation, using the procedures of the package (Binsted *et al.*, 1991).

For the analysis of the Ge local environment the Fourier-filtered data were fitted using the k and k^2 weighting procedure in the photoelectron wavevector interval from 2.5 $Å^{-1}$ to 13 $Å^{-1}$. The error in determining the interatomic distances with the fitting procedure was $\pm$0.01 Å. The amplitude-damping factor S_0^2 was determined by data fitting for massive Ge and was equal to 0.8.

3. Results and discussion

While the amplitude and phase characteristics of $k\chi(k)$ for the spectra of the Ge_xSi_{1-x} films with different stoichiometries are significantly different, comparison of $k\chi(k)$ of the EXAFS spectra of a film of the $Ge_{0.50}Si_{0.50}$ solid solution and the 4 ML film show a complete similarity both in the amplitude and phase. This does not mean that the four monolayers that grew are a uniform solid solution; but this does establish the presence of an appreciable exchange of atoms between the Ge and Si phases, which decreases the elastic strain in the system during the deposition of the blocking Si layer (773 K). Thus the monolayers forming the so-called pseudomorphous Ge films embedded in an Si matrix contain up to 50% of Si atoms. It is essential that our results (see below) show that only the atoms in the immediate vicinity of the boundary are really participating in the exchange. On processing our data the fitting was performed using the experimental data Fourier-filtered in the interval 1.5 Å < R < 2.6 Å. The values of the Debye–Waller factor, σ^2 = 0.0034 $Å^2$, and of the energy, E_o = 10.6 eV, were determined as a result of fitting for pure Ge with interatomic distances R(Ge—Ge) = 2.450 Å and coordination number n = 4, and were fixed in all other cases.

Table 1
Parameters obtained by the fitting procedure for pseudomorphous Ge films and structures with pyramid-like Ge islands on Si(001).

R_1(Ge—Ge) and R_2(Ge—Si) are interatomic distances. n_1(Ge) and n_2(Si) are the coordination numbers of Ge with respect to Ge atoms and to Si atoms, respectively. The quality of the fit is determines by the index F (Binsted *et al.*, 1991).

N	Sample	R_1(Ge—Ge)	R_2(Ge—Si)	n_1(Ge)	n_2(Si)	F
1	c-Ge	2.45 Å		4		0.8
2	Film ($\|$**E**)	2.41 Å	2.37 Å	1.70	2.35	0.6
3	QD ($\|$**E**)	2.40 Å	2.38 Å	3.16	1.67	1.0
3*a*	QD ($\|$**E**)	2.41 Å	2.37 Å	1.70	2.34	1.7
		2.40 Å	2.38 Å	4.14	0.54	
4	Film ($\perp$**E**)	2.41 Å	2.36 Å	1.78	2.00	3.9
5*a*	QD ($\perp$**E**)	2.41 Å	2.36 Å	1.78	2.00	1.1
		2.41 Å	2.38 Å	4.5	0.10	

The simplest models, *N*2, 3, 4, included one averaged variant of the environment for the Ge atoms with distances R_1(Ge—Ge), R_2(Ge—Si) and coordination numbers of Ge with respect to germanium atoms [n_1(Ge)] and to silicon atoms [n_2(Si)] (Table 1). To a certain degree, such models are correct for the 4 ML films. The models should include at least two types of Ge atoms for heterostructures with quantum dots: the atoms at the boundary and those within the bulk of the Ge nanoclusters. For the samples with QDs, the models included two types of Ge atoms: (i) Ge atoms at the boundary in the 2 ML-thick transition layer (such atoms account for about half of all the Ge atoms); (ii) the atoms inside the quantum dots accounting for the other half of the Ge atoms. The thickness of the transition layer was estimated using the conclusion of this work, that the pseudomorphous 4 ML Ge films embedded in the Si matrix and having a thickness of two transition layers contain about 50% of Si atoms. This assumption turned out to be true, since with the use for the quantum dots of the same transition-layer parameters [of the interatomic distances R_1(Ge—Ge), R_2(Ge—Si) and the coordination numbers n_1(Ge) in germanium and n_2(Si) in silicon] as in the 4 ML films, the Ge atoms in the quantum dots have practically no Si atoms in the first sphere of their environment.

