X-ray study of $Nd_{0.5}Sr_{0.5}MnO_3$ manganite structure above and below the ferromagnetic metal–antiferromagnetic insulator spontaneous phase transition

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The crystal structure of the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ is studied at temperatures $T = 300$ and 77.3 K by means of an x-ray diffractometer. It is shown that the transition from the ferromagnetic metallic state to the antiferromagnetic insulating charge-ordered state is accompanied by a lowering of the symmetry of the structure from orthorhombic to monoclinic. The space-group symmetry of the orthorhombic and monoclinic phases is identified as *Imma* and $P2_1/m$, respectively. Twinning of the crystal and the formation of a twin domain structure with coherent boundaries in the (00*l*) crystallographic planes are found.

Introduction

Keen interest in the investigation of the manganese-based compounds ($R_{1-x}A_xMnO_3$) with perovskitelike structures is connected with their high potentialities for technical applications due to their colossal negative magnetoresistance [1]. The manganites are also attractive objects for basic physical research primarily for a combination of different phase transformations in the electronic, magnetic, and crystallographic subsystems.

Recent studies of $Nd_{0.5}Sr_{0.5}MnO_3$ have revealed a number of spontaneous phase transitions observed on decreasing temperature. At a temperature $T = 250$ K the crystal transforms from a paramagnetic (PM) metallic state to ferromagnetic (FM) metallic one, and at a temperature of about 158 K a first-order phase transition to an antiferromagnetic (AFM) insulating charge-ordered state was observed in this crystal [2]. In a temperature range below $T < 158$ K a magnetic field induces the reverse transition to the FM metallic state [3].

At room temperature the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ is characterized by a perovskitelike orthorhombic structure (Fig. 1), though there is a

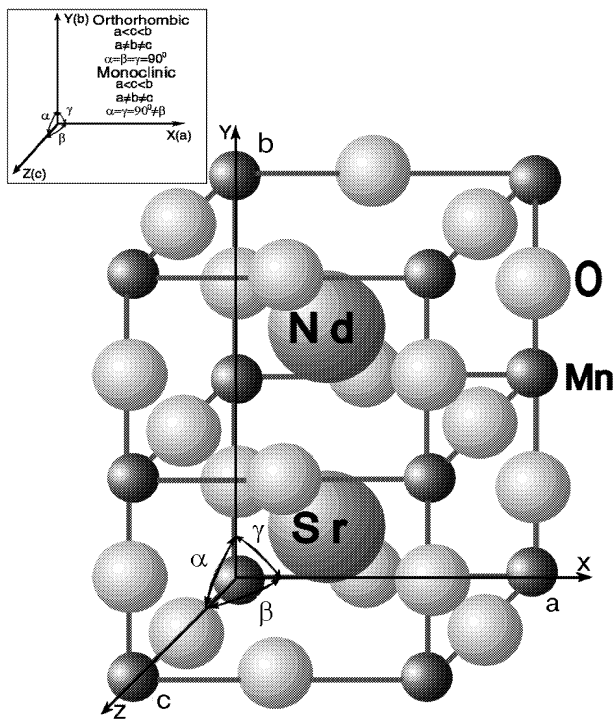*Fig. 1.* The unit cell of the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ (the inset shows the chosen spatial axes for the orthorhombic and monoclinic systems).

discrepancy in the published data on identification of the symmetry space group of this crystal. In [2–5] the $Nd_{0.5}Sr_{0.5}MnO_3$ compound is attributed to the space group *Imma*. In this case its crystal structure is the perovskite one, distorted by rotation of the octahedra with respect to the [101] direction in the perovskite structure. At the same time, in [1,6,7] the space group of the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ was determined as *Pmma*. This group has a lower symmetry as compared with *Imma* and corresponds to a distortion of the ideal cubic perovskite structure by rotation of the octahedra with respect to the [101] and [010] directions.

As the temperature is decreased below 250 K an increase of the lattice cell parameters *a* and *c* and a decrease of the *b* parameter is observed [3,6]. The lattice symmetry does not change.

The ideas about the crystal structure of $Nd_{0.5}Sr_{0.5}MnO_3$ in the AFM insulating state also diverge. According to the results of [6–8] the structure of this compound does not change during transition to AFM insulating phase and stays orthorhombic. However, in [2–5] results were obtained which suggest that the crystal structure in this state becomes monoclinic with the space group $P2_1/m$.

