Anisotropic magnetic, magnetoresistance, and electrotransport properties of GdBaCo₂O_{5.5} single crystals

D. D. Khalyavin,^{*} S. N. Barilo, S. V. Shiryaev, G. L. Bychkov, and I. O. Troyanchuk[†] Institute of Solid State and Semiconductors Physics, National Academy of Sciences, P. Brovka Street 17, 220072 Minsk, Belarus

A. Furrer and P. Allenspach

Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institute, CH-5232 PSI Villigen, Switzerland

H. Szymczak and R. Szymczak

Institute of Physics, Polish Academy of Sciences, Lotnikow Street 32/46, PL 02-668 Warsaw, Poland (Received 22 January 2003; published 18 June 2003)

Single crystals of GdBaCo₂O_{5.5} layered perovskites have been grown from a flux melt of Gd₂O₃-BaO-CoO oxides. Magnetic data showed that the GdBaCo₂O_{5.5} single crystals exhibit a magnetic phase transition from an antiferromagnetic state to a ferromagnetic one with spontaneous magnetization around 0.41 μ_B per Co ion at $T_i \sim 160$ K. Direction of spontaneous magnetic moment coincides with either the *a* or *b* axis. It is assumed that Co³⁺ ions adopt low- and intermediate-spin states in the ratio of 1:1. The giant magnetoresistance effect connected closely with a spontaneous magnetic properties. On the basis of electrical resistivity data the quasi-two-dimensional character of conductivity, above the metal-insulator transition temperature $T_{MI} \sim 370$ K, was assumed.

DOI: 10.1103/PhysRevB.67.214421

PACS number(s): 75.50.Dd, 75.30.Gw, 75.30.Cr, 75.47.De

Unusual magnetic and electrical properties have been reported for oxygen-deficient orthocobaltites with a common chemical formula $LnBaCo_2O_{5+\delta}$ (Ln represents lanthanide).¹⁻⁴. These compounds have recently been synthesized and have attracted considerable attention of many investigators. Its crystal structure is related closely to YBaFeCuO₅-type structure and it represents a consequence of $[CoO_2]$ -[BaO]- $[CoO_2]$ - $[LnO_{\delta}]$ layers stacked along the c axis. In the case of $\delta = 0$, all the cobalt ions are located within square pyramids with a fivefold coordination. As δ increases an excess of oxygen ions occupies the [LnO_{δ}] layers, providing an octahedral environment for a part of Co ions. At the highest limit $\delta = 1$, all the cobalt ions have an octahedral environment. In the $\delta = 0.5$ case, oxygen ions and oxygen vacancies are located in chains along the a axis within $[LnO_{\delta}]$ layers. Thus, Co^{3+} ions are present in both CoO_6 -octahedral (Co_{oct}) and CoO_5 -pyramidal (Co_{pyr}) coordinations in an ordered manner. As a result of the ordering, a consequent alternation of the planes formed by either Co_{oct} or Co_{pyr} ions takes place along the *b* axis (inset in Fig. 1). Depending on the δ value an interesting variety of magnetic and structural phase transitions has been revealed together with charge and orbital ordering phenomena.⁵⁻⁷ In particular, the LnBaCo₂O_{5.5} perovskites have been found to exhibit first-order phase transitions from an antiferromagnetic state to that with spontaneous magnetization at $T_i \approx 250$ K and metal-insulator (MI) ones at $T_{MI} \approx 340$ K.¹⁻⁴ The nature of these transitions is a matter of discussion now. The value of spontaneous magnetization 0.18 μ_B per cobalt ion, found in ceramic samples is too low for parallel ordering of magnetic moments of Co³⁺ ions in the case of the intermediate-spin (IS) $(t_{2g}^5 e_g^1 S=1)$ or high-spin (HS) $(t_{2g}^4 e_g^2 S=2)$ states.

Several models have been proposed to explain these transitions, most of them being based on the idea of the spinstate transition of Co^{3+} ions.^{8,9} Two nonequivalent cobalt positions in the LnBaCo₂O_{5.5} lattice and three possible spin states of Co³⁺ ions [LS (low spin) IS, and HS states] give a wide field for speculations. The above-described crystal structure of LnBaCo₂O_{5.5} layered perovskites presumes a strong anisotropy of physical properties. Therefore, the investigations performed on the high quality single crystals will be able to represent useful information on the nature of the aforementioned transitions. The present paper is devoted to an investigation of growth conditions and anisotropy of physical properties of GdBaCo₂O_{5.5} single crystals.

