ISSN 0021-3640, JETP Letters, 2013, Vol. 97, No. 11, pp. 616–620. © Pleiades Publishing, Inc., 2013.
Original Russian Text © M.G. Kostenko, A.A. Rempel, S.V. Sharf, A.V. Lukoyanov, 2013, published in Pis'ma v Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2013, Vol. 97, No. 11, pp. 712–717.

Simulation of the Short-Range Order in Disordered Cubic Titanium Monoxide $TiO_{1.0}$

M. G. Kostenko[a], **A. A. Rempel**[a, b], **S. V. Sharf**[c], **and A. V. Lukoyanov**[b, d]
[a] *Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620990 Russia*
e-mail: rempel@ihim.uran.ru
[b] *Ural Federal University, Yekaterinburg, 620002 Russia*
[c] *Institute of Mathematics and Mechanics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620990 Russia*
[d] *Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620990 Russia*

Received March 12, 2013; in final form, April 19, 2013

A model of the atomic structure with the short-range order in the vacancy distribution for the disordered cubic phase of titanium monoxide $TiO_{1.0}$ has been proposed. The effect of the short-range order on the electronic structure and the stability of the compound has been studied by the supercell method within the DFT–GGA approximation with the use of pseudopotentials. It has been established that the appearance of the short-range order considerably decreases the total energy. The decrease in the energy is comparable with the energy gain during the ordering of the vacancies according to the type of monoclinic superstructure Ti_5O_5 to the long-range order parameter $\eta = 0.7$. It has been shown that the discrepancies between the theoretical and experimental electronic spectra of titanium monoxide can be explained by allowance for the short range order.

DOI: 10.1134/S0021364013110076

Oxides, carbides, and nitrides of transition metals having a wide range of homogeneity at high temperature owing to the high concentration of structural vacancies are conventionally singled out into a separate class of strongly nonstoichiometric compounds [1]. An important feature of such compounds is the atomic-vacancy ordering, which leads to the formation of new phases. The effect of ordering on the properties of the compound in some cases is comparable with the effect of nonstoichiometry. The structures of the ordered phases have been studied rather thoroughly to date. Their description can be found in [1].

At the same time, the features of the structure of the disordered phases have been studied insufficiently. The assumption that the vacancies are distributed statistically in the disordered phases, i.e., the short-range order is absent, is used most often. However, this assumption is not substantiated theoretically and experimentally. Effects of diffuse scattering indicating the existence of the short-range order were found in experiments on X-ray and electron diffraction on the samples of the disordered oxides, carbides, and nitrides of transition metals [2–6]. However, no models of the disordered structures with the short-range order were proposed. The effect of the appearance of the short-range order in the distribution of vacancies on the properties of strongly nonstoichiometric compounds remains unknown.

This work is aimed at the simulation of the short-range order in the distribution of vacancies for the disordered cubic phase of titanium monoxide of the equiatomic composition $TiO_{1.0}$ and the study of the effect of the short-range order on the electronic structure and total energy of this compound.

It is known that titanium monoxide TiO_y has the basic structure of the *B*1 type. In contrast to the majority of other strongly nonstoichiometric compounds, it contains vacancies in both metal and nonmetal sublattices. In the case of equiatomic composition ($y = 1.0$), their fraction is about 15% in each sublattice [7–10]. The concentration of vacancies can be decreased only by annealing at high pressures and temperatures [11]. Vacancies can be distributed over the sites of the basic structure regularly or randomly. The disordered state is thermodynamically equilibrium at temperatures above 1263 K. The ordered state is formed as a result of slow annealing at temperatures below 1263 K [8, 9]. It was earlier accepted that the ordering of vacancies in titanium monoxide of the stoichiometric composition leads to the formation of only the monoclinic ordered phase, considered in detail in [8–10]. In [12], an alternative variant of the ordering was analyzed and the model of the ordered phase with the cubic symmetry was proposed.

All these features make titanium monoxide the most interesting object among other strongly nonstoichiometric compounds for the study of the features of the ordering, simulation of the short- and long-range orders, and analysis of the effect of the ordering on the properties of the compound.