Table 1 shows that the interatomic distances R_1(Ge—Ge) decrease in the thin films and structures with QDs by 0.04 Å compared with pure Ge and are equal to 2.41 Å. The R_2(Ge—Si) distances decrease by 0.03 Å compared with the sum of the covalent radii of Ge and Si and are equal to 2.37 Å. Fig. 1 illustrates the monotonic growth of the fraction of Ge atoms inside purely germanium islands with entirely Ge atoms in their environment as the effective thickness of the germanium film increases from 4 to 10 ML, *i.e.* the monotonic size evolution of germanium nanoclusters as a function of film thickness in this series. It was of interest to study analogous systems prepared using slightly different temperatures for the film growth and the deposition of the blocking silicon layer.

Table 2
Comparison of parameters obtained by the fitting procedure for pseudomorphous Ge films and structures with pyramid-like Ge islands on Si(001) with blocking Si layer deposited at 773 K and 573 K.

R_1(Ge—Ge) and R_2(Ge—Si) are interatomic distances. n_1(Ge) and n_2(Si) are the coordination numbers of Ge with respect to Ge atoms and to Si atoms, respectively. T is the blocking Si layer deposition temperature. The quality of the fit is determines by the index F [**E** || Si(001)].

T (K)	Sample	R_1(Ge—Ge) (Å)	R_2(Ge—Si) (Å)	n_1(Ge)	n_2(Si)	F
773	Film	2.41	2.37	1.7	2.3	1.0
573	Film	2.42	2.37	2.7	1.3	2.2
773	QD	2.40	2.36	2.6	1.4	0.5
773	QD	2.41	2.37	1.7	2.3	1.4
		2.41	2.37	3.7	0.3	
573	QD	2.42	2.37	2.7	1.3	2.9
		2.42	2.38	4.0	0.0	

At first, structures were prepared using the same temperature for the film growth (573 K) but a lower (573 K) deposition temperature of the blocking Si layer. Table 2 shows the influence of the blocking Si-layer deposition temperature on the local structure parameters [n_1(Ge), n_2(Si)]. As seen from Table 2, with a change in the temperature conditions there is no appreciable change in interatomic distances but the partial coordination numbers of germanium with respect to Ge, n_1(Ge), and Si, n_2(Si), are seriously altered, *i.e.* such a decrease in the temperature leads to a substantial decrease in the diffusion between the phases Ge/Si and the formation of sharper phase boundaries.

As seen from Fig. 2, the amplitude characteristics of the EXAFS spectra for such films do not differ from those of the massive Ge and there is only a small phase shift. This effect may be explained by the scattering potentials of the environment for the absorbing atoms being similar not only in the first sphere of its environment. Therefore in this case we have structural similarity not only for the first coordination sphere of Ge but also an ordering in the further coordination spheres of Ge in thin films analogous to that in the massive Ge. On the other hand, the phase shift at large energies for the nanoclusters relative to the massive Ge is apparently due to a decrease in the Ge—Ge interatomic distances.

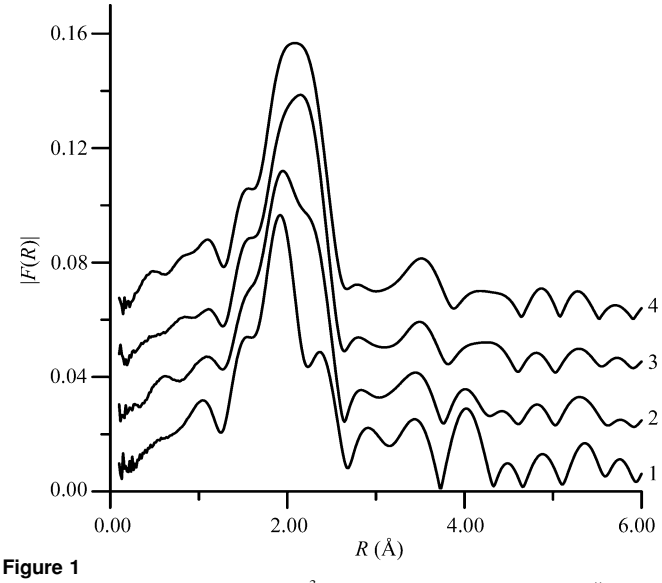

Figure 1
Fourier transform magnitude of $k^3\chi(k)$ Ge K EXAFS data at **E**||Si(001). Curve 1: pseudomorphous 4 ML two-dimensional films on Si(001). Curve 2: Ge nanoclusters on pseudomorphous 4 ML films on Si(001) with effective thickness equal to 6 ML, to 8 ML (curve 3) and to 10 ML (curve 4).