We have grown the single crystals of GdBaCo₂O_{5+ δ} from



FIG. 1. A primary crystallization field of the $GdBaCo_2O_{5.5}$ phase in the Gd_2O_3 -BaO-CoO system. Inset shows a schematic representation of the crystal structure of $GdBaCo_2O_{5.5}$.

a nonstoichiometric solution of starting oxides. The flux method used here has been successfully applied previously to grow single crystals of high- T_C superconducting copper oxides such as $YBa_2Cu_3O_{7-\gamma}$ (123)¹⁰ and $Nd_{2-x}Ce_xCuO_{4-\gamma}$.¹¹ A sufficiently low melting point 1100°C of the $(BaO)_{1-x}$ - $(CoO)_x$ mixture near eutectic point,¹² which one can expect for the composition close to $x = 0.6 \pm 0.05$, allows one to use this mixture as a solvent to grow LnBaCo₂O_{5+ δ} layered cobaltites. In our experiments, the following growth conditions were used. First, Gd_2O_3 , BaCO₃, and CoO powders with a purity of 99.99 % were mixed in an appropriate ratio. The corresponding mixture was placed into an Al₂O₃ crucible and heated up to 1300-1350 °C. After homogenization for 2 h the flux melt was slowly cooled down to 1000 °C at the rate of 1 °C/h and then the furnace was cooled to room temperature. In Fig. 1 the primary crystallization range of $GdBaCo_2O_{5+\delta}$ (112) phase) is presented on the GdO_{1.5}-BaO-CoO Gibbs triangle. The highest quality crystals were grown in a case of a flux melt containing a small amount of Gd₂O₃ solved in the BaO-CoO mixture close to eutectic. The hypothetical composition of the flux melt was estimated as $GdBa_6Co_9O_7$. It is worth noting that at a lower Gd₂O₃ content there is a phase crystallized with the composition identified as GdBaCo₄O₇. To our knowledge there was not any report an this kind of cobalt oxides up to now. A calculation of the crystal structure showed this compound to be isostructural to hexagonal $Ba_2Er_2Zn_8O_{13}$ oxide with space group P63mc. A detailed description of the crystal structure and physical properties of the family of LnBaCo₄O₇ compounds will be presented in a separate paper. Using the above-described method we have also grown LnBaCo₂O_{5+ δ} single crystals on the basis of other rare-earth elements Ln=Pr, Eu, Tb, and Dy. The primary crystallization field for the $LnBaCo_2O_{5+\delta}$ phase strongly depends on rare-earth ions and it is necessary to provide additional investigations in order to constant correct diagrams.

Crystal phase purity and cationic composition of obtained crystals were checked by x-ray diffraction (XRD) and x-ray fluorescent analysis, respectively. Oxygen content was determined by iodinemetric titration. For this procedure several crystals (total weight 150 mg) annealed together were used. The magnetization studies were performed by a superconducting quantum interference device magnetometer quantum design MPMS-5. The conventional four-probe method in dc configuration was used to measure the crystal's resistivity and its magnetic-field dependence.

Grown crystals had a rectangular shape with a welldeveloped (*ab*) plane. An average edge length of these crystals was of several millimeters (the largest size was $5 \times 5 \times 2 \text{ mm}^3$). XRD data revealed that the as-grown crystals had a tetragonal symmetry of crystal structure (space group *P4/mmm*). Annealing for several days in oxygen flow at 600 °C changed the symmetry from tetragonal to orthorhombic (space group *Pmmm*). As it was shown,⁴ orthorhombic distortions in the LnBaCo₂O_{5+δ} perovskites are caused by the oxygen ions ordering within the [LnO_δ] layers as a result of a doubling of the unit cell along the *b* axis (inset in Fig.



FIG. 2. Image of twins in the $GdBaCo_2O_{5.5}$ single crystal obtained in polarized microscope in the normal-reflection mode.