The aim of this work is the investigation and identification of the $Nd_{0.5}Sr_{0.5}MnO_3$ crystal struc-

ture in the metallic state at room temperature and in the insulating state below the charge-ordering temperature by means of x-ray scattering measurements.

Experimental technique

Single-crystal and powder samples of the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ were studied. The single crystals were obtained by the floating zone technique at the University of Warwick as well as at the Institute of Physics of the Polish Academy of Sciences. The single crystals were used for analysis of Laue patterns and also for observation and investigation of the twin domain structure by means of ω-scanning. For x-ray diffraction analysis the powders were prepared from single crystals in commercial dispergator. It should be noted at once that the results obtained for the samples prepared at the University of Warwick and at the Institute of Physics of the Polish Academy of Sciences coincide fairly well.

The single-crystallinity of the samples under study was proved by the Laue patterns. This way of characterizing the samples was chosen as an express and direct one. A thick sample with high x-ray absorption was studied; the reverse Laue patterns were taken, because the reflections in the sample at low angles θ are strongly weakened and are not observed.

The x-ray spectra $I(\theta)$ were registered on a DRON-2.0 diffractometer, using the Bragg–Brentano scheme of focusing (θ–2θ scheme). The complete spectra of the diffracted radiation were obtained, with a subsequent identification of the unit cell system and parameters. The accuracy of the intensity measurements was 0.5%. The lattice parameters were determined to within ± 0.01%. The other used technique was ω-scanning, when the sample only rotates around the goniometer axis, while the counter is immobile and is mounted at a fixed double angle of diffraction with respect to the primary beam. The latter registering technique was used to obtain the «reflection curves» of the single crystal.

The DRON-2.0 diffractometer was also used in the cryogenic experiments: in this case the small-size cryostat for x-ray powder measurements in a temperature range 4.2–300 K was installed.

In the experiment an x-ray tube with a copper anode was used (λ_{CuK_α} = 1.54178 Å). The spectra were registered in the angle range 2θ = 20°–80°.

In principle the problem of structure analysis is solved for the crystals. However, utilization of the

known techniques in structure identification for complex compounds often turns out to be inefficient without computer aids. Accordingly, it is important to modify the common methods of x-ray data processing using modern computer techniques. Here we used an approach [9] based on the differential Lipton technique for indexing the diffraction patterns and estimation of the unit cell parameters a_i ($i = 1, 2, 3$) for the orthorhombic and monoclinic systems. The classic techniques allow one to estimate only the order of the complex crystal lattice parameter. The differential Lipton technique was used as a basis for the algorithm of the program in order to estimate the parameters a_i and confine them by the least-squares technique. This algorithm included probability distribution for estimations of the lattice parameters and preliminary analysis of the measured and computed amplitudes of scattering. Such values of lattice parameters were selected, which corresponded to the local maxima of the probability distribution function. As the latter may have the false maxima, which are not attributed to real values of the cell parameters, the proposed algorithm provided additional procedures for estimation of the reliability of proposed structure models, which allowed one to exclude false maxima.

Experimental results and discussion

The Laue patterns registered at room and low temperatures are presented in Fig. 2. The point Laue patterns, shown in the picture, unambiguously identify the sample as being a single crystal. In order to avoid the situation in which the sample is a large-grained polycrystal and the incident beam reaches only one of the grains, the sample was shifted by small distances parallel to the film plane. The fact that the patterns obtained in various positions of the sample did not differ proves the single-crystallinity of the sample.

It is important to note that all the reflections on the Laue patterns are double, as is seen from Fig. 2. This circumstance may be explained by mosaicity of the crystal, i.e., it consists of blocks. The misorientation angle calculated from the Laue pattern is about ~ 0.13°, which is in good agreement with the low-angle boundary between the blocks.

The low-temperature Laue pattern shows changes in the reflection positions, though it is difficult to estimate the structure change correctly. For that the more accurate and informative x-ray diffraction analysis is required.

Figure 3 presents the diffraction patterns obtained at temperatures of 300 and 77.3 K for the powder sample of $Nd_{0.5}Sr_{0.5}MnO_3$. The low-tem-

