Solid-Phase Synthesis of L1$_0$-FePd(001) Epitaxial Thin Films: Structural Transformations and Magnetic Anisotropy

V. G. Myagkov[a], V. S. Zhigalov[c], L. E. Bykova[a], L. A. Solov'ev[b], and G. N. Bondarenko[b]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,*
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: miagkov@iph.krasn.ru

[b] *Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences,*
Krasnoyarsk, 660036 Russia

[c] *Siberian State Aerospace University, Krasnoyarsk, 660014 Russia*

Received April 1, 2010

The solid-phase synthesis of the L1$_0$-FePd magnetically hard phase in Fe(001)/Pd(001) epitaxial films has been experimentally investigated. The formation of three types of L1$_0$-FePd ordered crystallites whose c axes coincide with the $\langle 100 \rangle$ directions of the MgO(001) substrate begins at the Fe/Pd interface at a temperature of 450°C. After an increase in the annealing temperature to 500°C, structural rearrangement occurs and gives rise to the predominant growth of L1$_0$-FePd crystallites with the c axis perpendicular to the film plane. After 10-h annealing, the fraction of such crystallites becomes dominant, leading to large perpendicular anisotropy. The first magnetocrystalline-anisotropy constant of the L1$_0$-FePd phase has been determined and the second constant has been estimated. It has been shown that magnetic anisotropy in the L1$_0$-FePd(001) basal plane cannot be described by the biaxial anisotropy of the tetragonal crystal. The annealing above 500°C results in the evolution of L1$_0$-FePd to a disordered cubic phase.

DOI: 10.1134/S0021364010090109

INTRODUCTION

The structural and magnetic properties of FePd, FePt, and CoPt thin films and L1$_0$-type ordered nanoparticles are actively investigated in view of the potential possibility of their use for high-density magnetic recording of information, special magnetic media [1, 2], and biological and medical purposes [3]. The initial FePd film samples and nanoparticles prepared by various methods usually have a disordered lattice, and long-term high-temperature annealings are necessary for obtaining the L1$_0$-FePd ordered structure [2]. Significant efforts are focused on the investigation of the correlation of perpendicular anisotropy K_U and magnetization M_S with the structural properties of L1$_0$-FePd thin films [4–8] and nanoparticles [9–11]. However, solid-phase reactions between Fe and Pd element reagents were investigated only in a few works. In particular, the L1$_0$-FePd phase was revealed after annealing in bilayer Fe/Pd films [6], multilayers [7], after irradiation by helium ions [8], and in nanoparticles prepared by the mechanical melting of Fe and Pd powders [11]. Owing to the tetragonal distortion, the L1$_0$ phases have a large uniaxial magnetocrystalline-anisotropy constant K_1 with the easy magnetization direction coinciding with the c axis. The magnetocrys-

talline-anisotropy energy E_K for the tetragonal crystal per unit volume of the sample has the form [12]

$$E_K = E_0 + K_1 \sin^2 \varphi + K_2 \sin^4 \varphi + K_3 \cos^2 \alpha \cos^2 \beta, \quad (1)$$

where φ is the angle between the magnetization M_S and [001] c axis and α and β are the angles between the magnetization M_S and the [100] and [010] axes, respectively. The maximum K_1 values are observed in the L1$_0$ phases of the FePt (6.6×10^7 erg/cm^3) and CoPt (4.9×10^7 erg/cm^3) melts and the value for FePd is somewhat smaller (1.8×10^7 erg/cm^3) [13]. When the constant K_1 of the L1$_0$ phases in FePd, FePt, and CoPt samples is measured by various methods, either the constant K_2 is neglected or the sum $K_1 + K_2$ is determined. The anisotropy constants are the fundamental characteristics of magnetic materials, and knowledge of them is very important for both scientific and engineering applications.