In addition, the interatomic distances R_1(Ge—Ge) and R_2(Ge—Si) obtained from the EXAFS data are in agreement with the interatomic distances derived from the spatial distribution of elastic deformation calculated within the valence force field (VFF) model. The calculation was performed by a procedure based on the use of the Green function of the 'atomistic' elastic problem, which was further developed by Nenashev & Dvurechenskii (2000). The calculation was performed for the QD model with sharp Ge/Si boundaries.

In conclusion, the first attempt at extracting the spectral information on the energy structure of the free states of the quantum dot itself from X-ray absorption spectra should be mentioned. XANES spectra of two samples were compared: one sample was synthesized under conventional conditions; the other was doped with boron by a special procedure so that Ge in the nanoclusters had a substantial deficit of electron charge.

A detailed comparative analysis of the obtained spectra showed the presence of a maximum A in the spectrum of the doped sample at a distance of −1.8 eV from the point of inflection of the main Ge K absorption edge (the position of the Ge K absorption edge) (Fig. 3).

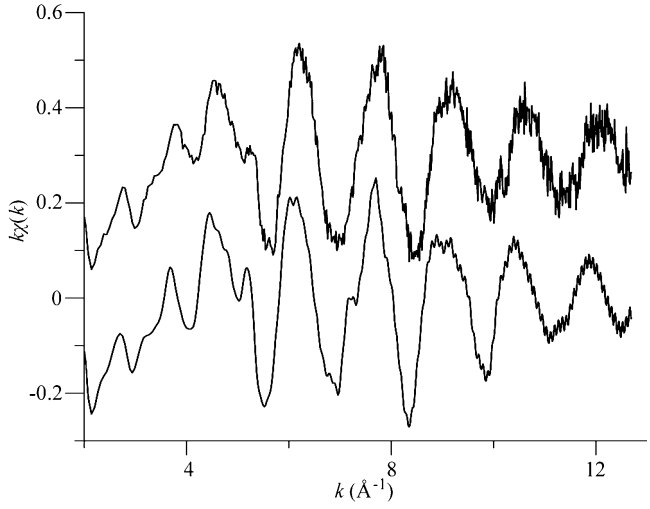

Figure 2
Ge K k-weighted normalized oscillating part of the X-ray absorption coefficient measured on pure Ge film (1000 Å) (bottom curve) and on Ge nanoclusters (∼15 nm × ∼1.5 nm) on Si(001) with blocking Si layer deposited at 573 K (top curve).

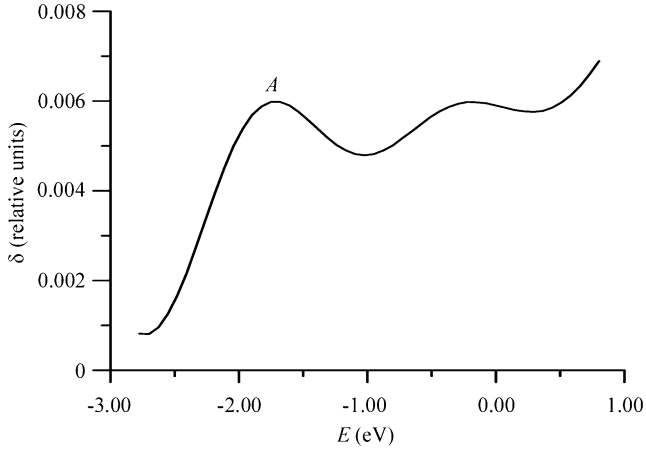

Figure 3
Relative difference absorption intensity of 8 ML Ge samples with and without boron dopants.

Such a maximum is absent in the sample with no dopant. The maximum has an intensity of the order of 0.2% of the absorption jump in the main Ge *K* absorption edge. It was suggested that the maximum is due to the appearance of free levels in the QD at a depth of the order of 1.1 eV from the bottom of the Ge conduction band (Fig. 4) in accordance with previous experimental and calculation results (Dvurechenskii *et al.*, 2002).

4. Conclusion

The microstructural parameters of Ge/Si heterosystems, largely influenced by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters of the nanocluster and substrate, were detected by direct methods showing that EXAFS spectroscopy is a very useful tool for studying materials containing nanostructures.

Financial support from the Russian State Scientific and Engineering Program on Basic Researches in Physics (theme 01.40.01.09.04, public contract 40.072.1.1.1176) and the Russian State Scientific Program 'Integration' is greatly appreciated.