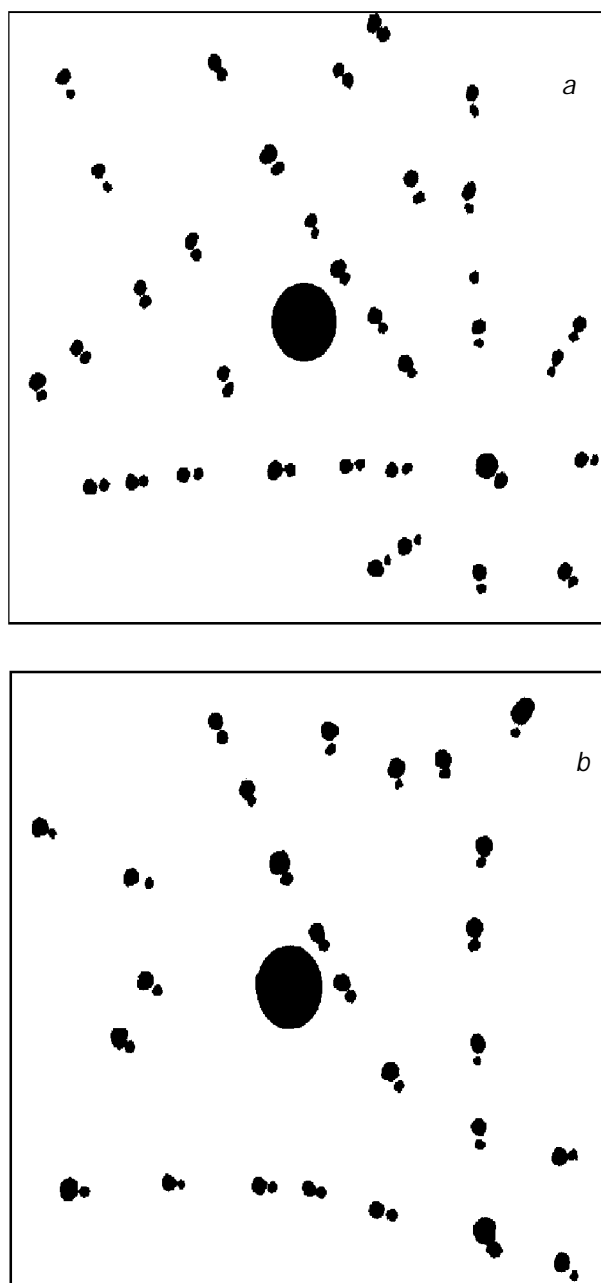*Fig. 2.* The Laue patterns for single-crystal $Nd_{0.5}Sr_{0.5}MnO_3$ at $T = 300$ (*a*) and 77.3 (*b*) K.

perature scanning was similar to that at room temperature, which simplifies considerably a comparative analysis of both diffraction patterns from the same sample at different temperatures. The chosen spatial axes for the unit cells in the orthorhombic and monoclinic systems are presented in Fig. 1 [10].

The quantities 2θ and the reduced intensities were derived for each maximum from the diffraction pattern at room temperature. Every peak was indicated using computer data processing and the space system was determined. In Fig. 3 the indices of the reflecting plane are indicated near every peak. To-
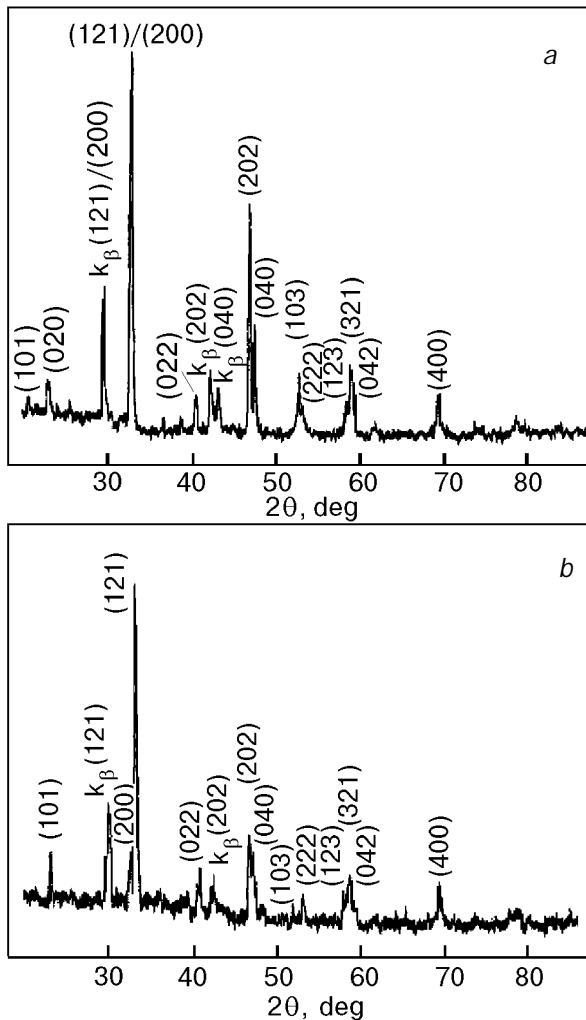
Fig. 3. The diffraction patterns for the $Nd_{0.5}Sr_{0.5}MnO_3$ powder sample at $T = 300$ (*a*) and 77.3 (*b*) K.