In this work, the solid-phase synthesis of the L1$_0$-FePd phase and the structural rearrangement of L1$_0$-FePd crystallites are investigated at various temperatures and times of annealing in Pd(001)/Fe(001) film systems. The structural features of L1$_0$-FePd films make it possible to determine the K_1 value and estimate the second magnetocrystalline-anisotropy constant K_2.
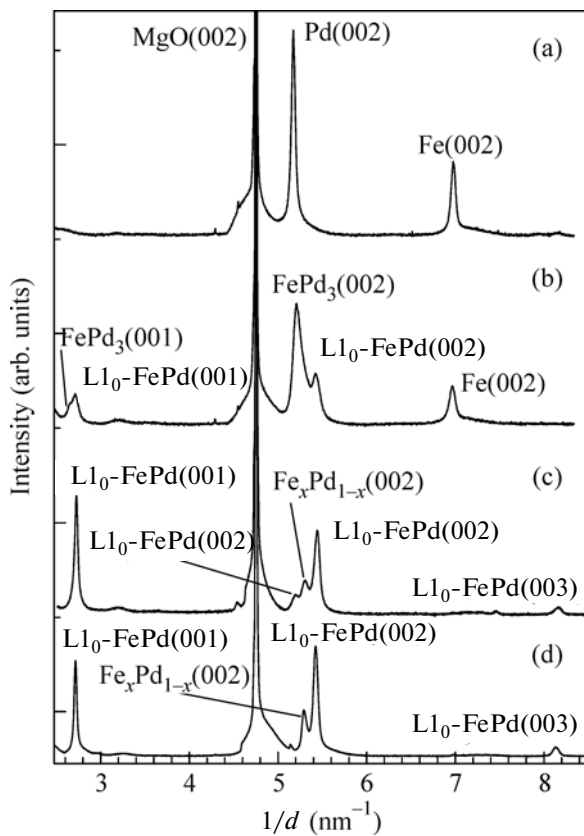
Fig. 1. Diffraction patterns of the Fe(001)/Pd(001)/MgO(001) film system (a) in the initial state and after annealing (b) for 0.5 h at 450°C, (c) for 3 h at 500°C, and (d) for 10 h at 500°C.

Fig. 2. Curves of the torque $L_{\parallel}(\varphi)$ in the plane of the Fe(001)/Pd(001)/MgO(001) film system ($\triangle$) in the initial state and after annealing at 500°C for ($\square$) 0.5 and ($\blacksquare$) 10 h.

SAMPLES AND THE EXPERIMENTAL PROCEDURE

The initial Fe(001)/Pd(001) film structures were obtained by the successive thermal deposition of Pd and Fe layers onto the MgO(001) single-crystal substrate in a vacuum of 10^{-6} Torr. The samples with a Fe : Pd atomic ratio of 1 : 1 and a general thickness of 200 nm were used in the experiments. The layers were deposited at temperatures of 220–250°C, at which the epitaxial growth of Fe(001) and Pd(001) on the MgO(001) surface occurs without the solid-phase reaction between the layers. The saturation magnetization M_S and magnetocrystalline-anisotropy constants were measured using the torque method with a maximum magnetic field of 18 kOe. The torques perpendicular to the film plane $L_{\perp}(\varphi)$ and in the plane $L_{\parallel}(\varphi)$ are presented per unit volume of the film. The X-ray fluorescence analysis was used to determine the thicknesses of the Fe and Pd layers. The appearing phases were identified using a DRON-4-07 diffractometer (CuK_α radiation). X-ray diffraction investigations of the epitaxial orientation of the phase were performed with a PANalytical X'Pert PRO diffractometer with a PIXcel matrix solid-state detector. The order
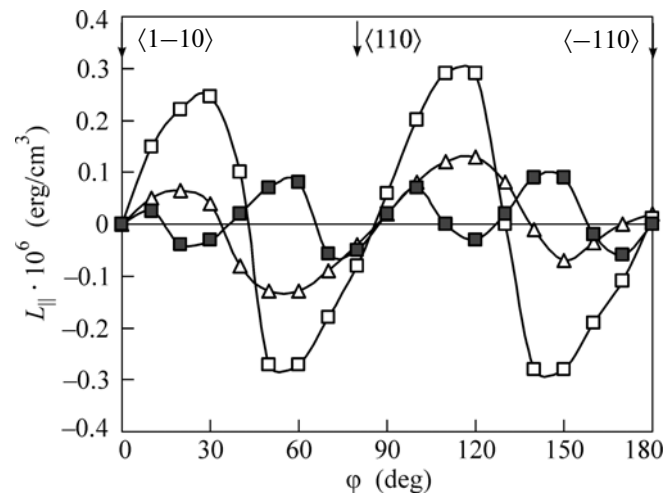
degree η of the $L1_0$-FePd phase was determined by the refinement of the occupation of the corresponding Fe and Pd atomic position in the structure by the full-profile X-ray diffraction analysis. The initial Fe(001)/Pd(001)/MgO(001) samples were annealed from 300 to 550°C with a step of 50°C and aging for 30 min at each step.