The high concentration of vacancies makes it possible to use the supercell method when studying the

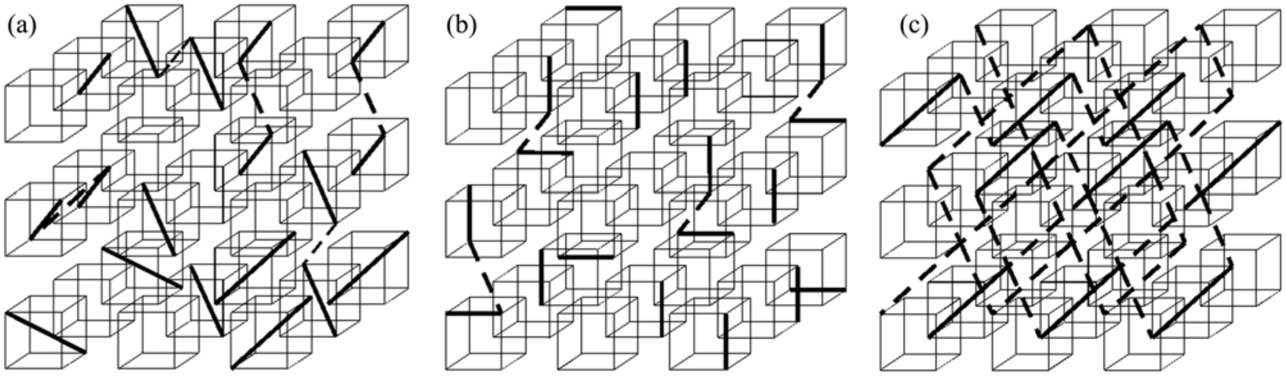

Fig. 1. Models of the structure of (a, b) the disordered cubic phase with the short-range order and (c) the ordered monoclinic phase. Solid bold lines show titanium–oxygen pairs of vacancies in separate clusters. Dashed bold lines are pairs of vacancies distributed between clusters. Each vacancy in the ordered structure (c) has four neighboring vacancies in the third coordination sphere. Vacancies in structures (a) and (c) are located at a distance larger than the radius of the first coordination sphere. Each vacancy in the structure (b) has only one neighboring vacancy in the first coordination sphere.

electronic structure of the compound with the short-range order. In turn, this allows the application of the most exact and convenient approaches on the basis of the density functional theory and pseudopotentials.

When building the model of the structure with the short-range order, first of all it is necessary to solve the problem of what correlations and in what coordination spheres they arise between defects. The simplest variant is to take into account only the pair correlations at short distances. In this case, this is the interaction between the titanium vacancy and the oxygen vacancy in the vacancy–vacancy pair. The distance between vacancies in the pair can differ. The concentration of defects in titanium monoxide is so high that most of the vacancies of one of the sublattices have at least one neighboring vacancy at the distance corresponding to the radius of the first or third coordination sphere. To determine what distance is the most energy favorable, two supercells in the shape of a cube containing 216 sites of the *B*1 basic structure were built. Each supercell contained one titanium vacancy and one oxygen vacancy. In one case, the distance between them was the radius of the first coordination sphere, and in the other case, the radius of the third coordination sphere. The translation of the supercell of a given size gives a crystal structure, in which the titanium–oxygen pairs of vacancies are rather distant from each other.

The ab initio quantum mechanical calculations within the density functional theory were performed for the model structures built in this manner. The exchange-correlation interaction was taken into account in the GGA approximation of the PBE version [13]. The PWSCF code of the Quantum ESPRESSO suite [14], which assumes the use of pseudopotentials based on plane waves, was used in the calculations.

The calculations showed that the total energy of the crystal with the structure in which the vacancies are distributed at the distance of the radius of the third coordination sphere is less than the energy of the crystal with the vacancies at the distance of the radius of the first coordination sphere. Thus, the distribution of the vacancies at the distance of the radius of the third coordination sphere in the titanium vacancy–oxygen vacancy pair is preferable.

The vacancies located at the distance of both the first and third coordination spheres should be present with a definite probability in the completely disordered structure of titanium monoxide. The exclusion of one of the variants as the energy unfavorable one leads to the appearance of the short-range order or the short- and long-range orders simultaneously. The simplest energy favorable structure, in which only the short-range order is present, is the structure where titanium–oxygen pairs of vacancies are located chaotically with respect to each other and at the same time uniformly over the total volume of the *B*1 lattice but so that the distance between two vacancies is always larger than the radius of the first coordination sphere. It is convenient to use the cluster approach [15–17] in order to simulate such a structure. The *B*1 basic structure may be represented as an ensemble of noncontact cubic clusters, each of which is 1/8 fraction of the unit cell of the basic structure (Fig. 1). A vacancy may be located at the end of one of four diagonals of the cluster. Its appearance automatically leads to the appearance of the vacancy at the other end of the diagonal and the exclusion of vacancies at all six sites of the first coordination sphere of all vacancies. The probability of the cluster with a pair of vacancies is 2/3. It corresponds to the concentration of vacancies in the compound of 1/6, the same as in the ideal structure of the ordered phases [7–12]. All four possible orientations of the pair of vacancies in the cluster are of equal probability. No exclusion for each vacancy to have more than one neighboring vacancy at the distance of the radius of the third coordination sphere was estab-