Fig. 4. The results of the discrete recording of the (121) and (200) reflections at $T = 300$ and 77.3 K.

gether with the extinction laws for the orthorhombic system it clearly shows that at room temperature the $Nd_{0.5}Sr_{0.5}MnO_3$ belongs to the space group *Imma*. For this space group the following laws are valid: $h + k + l = 2n$ for lines of the (*hkl*) type, and $k + l = 2n$ for lines of the (0*kl*) type [11].

The unit cell parameters derived from the diffraction pattern at room temperature were $a = 5.4302$ Å, $b = 7.6177$ Å, $c = 5.4860$ Å.

From a comparison of the diffraction patterns in Fig. 2 the change of the diffraction spectrum in the low-temperature state relative to that at room temperature is clearly seen. However, the large number of superimposed lines does not allow one to perform a qualitative analysis of the crystal lattice modification in the AFM insulating state. Therefore, in the next stage of the investigation the most intense lines were recorded in a discrete mode at both room and low temperatures. The results obtained are
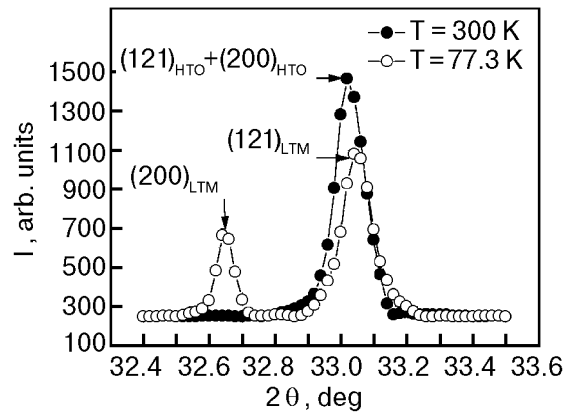
presented in Fig. 4. It clearly demonstrates that at low temperature the double maximum (200) ∕ (121) splits into two separate maxima.

The shift and splitting of the diffraction maxima may be induced both by the change of space group and by the thermal expansion anisotropy. Cooling of our samples is accompanied by decrease of the cell parameters which in it is turn results in the shift of corresponding diffraction lines. However, the shift of the diffraction lines, induced by thermal expansion anisotropy is lower than that, induced by a change of a space symmetry group. Besides, the change of lattice parameters due to thermal expansion is smooth, while near 160 K we have a jump-like change of cell parameters, which is attributed with the change of the space group symmetry. The above consideration are based on the data [3].

The AFM insulating state, which is observed in the $Nd_{0.5}Sr_{0.5}MnO_3$ manganite below 158 K, is characterized by a monoclinic structure and belongs to the space group $P2_1/m$. The processing of the diffraction spectrum gave the following unit cell parameters of the monoclinic phase: $a = 5.4851$ Å, $b = 7.5223$ Å, $c = 5.5186$ Å and the angle $\beta = 89.455$ Å.

It is important to note that, as is clearly seen from Fig. 4, in this angle range the diffraction reflections corresponding to the orthorhombic phase are not observed. This suggests that in our case the state of the sample at $T = 77.3$ K is homogeneous, i.e, phase separation [5] is not observed.

Consequently, the transition from the FM metallic state to the AFM charge-ordered insulating state is accompanied by a structural transformation. It should be mentioned that at the transition from the orthorhombic phase with space group *Imma* to the monoclinic phase with space group $P2_1/m$ the crystal loses some elements of symmetry, namely

2 reflection planes of the *m* type and, consequently, 2 twofold rotation axes normal to these planes. It is known that at a phase transition with symmetry lowering a twin domain structure may appear in the low-symmetry phase. In the situation considered the twins may form in the monoclinic phase, which are separated by coherent domain boundaries along the planes of the (00*l*) type. Then in the monoclinic phase of the $Nd_{0.5}Sr_{0.5}MnO_3$ single crystal 2 sets of (*h*00) planes will exist, with an interplane angle 2β (Fig. 5).