EXPERIMENTAL RESULTS AND DISCUSSION

Only the Fe(001) and Pd(001) reflections are manifested on the diffraction pattern of the initial Fe(001)/Pd(001)/MgO(001) sample (see Fig. 1a), indicating the cube-per-cube epitaxial growth. The initial samples have magnetic anisotropy in the film plane whose easy axes coincide with the [110 and [1–10] direction of the MgO(001) substrate and the constant is equal to the first magnetocrystalline-anisotropy constant of bulk iron (see Fig. 2). The analysis of magnetic and X-ray measurements indicates that Fe and Pd layers grow according to the orientation relations Fe(001)[110] ∥ Pd(001)[001] ∥ MgO(001)[001]. The magnetization and magnetic anisotropy constant remain unchanged up to a temperature of 400°C and change sharply after annealing at 450°C. This indicates the initiation of the solid-phase reaction between the Fe and Pd layers. The magnetic anisotropy constant in the film plane increases in this case by a factor of about 3 ($2L_{\parallel}^{max} \sim (0.6 \pm 0.1) \times 10^6$ erg/cm^3) without a change in the directions of the easy axes; this increase is attributed to the formation of the high-anisotropy phase (see Fig. 2). After annealing at 450°C, a decrease in the intensities of the Fe(00l) and Pd(00l) reflections is observed on the diffraction pattern (see Fig. 1b) and new (001) and (002) peaks of the

ordered L1$_0$-FePd and L1$_2$-FePd$_3$ phases, respectively, appear. This indicates that these phases are formed at close temperatures. It is worth noting that the (002) peak of the L1$_2$-FePd$_3$ phase can partially mask the peak of unreacted Pd, the disordered cubic Fe$_x$Pd$_{1-x}$ phase, and the (200) reflection of the L1$_0$-FePd phase.

As the annealing temperature was increased to 500°C, the reflections of the L1$_0$-FePd phase continued to increase, whereas the Fe(002) peak decreased and completely disappeared after 3-h annealing in view of the end of the synthesis (see Fig. 1c). The appearance of the (200) reflection of the L1$_0$-FePd phase implies that the structure of the layer of the reaction products contains three variants of crystallites of the L1$_0$-FePd phase with three orthogonal axes parallel to three main $\langle 100 \rangle$ aces of the MgO substrate (see Fig. 1c). Such a structure is often observed in L1$_0$-FePd, CoPt, and FePt thin films [5] and nanoparticles [10]. The presence of three types of the orientations of the L1$_0$-FePd crystallites were confirmed by the asymmetric scanning of the (113), (311), and (201) reflections of the L1$_0$-FePd phase and the (113) reflection of the MgO substrate. This implies that three types of crystallites are formed at the initial stage of the synthesis of the L1$_0$-FePd phase at 450°C.

The magnetic anisotropy in the film plane increases slightly at short annealing times at a temperature of 500°C and begins to decrease after 3-h annealing. The magnetic anisotropy constant of the disordered FePd phase is estimated as ~10^5 erg/cm^3 [14]. This value is much smaller than the effective biaxial constant ($2L_\parallel^{max}$ ~ $(0.6 \pm 0.2) \times 10^6$ erg/cm^3) of the samples under investigation, in agreement with the formation of three types of crystallites of the L1$_0$-FePd high-anisotropy disordered phase. When the magnetic field H rotates in the plane of the sample, the contribution to the total anisotropy energy E_K from the crystallites whose c axes are perpendicular to the film plane is small, because it is described by the term $K_3 \cos^2 \alpha \cos^2 \beta$. The main contribution comes from the crystallites whose c axes are in the film plane. Assuming that L1$_0$-FePd crystallites are coupled by the exchange interaction and $K_2 \gg K_3$, we transform Eq. (1) for the anisotropy energy into the expression [15]