1). The stoichiometric phase with such a type of oxygen ordering corresponds to oxygen content 5.5. An iodinemetric titration of GdBaCo₂O_{5+ δ} crystals after annealing gives an oxygen content δ =0.46±0.03 close to the stoichiometric one. The somewhat lower value of the oxygen index obtained in our experiment in comparison with the ceramic samples (δ =0.53) (Ref. 9) is probably caused by a much less diffusion coefficient of oxygen in the case of the single-crystal sample.

single crystals of high T_C cuprates In the $LnBa_2Cu_3O_{7-\gamma}$, the similar crystal structure transformation from tetragonal (P4/mmm) to orthorhombic (Pmmm) symmetry as oxygen content increases is known to be accompanied with an appearance of a developed twinning structure.¹³ The twinning was found to affect strongly the anisotropy of electrical and magnetic properties, especially in the (ab)plane. To observe the twin structure in the 123 crystals the polarization-optical method based on the effect of a light polarization change while reflecting from an anisotropic medium has been successfully applied.¹⁴ In Fig. 2, the polarization-optical contrast is presented from twins of the GdBaCo₂O_{5.5} crystal in a normal-reflected light. For the basic (001) plane, one can clearly see the typical picture with two systems of bright and dark stripes along [110] and $[1\overline{1}0]$ directions. The very similar polarization-optical contrast has been observed for orthorhombic 123 crystals.¹⁴ In these crystals, CuO chains appear as a result of an oxygen ordering along the b axis and directions of a and b axes have been found to differ by 90° in the neighboring twins. Taking into account that the orthorhombic distortions of the crystal structure of LnBaCo₂O_{5.5} perovskites are also caused by the oxygen ordering along a certain direction (along the *a* axis), one can suggest the twin structure of both types of 112 and 123 crystals to be similar, too. In other words, the polarizationoptical contrast in the GdBaCo₂O_{5.5} crystals is connected with a 90° turn of the *a* and *b* axes in the neighboring twins. However, it is necessary to carry out a further detailed investigation of the twin structure in the LnBaCo₂O_{5.5} crystals to clarify its role in forming properties of these crystals as well as to optimize conditions for the detwinning procedure.



FIG. 3. Temperature dependences of magnetization of GdBaCo₂O_{5.5} single crystal at magnetic fields applied parallel and perpendicular to *c* axis. Inset shows angle dependences of magnetization in $H \perp c$ geometry.

According to our magnetic measurements, the GdBaCo₂O_{5.5} single crystals exhibit a strong anisotropic behavior (Fig. 3). In magnetic fields perpendicular to the basal (ab) plane (H||c) axis), the crystal behaves as an antiferromagnet in the whole temperature range 4.2 < T < 300 K. However, in the case of $H \perp c$ axis, the curves of magnetization temperature dependences M(T) have a character similar to that of polycrystalline samples with transition to a state with spontaneous magnetization at $T_i = 160$ K. These results point that an uncompensated magnetic moment lies in the (ab) plane. A rotation of the crystal in the magnetic fields $H \perp c$ axis gives four equivalent maxima and four nonequivalent minima (inset in Fig. 3). The minima alternate via every 90°, whereas angles between maxima are different.

Taking into account the above-considered twin structure of the crystal, the angle dependence of magnetization shown in Fig. 3 can be explained by suggesting GdBaCo₂O_{5.5} to be a single-axis strong anisotropic magnet with easy magnetization axis coinciding with either the *a* or *b* axis. In addition to explaining the nonequivalent minima it is necessary to suggest that the twins with different orientations of the a and b axes occupy different volumes of the crystal (partial detwinning). In this case by attaching effective magnetic moments of saturation to different types of the twins $(\tilde{M}_{min1}$ and M_{min2} ; $M_{min1} \neq M_{min2}$) and excluding its rotation in the magnetic field we can construct a vector diagram (Fig. 4, inset of top panel) explaining the angle dependence of magnetization. One can see from this diagram that there should be the following correlations between M_{min1} , M_{min2} , M_{max} , and φ :

$$M_{max} = \sqrt{M_{min1}^2 + M_{min2}^2}, \quad \varphi = \tan^{-1} \frac{M_{min1}}{M_{min2}}.$$
 (1)

Having determined from Fig. 4 (top panel) the magnetization of saturation at different orientations of the GdBaCo₂O_{5.5} crystal ($M_{min1}=0.18\mu_B$ and $M_{min2}=0.23\mu_B$ per Co ion), we can find from Eq. (1) that $M_{max}=0.29\mu_B$ per Co ion and $\varphi = 40^\circ$. Comparison of these values with experi-



FIG. 4. Magnetization of the GdBaCo₂O_{5.5} single crystal vs magnetic-field value at its different orientation in the (ab) plane (top panel). Isotherms of in-plane and out-of-plane magnetization (bottom panel).