The domain structure in the AFM insulating phase of $Nd_{0.5}Sr_{0.5}MnO_3$ was observed visually in [12,13]. It was assumed that the observed nonuniform state is connected with the formation of the twin domain structure at the transition from the orthorhombic to the monoclinic phase. However, the final conclusions as to the nature of the observed domain structure could be derived only from the more direct measurements, in part from the x-ray study.
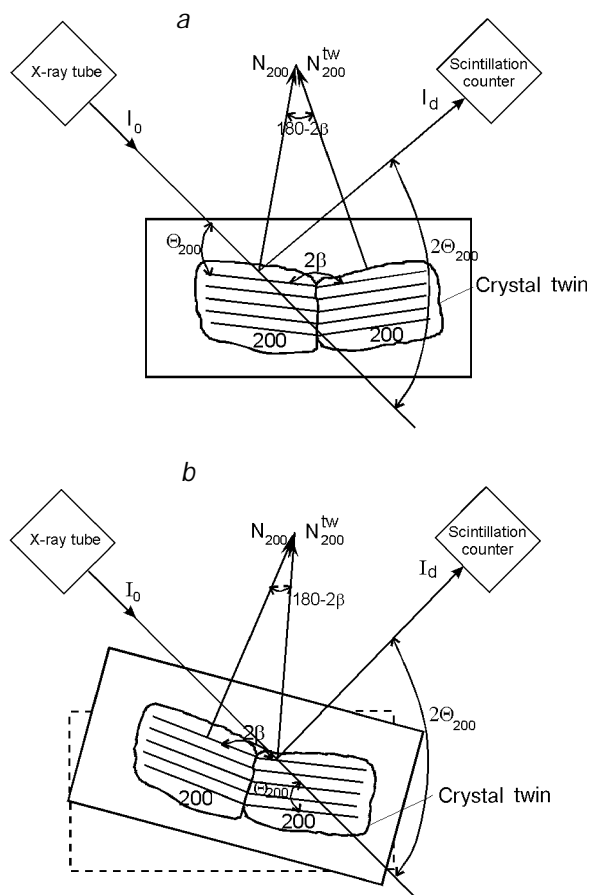
In order to reveal the twins, an ω-scanning of the single-crystalline sample relative to the (200) planes was performed. The orthorhombic and monoclinic phases were examined at room ($T = 300$ K) and low ($T = 77.3$ K) temperatures, respectively.

The principle of the twin structure revelation by ω-scanning is demonstrated schematically in Fig. 5.

The profiles of the interference lines obtained by means of ω-scanning at room ($2\theta = 33.04°$) and low ($2\theta = 32.65°$) temperatures for the (200) planes are shown in Fig. 6. The curves presented clearly indicate that at low temperature an additional reflection appears, corresponding to the occurence of the twinned domain structure. Thus the results of an x-ray structural investigation unambiguously prove the formation of the twinned domain structure at the transition from the orthorhombic to the monoclinic phase.
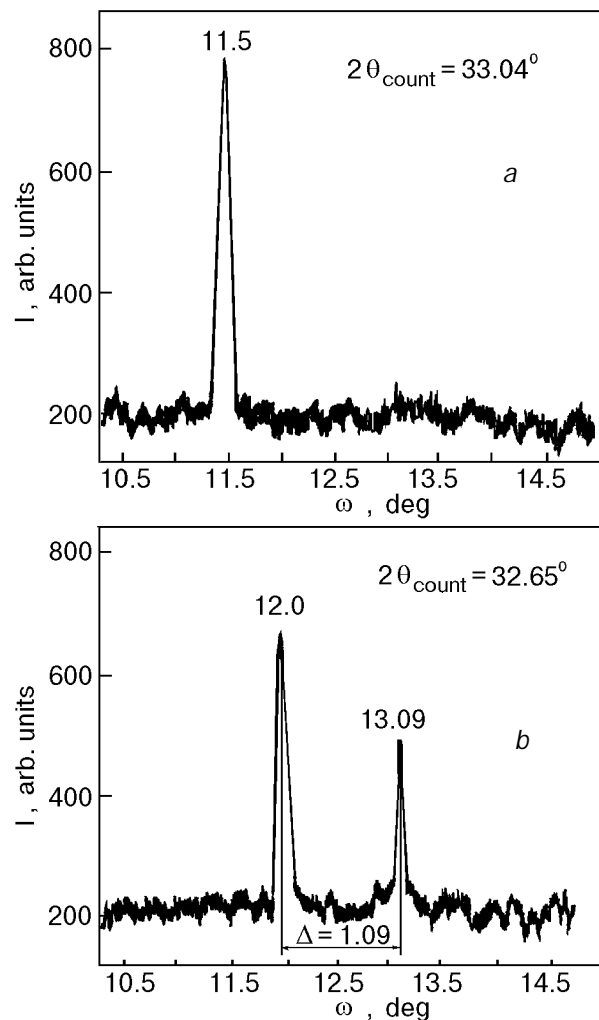

Fig. 5. The principle of twin structure observation in ω-scanning: *a* — the initial position; *b* — rotating the sample into position corresponding to the crystal twin.