$$E_K = -(f_1 + f_2)K_2 \sin^2 \varphi \cos^2 \varphi. \qquad (2)$$

According to the analysis of the relative decrease in the Fe(002) peak, the residual Fe(001) layer can occupy 0.25−0.5 of the film volume. Under the assumption that the relative volumes of three types of crystallites are the same, $f_1 = f_2 = 1/3$, and the effective anisotropy constant is $2L_\parallel^{max} = (1/2 - 1/3)K_2$, we obtain $K_2 = (1.5 \pm 0.5) \times 10^6$ erg/cm^3. This estimate of K_2 is in good agreement with the value of $2K_2/M_S = (3.5 \pm 0.5) \times$
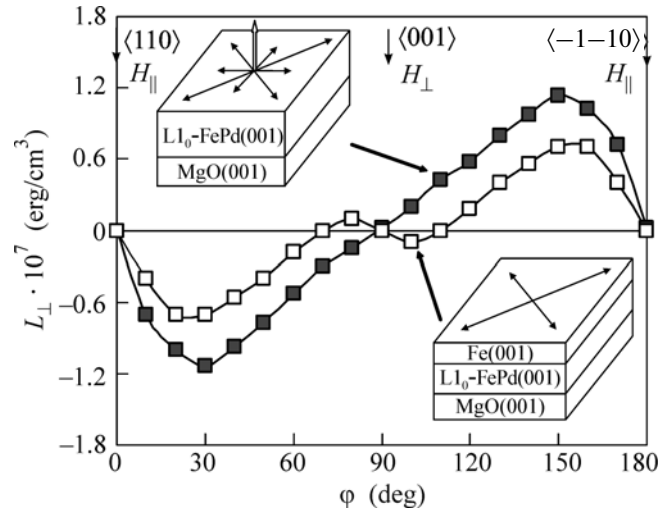

Fig. 3. Curves of the torque $L_\perp(\varphi)$ perpendicular to the plane of the Fe(001)/Pd(001)/MgO(001) film system obtained by the rotation about the $\langle -110 \rangle$ axis and the schematic picture of the evolution of the L1$_0$-FePd phase and easy magnetization axes after annealing at 500°C for (□) 0.5 and (■) 10 h.

10^3 Oe obtained from the measurement of the anisotropy field by the method that is modified to biaxial anisotropy and is presented in [16]. Taking $M_S = 900$ G for the L1$_0$-FePd films [7], we obtain $K_2 = (1.6 \pm 0.4) \times 10^6$ erg/cm^3. The K_2 value is positive, because the easy axes of effective anisotropy coincide with the [110] and [1−10] direction of the MgO(001) substrate and Eq. (2) contains a negative sign.

The predominant formation of the L1$_0$-FePd(001) crystallites begins at 500°C as is indicated by the presence of perpendicular anisotropy in the samples, which increases with the annealing time. The measurements of the torque perpendicular to the sample plane, $L_\perp$, with the rotation of the magnetic field about the $\langle -110 \rangle$ axis from the $\langle 110 \rangle$ direction to the $\langle -1-10 \rangle$ direction reveal the effective biaxial anisotropy with the easy axes making a certain angle with the film normal (see Fig. 3). This result indicates the structural rearrangement in the samples. As the annealing time increases, the crystallites with the c axis in the plane are transformed to the crystallites whose c axis is perpendicular to the film plane. As a result, large perpendicular anisotropy appears in the L1$_0$-FePd(001) films. However, owing to the anisotropy of the shape of the residual Fe(001) layer, the easy magnetization direction deviates from the vertical direction (see Fig. 3). Mutually perpendicular uniaxial particles separated in Fe$_2$NiAl single crystals exhibit a similar effective biaxial anisotropy. Such an anisotropy can be described using two noninteracting magnetic wires crossing at an angle of 90° [17].

The formation of the bulk fraction of the $L1_0$-FePd(001) crystallites increases with the annealing time. After 10-h annealing at 500°C, the diffraction pattern in Fig. 1d has only the (00l) peak of the $L1_0$-FePd phase and the residual peak of the Fe_xPd_{1-x} disordered solid solution; this indicates the completion of the structural rearrangement at which only the $L1_0$-FePd(001) crystallites with the c axis perpendicular to the film plane remain in the sample. The epitaxial relations $L1_0$-FePd(001)[100] ∥ MgO(001)[100] and Fe_xPd_{1-x}(001)[100] ∥ MgO(001)[100] were determined by asymmetric scanning. The lattice parameters $\mathbf{a} = \mathbf{b} = 0.384$ nm and $\mathbf{c} = 0.368$ nm of the $L1_0$-FePd phase determined from the positions of the (002) and (200) peaks are close to the respective parameters $\mathbf{a} = \mathbf{b} = 0.385$ nm and $\mathbf{c} = 0.3731$ nm of the bulk samples. The long-range order parameter is estimated as $\eta = 0.8 \pm 0.1$, which indicates the high degree of chemical ordering in the $L1_0$-FePd phase obtained by the solid-phase synthesis.