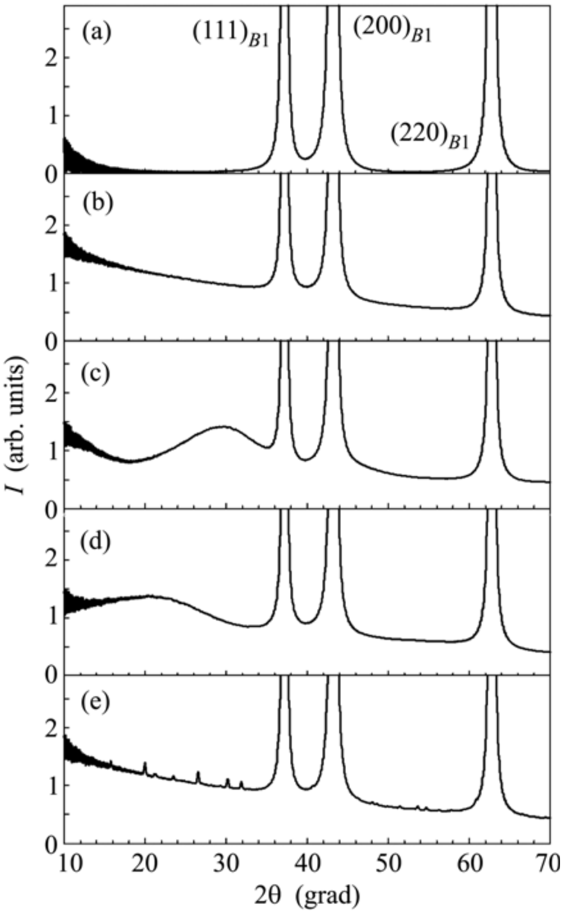

Fig. 2. Theoretical X-ray diffraction spectra of titanium monoxide (a) without vacancies, (b) with vacancies distributed randomly, with the short-range order according to models (c) 1 and (d) 2, and (e) with vacancies partially ordered according to the type of monoclinic superstructure Ti_5O_5 to the long-range order parameter $\eta = 0.1$.

lished. Therefore, the vacancies with one neighboring vacancy in the third coordination sphere and with two or more vacancies should be met in the structure with a certain probability. When the long-range order appears according to the type of monoclinic superstructure Ti_5O_5, pairs of vacancies are arranged so that each vacancy has exactly four neighboring vacancies at the distance of the radius of the third coordination sphere (Fig. 1c). The vacant sites are located only in every third (101) plane of the sublattices of the basic structure [10]. Thus, the essence of the proposed model is that, in the process of temperature-induced disordering, vacancies tend to be distributed in the *B*1 basic structure in disorder and homogeneously but with the conservation of the pair correlations between them, which were present in the ordered phase. This model of the structure is called model 1.

Figure 1b shows the necessarily energy unfavorable model of the short-range order (model 2). It is built in analogy with model 1 (Fig. 1a), but here the vacancies in a pair are located at the distance of the radius of the first coordination sphere from each other, i.e., on the edges of clusters rather than on their diagonals.

To test that the proposed short-range order does not lead to the automatic appearance of the long-range order, the X-ray scattering spectra for the crystals with the model structures described above were calculated by the Debye formula:

$$I(\theta) = N_{\mathrm{Ti}} f_{\mathrm{Ti}}^2(\theta) + N_{\mathrm{O}} f_{\mathrm{O}}^2(\theta) + 2\sum_{j=0}^{N-1}\sum_{i>j}^{N-1} f_j(\theta) f_i(\theta)\frac{\sin(C\sin\theta R_{ij})}{C\sin\theta R_{ij}}, \quad (1)$$

where I is the scattering intensity; θ is the diffraction angle; N_{Ti} and N_{O} are the numbers of titanium and oxygen atoms in the crystal, respectively; N is the total number of atoms in the crystal; f_i is the atomic scattering factor [18] of the ith atom (f_{Ti} or f_{O}); R_{ij} is the distance between the ith and jth atoms; and C is a constant. Crystals had the shape of a sphere and contained about 4×10^6 sites of the *B*1 basic structure. Five types of structures were simulated: (i) without vacancies, (ii) with complete disorder in the distribution of vacancies, (iii) with the short-range order according to model 1, (iv) with the short-range order according to model 2, and (v) with the long-range order according to the type of monoclinic superstructure Ti_5O_5 with the long-range order parameter $\eta = 0.1$. The calculated spectra are shown in Fig. 2. In all cases, the reflections from the *B*1 basic structure are present in the spectrum. The appearance of vacancies leads to the appearance of the Laue background (Figs. 2b–2e). The short-range order gives the variations of this background. According to the type of variation or, in other words, the shape of the spectrum, one disordered structure can be distinguished from the other (Figs. 2c, 2d). In the spectrum corresponding to model 1, the maximum at $2\theta = 29.6°$ and the minimum at $2\theta = 17.6°$ arise, and in the spectrum corresponding to model 2, only the maximum at $2\theta = 20.4°$ arises. The long-range order leads to the appearance of superstructural reflections (Fig. 2e). In the spectra corresponding to models 1 and 2, no superstructural reflections were found. This fact indicates that the proposed model structures indeed have only the short-range order.