mental data $\varphi \approx 40^{\circ} \pm 1^{\circ}$ (inset in Fig. 3) and $M_{max} \approx 0.29 \pm 0.01 \mu_B$ per Co ion (Fig. 4 top panel) gives a good agreement. It is obvious that if the easy magnetization axis does not coincide with either the *a* or *b* axis the angle dependence shown in Fig. 3 would not change qualitatively but the correlation between M_{min1} , M_{min2} , M_{max} , and φ would have a more complex character. On the basis of the obtained results it is easy to account for the real value of spontaneous magnetization (M_S) $M_S = M_{min1} + M_{min2} = 0.41 \mu_B$ per Co ion for the single domain crystal without twinning. It is obvious for polycrystalline samples of GdBaCo₂O_{5.5} that the value of spontaneous magnetization (M_{pol}) can be written in the same way as for a single-axis magnet with a random distribution of the magnetic moments within a half sphere of radius M_S :

$$M_{pol} = \int_0^{\pi/2} M_S \sin \varphi \cos \varphi \, \partial \varphi = \frac{M_S}{2}.$$
 (2)

At $M_s = 0.41 \mu_B$ per Co ion, $M_{pol} \approx 0.2 \mu_B$ per Co ion, which is in a good agreement with literature data. Thus, from obtained data we can conclude that the single-crystal GdBaCo₂O_{5.5} shows a phase transition at T_i from an antiferromagnetic state to that with spontaneous magnetization $0.41 \mu_B$ per Co ion. Moreover, the spontaneous moment is directed along either the *a* or *b* axis.

Let us further consider field isotherms of the GdBaCo₂O_{5,5} single crystal registered at different directions of the crystal (Fig. 4, bottom panel). One can see the out-ofplane $(H \| c)$ and in-plane $(H \perp c, \text{ linear part})$ susceptibility values are very close in both temperature ranges $T < T_i$ and $T > T_i$. In addition, there is no anomaly in the curve of temperature dependence of out-of-plane magnetization for the GdBaCo₂O_{5.5} crystal at T_i (Fig. 3). In other words, the outof-plane susceptibility does not change at the temperature of the phase transition. Qualitatively, the same results have been obtained for the Eu-based crystal for which there is not paramagnetic contribution of the rare-earth sublattice into magnetization (for Eu^{3+} ions, J=0). In addition, one can see from Fig. 4 (bottom panel) that the 50 kOe field is not enough to overcome the magnetic anisotropy and direct the magnetic moment along the field even at high temperatures. Apparently, in this compound, energy of the magnetic anisotropy is comparable or higher than the energy of the exchange interactions.

The magnitude of spontaneous magnetization $(0.41 \mu_B \text{ per}$ Co at T = 190 K) is too large for a weak ferromagnetic state which may appear as a result of canting due to the Dzialoshinsky-Moria exchange. Moreover, a coarse estimate of the spontaneous magnetization at T=0 K obtained by extrapolation of the high-temperature dependence of the magnetization gives the value $\sim 0.75 \mu_B$ per Co ion. Hence, we assume that a part of Co^{3+} ions adopts the low-spin state. Another part of ferromagnetically ordered Co³⁺ ions is in the intermediate-spin state. Having analyzed the inverse paramagnetic susceptibility in the temperature range $T_C < T$ $< T_{MI}$ for a polycrystalline GdBaCo₂O_{5.5} sample and excluded a paramagnetic contribution of the Gd sublattice, Respaud *et al.*¹⁵ obtained the value of effective paramagnetic moment $\mu_{eff(Co)} = (1.9 \pm 0.1) \mu_B$ per Co. As it was also noted,¹⁵ this value of $\mu_{eff(Co)}$ is well consistent with a model assuming a 50% mixture of LS Co (S=0) and IS Co (S=1) ions. However, the value of spontaneous magnetization $(=0.45\mu_B$ per Co at T=4.2 K) obtained from high-field measurements made the authors reject the idea of ferromagnetic ordering of cobalt ions adopting an intermediate-spin state because in this case the expected value of spontaneous magnetization should be $1\mu_B$ per Co. Taking into account expression (2), one can obtain from data of the work 15 the real value of spontaneous magnetization (= $0.9\mu_B$ per Co at T=4.2 K). Thus, we can conclude that the model assuming a mixture of cobalt ions in the low-spin state and ferromagnetically ordered ones in the intermediate-spin state can reasonably explain the value of spontaneous magnetization in the GdBaCo₂O_{5.5} perovskite.