Structural transformations significantly change the magnetic properties of the samples after 10-h annealing at a temperature of 500°C. According to the measurements of the torque $L_\perp$ perpendicular to the sample plane, the saturation magnetization M_S is strictly perpendicular to the film plane (see Fig. 3). Neglecting the volume of the Fe_xPd_{1-x} solid solution and the contribution of the magnetoelastic energy, the perpendicular-anisotropy constant was determined as the maximum value of $L_\perp^{max}$ as a function of the rotation angle $L_\perp^{max} = K_U = (1.1 \pm 0.3) \times 10^7$ erg/cm³. Assuming that $K_1 \gg K_2 > K_3$, we determined the first magnetocrystalline-anisotropy constant $K_1 = K_U + 2\pi M_S^2 = (1.7 \pm 0.3) \times 10^7$ erg/cm³, which is close to the value for bulk samples [13, 14, 18]. As the annealing time at a temperature of 500°C is increased, the magnetic anisotropy in the film plane decreases and changes its symmetry after 10-h annealing (see Fig. 2). This is a consequence of the complete structural transformation of crystallites with the c axis in the film plane to crystallites with the c axis perpendicular to the film plane. The anisotropy energy of $L1_0$ crystallites in the (001) basal plane is given by the term $K_3\cos^2\alpha\cos^2\beta$ in Eq. (1), which corresponds to the biaxial anisotropy. However, the torque curves $L_\parallel(\varphi)$ measured in the sample plane exhibit quadriaxial anisotropy, which is atypical for single crystals (see Fig. 2). Therefore, the anisotropy energy of the $L1_0$-FePd crystallites in the (001) basal plane is not described by the term $K_3\cos^2\alpha\cos^2\beta$ in Eq. (1) and is a fourth-order polynomial of the direction cosines.

An increase in the sample annealing temperature to 550°C gives rise to the degradation of the $L1_0$-FePd phase and the growth of the phase of the Fe_xPd_{1-x} disordered solid solution with the lattice parameter $\mathbf{a} =$ 0.379 nm. Such samples had a zero magnetocrystalline-anisotropy constant and saturation magnetization lying in the film plane.

As was previously shown, the initiation temperature T_0 of the solid-phase reaction in bilayer film systems and multilayers coincides with the minimum temperature of the structural solid-phase transformation in a given binary system [19, 20]. In particular, the solid-phase reaction between the Au and Cu films starts at the minimum order−disorder temperature (240°C) with the formation of the CuAu| and CuAu∥ ordered phases [20]. According to the above consideration, the initiation temperature ($T_0 \sim 450$°C) in the Fe/Pd films is the temperature of the order−disorder phase transition (Kurnakov point) of the FePd phase.

CONCLUSIONS

The investigations of phase formation in Fe(001)/Pd(001)/MgO(001) bilayer samples at various annealing temperatures indicate that the structure consisting of crystallites of the $L1_0$-FePd ordered phase with the c axes coinciding with the [100], [010], and [001] directions of the MgO(001) substrate is formed at ~450°C. Taking into account the volume of the residual Fe(001) layer and assuming that the crystallites of three types are coupled by the exchange interaction, we have determined the second magnetocrystalline-anisotropy constant $K_2 = (1.5 \pm 0.5) \times 10^6$ erg/cm³. The fraction of the crystallites with the c axis perpendicular to the film plane increases with the annealing time at a temperature of 500°C and their volume becomes dominant after 10-h annealing. The samples of the $L1_0$-FePd(001) phase have a long-range degree of $\eta = 0.8 \pm 0.1$ and a large perpendicular anisotropy from which the first magnetocrystalline-anisotropy constant $K_1 = (1.7 \pm 0.3) \times 10^7$ erg/cm³ has been determined.