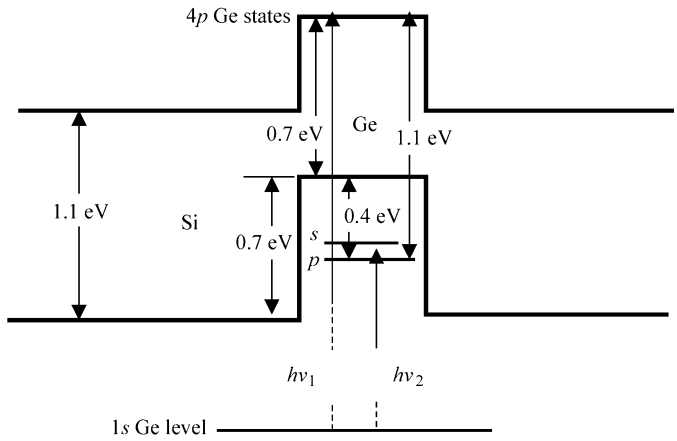

Figure 4
Scheme of hole states and X-ray absorption electron transitions in the Ge quantum dots with boron dopants.

References

Barenco, A., Deutsch, D., Ekert, A. & Jozsa, R. (1995). *Phys. Rev. Lett.* **74**, 4083–4086.
Binsted, N., Campbell, J. W., Gurman, S. J. & Stephenson, P. C. (1991). *The SERC Daresbury Laboratory EXCURVE Program*. SERC Daresbury Laboratory, Warrington WA4 4AD, Cheshire, UK.
Dvurechenskii, A. V., Nenashev, A. V. & Yakimov, A. I. (2002). *Nanotechnology*, **13**, 75–80.
Erenburg, S. B., Bausk, N. V., Mazalov, L. N., Nikiforov, A. I., Stepina, N. P., Nenashev, A. V. & Yakimov, A. I. (2001). *Solid State Ion.* **141**/**142**, 137–141.
Erenburg, S. B., Bausk, N. V., Nenashev, A. V., Stepina, N. P., Nikiforov, A. I. & Mazalov, L. N. (2000). *Russ. J. Struct. Chem.* **41**, 802–808.
Erenburg, S. B., Bausk, N. V., Stepina, N. P., Nikiforov, A. I., Nenashev, A. V. & Mazalov, L. N. (2001). *Nucl. Instrum. Methods Phys. Res. A*, **470**, 283–289.
Kakar, S., van Buuren, T., Treusch, R., Heske, C., Himpsel, F. J., Chase, L. L. & Terminello, L. J. (1998). *Abstracts of the MRS 1998 Spring Meeting*, Vol. 2.5, San Francisco, California, USA, p. 350.
Koninsberger, D. C. & Prins, R. (1988). *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, p. 710. New York: Wiley.
Nenashev, A. V. & Dvurechenskii, A. V. (2000). *JETP*, **117**, 570–578.
Oyanagi, H., Sakamoto, K. & Shioda, R. (1997). *J. Phys. IV France*, **7**(C2), 669–673.
Rieger, M. M. & Vogl, P. (1993). *Phys. Rev. B*, **48**, 14276–14287.
Shchukin, V. A. & Bimberg, D. (1998). *Appl. Phys. A*, **67**, 687–700.
Wei, S., Oyanagi, H., Sakamoto, K., Takeda, Y. & Pearsall, T. P. (1999). *J. Synchrotron Rad.* **6**, 790–792.
Yakimov, A. I., Adkins, C. J., Boucher, R., Dvurechenskii, A. V., Nikiforov, A. I., Pchelyakov, O. P. & Biskupskii, G. (1999). *Phys. Rev. B*, **59**, 12598–12603.
Yakimov, A. I., Dvurechenskii, A. V., Nikiforov, A. I. & Pchelyakov, O. P. (1998). *JETP Lett.* **68**, 125–130.
Yakimov, A. I., Dvurechenskii, A. V., Nikiforov, A. I. & Pchelyakov, O. P. (1999). *Phys. Low-Dim. Struct.* **3**/**4**, 99–109.
Yakimov, A. I., Dvurechenskii, A. V., Stepina, N. P. & Nikiforov, A. I. (2000). *Phys. Rev. B*, **62**, 9939–9942.

 Received 25 January 2003 • Accepted 23 June 2003