Taking into consideration that there are two different positions of the cobalt ions in the crystal structure of $GdBaCo_2O_{5.5}$, one can suggest that one of these positions is occupied by the cobalt ions in the low-spin state, whereas the other one by cobalt ions in the intermediate-spin state. On the basis of the results obtained here, it is impossible to make a choice between two probable situations. However, recent ultrahigh-resolution synchrotron-diffraction data reported by Frontera *et al.*⁹ for GdBaCo_2O_{5.5} showed that the low-spin electronic configuration is adopted by the cobalt ions with



FIG. 5. Temperature dependences of in-plane and out-of-plane resistivity of GdBaCo₂O_{5.5} single crystal. Inset shows out-of-plane magnetoresistance (MR) at different orientations of the crystal and magnetic field H = 10 kOe.

octahedral coordination. Thus, we have the model where consequent alternation of the ferromagnetic and diamagnetic layers takes place along the *b* axis. In this model, the ferromagnetic layers divided by the diamagnetic ones are coupled ferromagnetically and antiferromagnetically above and below T_i , correspondingly. One can suggest that the coupling between ferromagnetic layers is much weaker as compared with interactions within the layers, and the transition from the antiferromagnetic state to the ferromagnetic one can be easily induced by the external magnetic field or temperature.

The origin of the ferromagnetic ordering within layers can be explained by the orbital ordering satisfying the Goodenough-Kanomory rules for the positive superexchange interactions. However, in the case of the model, where ferromagnetic layers consist of the fivefold coordinated cobalt ions (Co_{pyr}), the exchange mechanism connecting magnetic moments of the ions located in separate double pyramidal chains is not clearly described. In this case it is rather correct to consider the double ferromagnetic chains than the ferromagnetic layers.

Let us consider electrical and magnetoresistance properties of the GdBaCo₂O_{5.5} crystals. From a previous study of ceramic samples the phase transition into the state with spontaneous magnetization is known to be accompanied with a resistivity jump. The resistivity of the highest quality ceramic samples sharply decreases almost by a factor of 2 at T_i . Application of an external magnetic field shifts the phase-transition temperature and the jump of resistivity to a low-temperature area, which leads to the giant negative magnetoresistance effect¹⁻⁴ (~15% at H=10 kOe). According to magnetotransport measurements of the GdBaCo₂O_{5.5} crystal, (Fig. 5) the anomaly of resistivity associated with a spontaneous magnetization appearance is the most developed in the curve of the resistivity temperature dependence registered along c axis [out-of-plane resistivity $\rho_{out}(T)$]. Maximal magnetoresistance effect (~5% at H=10 kOe) has also been observed along this direction (inset in Fig. 5). However, as one should expect from magnetic data the magnetoresistance shows a strong anisotropic behavior (inset in Fig. 5). Magnetic field influences considerably the resistivity only if it is applied parallel to (ab) plane. Magnetic field applied along the *c* axis does not change the magnetic state of the crystal and, consequently, its resistivity. It should be noted that the smaller value of magnetoresistance in our crystal in comparison with the ceramic samples is apparently connected with the diffusion phase transition to the ferromagnetic state. Such a behavior may be caused by nonuniform distribution of oxygen in the crystal and to obtain the welldefined phase-transition additional investigations directed to optimization of the annealing conditions are needed.

In the high-temperature paramagnetic area at T_{MI} \sim 370 K, the pronounced metal-insulator transition is observed in the curve of $\rho_{out}(T)$ (Fig. 5). In the temperature dependences of resistivity registered by in-plane geometry $[\rho_{in1}(T) \text{ and } \rho_{in2}(T)$ —current direction along two different edges of the crystal] the phase transitions at both T_i and T_{MI} are less pronounced. Authors of most papers devoted to an investigation of the MI transition in the LnBaCo₂O_{5.5} compounds conclude that the transition is induced by the change of spin state of Co³⁺ ions. The sharp increase of the effective paramagnetic moment at T_{MI} (Refs. 4,8 and 9) is a satisfactory argument in favor of this assumption. From crystal structure data obtained for Gd(Tb)BaCo₂O_{5.5} perovskites,^{8,9} the c/2 parameter of the unit cell is known to be less than the a and b/2 ones. It means a stronger d-p hybridization in the Co_{oct} planes between 3d orbitals of cobalt and 2p orbitals of oxygen in this direction and, consequently, a wider band-