REFERENCES

1. P. Gambardella, S. Rusponi, M. Veronese, et al., Science **300**, 1130 (2003); J.-P. Wang, Nature Mater. **4**, 191 (2005); O. Gutfleisch, J. Lyubina, K.-H. Müller, and L. Schultz, Adv. Eng. Mater. **7**, 208 (2005); M. Weisheit, S. Fähler, A. Marty, et al., Science **315**, 349 (2007); J.-L. Tsai, H.-T. Tzeng, and G.-B. Lin, Appl. Phys. Lett. **96**, 032505 (2010).

2. D. Alloyeau, C. Ricolleau, C. Mottet, et al., Nature Mater. **8**, 940 (2009).

3. A. G. Roca, R. Costo, A. F. Rebolledo, et al., J. Phys. D: Appl. Phys. **42**, 224002 (2009).

4. S. Guillous, M. Viret, C. Fermon, and H. Alloul, J. Appl. Phys. **89**, 6781 (2001); J. Buschbeck, I. Lindemann, L. Schultz, and S. Fähler, Phys. Rev. B **76**,

205421 (2007); C. Clavero, J. R. Skuza, Y. Choi, et al., Appl. Phys. Lett. **92**, 162502 (2008).

5. D. Halley, B. Gilles, P. Bayle-Guillemaud, et al., Phys. Rev. B **70**, 174437 (2004); V. Gehanno, A. Marty, B. Gilles, et al., Phys. Rev. B **55**, 12552 (1997).

6. A. Kovàcs, K. Sato, and Y. Hirotsu, J. Appl. Phys. **102**, 123512 (2007).

7. Y. Endo, Y. Yamanaka, Y. Kawamura, and M. Yamamoto, Jpn. J. Appl. Phys. **44**, 3009 (2005); D. H. Wei and Y. D. Yao, Appl. Phys. Lett. **95**, 172503 (2009).

8. H. Bernas, J.-Ph. Attané, K.-H. Heinig, et al., Phys. Rev. Lett. **91**, 077203 (2003).

9. K. Sato, K. Aoyagi, and T. J. Konno, J. Appl. Phys. **107**, 024304 (2010).

10. K. Sato, Bo Bian, and Y. Hirotsu, J. Appl. Phys. **91**, 8516 (2002); S. Farjami et al., J. Phys.: Conf. Ser. **165**, 012055 (2009).

11. J. Lyubina, O. Gutfleisch, and O. Isnard, J. Appl. Phys. **105**, 07A717 (2009).

12. R. M. Bozorth, *Ferromagnetism* (IEEE Press, 1978; Inostr. Liter., Moscow, 1956).

13. T. Klemmer, D. Hoydick, H. Okumura, et al., Scr. Metall. Mater. **33**, 1793 (1995).

14. H. Shima, K. Oikawa, A. Fujita, et al., Phys. Rev. B **70**, 224408 (2004).

15. E. Gu, M. Gester, R. J. Hicken, et al., Phys. Rev. B **52**, 14704 (1995).

16. S. Chikazumi, J. Appl. Phys. **32**, S81 (1961).

17. E. A. Nesbitt, H. J. Williams, and R. M. Bozorth, J. Appl. Phys. **25**, 1014 (1954).

18. V. V. Maikov, A. E. Ermakov, G. V. Ivanova, et al., Fiz. Mat. Mater. **67**, 79 (1989).

19. V. G. Myagkov, L. E. Bykova, G. N. Bondarenko, et al., Pis'ma Zh. Eksp. Teor. Fiz. **88**, 591 (2008) [JETP Lett. **88**, 515 (2008)]; V. G. Myagkov, V. C. Zhigalov, L. E. Bykova, et al., J. Magn. Magn. Mater. **305**, 334 (2006); V. S. Zhigalov, V. G. Myagkov, L. E. Bykova, et al., Pis'ma Zh. Eksp. Teor. Fiz. **89**, 725 (2009) [JETP Lett. **89**, 621 (2009)].

20. V. G. Myagkov, L. E. Bykova, G. N. Bondarenko, et al., Pis'ma Zh. Eksp. Teor. Fiz. **71**, 268 (2000) [JETP Lett. **71**, 183 (2000)]; V. G. Myagkov, Yu. L. Mikhlin, L. E. Bykova, et al., Pis'ma Zh. Eksp. Teor. Fiz. **90**, 121 (2009) [JETP Lett. **90**, 111 (2009)].

Translated by R. Tyapaev