Fig. 6. The results of ω-scanning of the (200) maximum at $T = 300$ (*a*) and 77.3 (*b*) K.

Conclusions

Our x-ray investigations of the manganite $Nd_{0.5}Sr_{0.5}MnO_3$ have shown the following:

1. In the orthorhombic phase the crystal structure of $Nd_{0.5}Sr_{0.5}MnO_3$ corresponds to the space group *Imma*. The unit cell of the orthorhombic phase is characterized by the lattice parameters $a = 5.4302$ Å, $b = 7.6177$ Å, $c = 5.4860$ Å.

2. At the transition to the AFM insulating charge-ordered state the crystal symmetry lowers to monoclinic. The symmetry of the crystal structure of the manganite in this state is described by the space group $P2_1/m$. The unit cell is characterized by the lattice parameters $a = 5.4851$ Å, $b = 7.5223$ Å, $c = 5.5186$ Å, and the angle $\beta = 89.455$ Å.

3. At the transition from the orthorhombic to the monoclinic phase a twinning of the crystal occurs. A twin domain structure with coherent boundaries in the crystal planes (00*l*) is formed.

1. H. Kuwahara, Y. Tomioka, Y. Moritomo, A. Asamitsu, M. Kasai, R. Kumai, and Y. Tokura, *Science* **272**, 80 (1996).
2. R. Mahendiran, M. R. Ibarra, F. Maigan, A. Arulraj, R. Mahesh, O. Revcau, and C. N. R. Rao, *Phys. Rev. Lett.* **82**, 2191 (1999).
3. P. M. Woodward, D. E. Cox, T. Vogt, C. N. Rao, and A. K. Cheetham, *Chem. Mater.* **11**, 3528 (1999).
4. M. R. Ibarra, J. M. DeTeresa, P. A. Algarabel, C. Marquina, B. Garcia-Landa, L. Morellon, C. Ritter, R. Mahendiran, A. Del Moral, *Magnetostriction in Mixed Valent Magnetic Oxides, NATO Science Series, ASI-2000, Modern Trends in Magnetostriction Study and Application* **5**, 171 (2000).
5. C. Ritter, R. Mahendiran, M. R. Ibarra, L. Morellon, A. Maignan, B. Raveau, and C. N. R. Rao, *Phys. Rev.* **B61**, 9229 (2000).
6. R. Kajimoto, H. Yoshizawa, H. Kawano, H. Kuwahara, Y. Tokura, K. Ohoyama, and M. Ohashi, *Phys. Rev.* **B60**, 9506 (1999).
7. H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Science* **270**, 961 (1995).
8. H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Phys. Rev. Lett.* **78**, 4253 (1997).
9. V. Bruk, A. Sirenko, and V. Sirenko, *Visualization of x-Ray Measurements of Complicated Structures,* in: *The Materials of Conf. «Teaching the Science of Condensed Matter and New Materials»,* M. Michelini (ed.), Udine, 24–30 August (1995), p. 463.
10. M. P. Shaskolskaya, *Cristallographia,* Vysshaya Shkola, Moscow (1984) [in Russian].
11. L. I. Mirkin, *Spravochnik po rentgenostructurnomu analizu polycristallov,* Gos. Izd.-vo Phys.-Math. Lit., Moscow (1961) [in Russian].
12. S. L. Gnatchenko, A. B. Chizhik, I. O. Shklyarevskiy, D. N. Merenkov, V. I. Kamenev, Yu. G. Pashkevich, K. V. Kamenev, G. Balakrishnan, and D. McK Paul, *Fiz. Nizk. Temp.* **25**, 992 (1999) [*Low Temp. Phys.* **25**, 744 (1999)].
13. I. O. Shklyarevskiy, M. Yu. Shvedun, S. L. Gnatchenko, P. J. M. van Bentum, P. C. M. Christianen, J. C. Maan, K. V. Kamenev, G. Balakrishnan, D. McK Paul, and J. Fink-Finowicki, *Fiz. Nizk. Temp.* **27**, 1250 (2001).