- *Corresponding author. Fax: (375-0172) 84-08-88. Electronic address: khalyav@ifttp.bas-net.by
- [†]Electronic address: troyan@ifttp.bas-net.by
- ¹C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, and B. Raveau, Appl. Phys. Lett. **71**, 1421 (1997).
- ²I.O. Troyanchuk, N.V. Kasper, D.D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, Phys. Rev. Lett. **80**, 3380 (1998).
- ³I.O. Troyanchuk, N.V. Kasper, D.D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, Phys. Rev. B **58**, 2418 (1998).
- ⁴A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, and B. Raveau, J. Solid State Chem. **142**, 247 (1999).
- ⁵T. Vogt, P.M. Woodward, P. Karen, B.A. Hunter, P. Henning, and A.R. Moodenbaugh, Phys. Rev. Lett. 84, 2969 (2000).
- ⁶E. Suard, F. Fauth, V. Caignaert, I. Mirebeau, and G. Baldinozzi, Phys. Rev. B **61**, R11 871 (2000).
- ⁷F. Fauth, E. Suard, V. Caignaert, B. Domenges, I. Mirebeau, and L. Keller, Eur. Phys. J. B **21**, 163 (2001).

width. Thus, apparently, the conductivity along the c axis is maximal in the LnBaCo₂O_{5.5} crystals. It was surprising to reveal an anisotropy of resistivity within the (ab) plane, which is apparently connected with a nonuniform defect distribution along the *a* and *b* directions due to strains caused by a growth rate anisotropy. This fact leads in turn to a partial detwinning of the crystal. From consideration of the LnBaCo₂O_{5,5} crystal structure (inset in Fig. 1) a strong anisotropy of the resistivity in the (ab) plane is expected for a crystal without twins. Unfortunately an in-depth analysis of the in-plane resistivity is complicated because of the twin structure. However, the fact is that the in-plane resistivity is much higher than the out-of-plane one above T_{MI} as well as the (ab) anisotropy of resistivity may be caused by one of the directions a or b remaining insulator at $T > T_{MI}$. Taking in consideration that b/2 is the largest lattice parameter it is reasonable to suggest that this direction is [010]. Thus, it is possible to suppose that the quasi-two-dimensional character of conductivity along octahedral (ac) planes realizes in the GdBaCo₂O_{5.5} crystal in the metallic temperature range $T > T_{MI}$.

This research was supported by SNSF in the framework of the SCOPES program under Grant No. 7BYPJ65732 and by INTAS Grant No. 01-0278. The work was also supported by the Polish State Committee for Scientific Researches (KBN Grant No. 5P03B01620) and the Belarus Fund for Basic Research (Grant No. F02R-069).

- ⁸H. Kusuya, A. Machida, Y. Moritomo, K. Kato, E. Nishibori, M. Takata, M. Sakata, and A. Nakamura, J. Phys. Soc. Jpn. **70**, 3577 (2001).
- ⁹C. Frontera, J.L. Garcia-Munoz, A. Llobet, and M.A.G. Aranda, Phys. Rev. B **65**, 180405(R) (2002).
- ¹⁰Y. Hidaka, Y. Enomoto, M. Suzuki, M. Oda, A. Katsui, and T. Murakami, Jpn. J. Appl. Phys., Part 2 26, L726 (1987).
- ¹¹Y. Hidaka and M. Suzuki, Nature (London) **338**, 635 (1989).
- ¹²V.A. Cherepanov, L.Ya. Gavrilova, E.A. Filonova, M.V. Trifonova, and V.I. Voronin, Mater. Res. Bull. **34**, 938 (1999).
- ¹³C.S. Pande, A.K. Singh, L. Toth, D.U. Gubser, and S. Wolf, Phys. Rev. B 36, 5669 (1987).
- ¹⁴B.N. Das, L.E. Toth, and A.K. Singh, J. Cryst. Growth 87, 588 (1987).
- ¹⁵M. Respaud, C. Frontera, J.L. Garcia-Munoz, Miguel Angel G. Aranda, B. Raquet, J.M. Broto, H. Rakoto, M. Goiran, A. Llobet, and J. Rodriguez-Carvajal, Phys. Rev. B 64, 214401 (2001).