Many works are devoted to the study of the effect of the vacancies on the electronic structure of titanium monoxide. The latest and most comprehensive studies are presented in [19–21]. However, nowhere was the relevant attention paid to the disordered phases. Moreover, the existence of the short-range order was not taken into account in them. It is convenient to simulate the structure of the compound using supercells, which are obtained during the twofold translations of the unit cell of the ordered monoclinic phase [10] along the crystallographic directions *a* and *b*, in order to study the effect of the short-range order on the electronic structure and to calculate the total

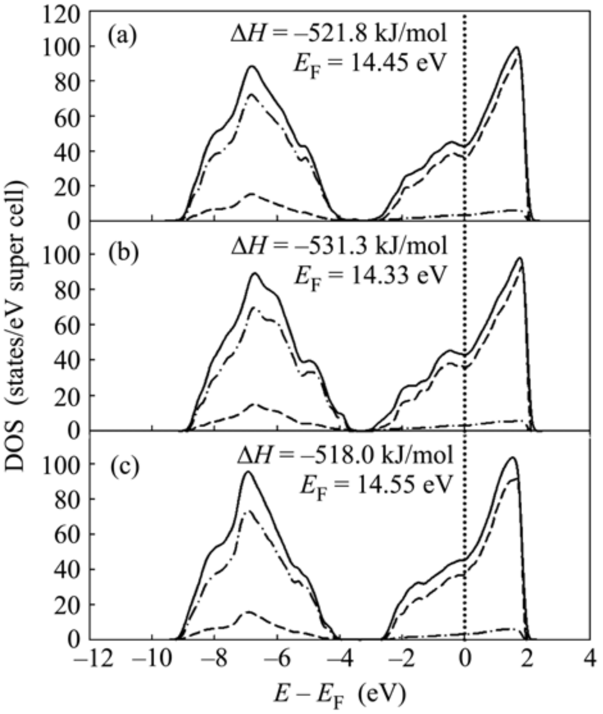

Fig. 3. Electron densities of states of titanium monoxide with (a) vacancies distributed randomly, as well as with vacancies distributed according to models (b) 1 and (c) 2. The solid line shows the total density of states, the dashed line is the partial density of the $3d$ states of titanium, and the dash-dotted line presents the partial density of $2p$ states of oxygen. The enthalpies of formation ΔH and the Fermi energies E_F found as a result of averaging over 20 supercells are given. The standard deviation σ of the calculated enthalpy of formation was 3.5 kJ/mol for the completely disordered structure and 2.2 and 2.3 kJ/mol for the structures with the short-range order according to models 1 and 2, respectively. In the calculation of the Fermi energy, σ did not exceed 0.06 eV.

energy. These supercells contain 96 sites of the $B1$ basic structure. The same supercells were used in [22, 23] for studying the effect of nonstoichiometry and the long-range order. In this case, the titanium and oxygen vacancies in the supercells were located so that during the translations the structure was formed corresponding to the requirements of models 1 and 2. The relaxation of the atomic positions was performed for all supercells.

Figure 3 shows the electronic spectra of the disordered cubic phase (a) with the complete disorder in the distribution of vacancies and with the short-range order according to models (b) 1 and (c) 2 built from the calculation results. The calculated enthalpies of formation and Fermi energies are given. For comparison, Fig. 4 shows the electronic spectra of titanium monoxide (a) without vacancies, as well as with the long-range order in the distribution of the vacancies according to the type of (b) monoclinic superstructure Ti_5O_5 and (c) cubic superstructure Ti_5O_5 recently proposed in [12]. In all cases, the low- and high-energy regions of the occupied states are mainly represented by the $2p$ states of oxygen and the $3d$ states of titanium, respectively. A distinct p–d gap is present in the spectra of the phase without vacancies, the ordered monoclinic phase, and the disordered cubic phase with the short-range order according to model 2. The gap boundaries are smeared in the phase with the complete disorder and states with a low density appear in its place. The appearance of the short-range order according to model 1 leads to the nearly complete vanishing of the p–d gap owing to a decrease in the energy of some $3d$ electrons of titanium. It should be noted that the calculated electronic spectrum of the disordered monoclinic phase (Fig. 3b) is in agreement with the results reported in [19–21].

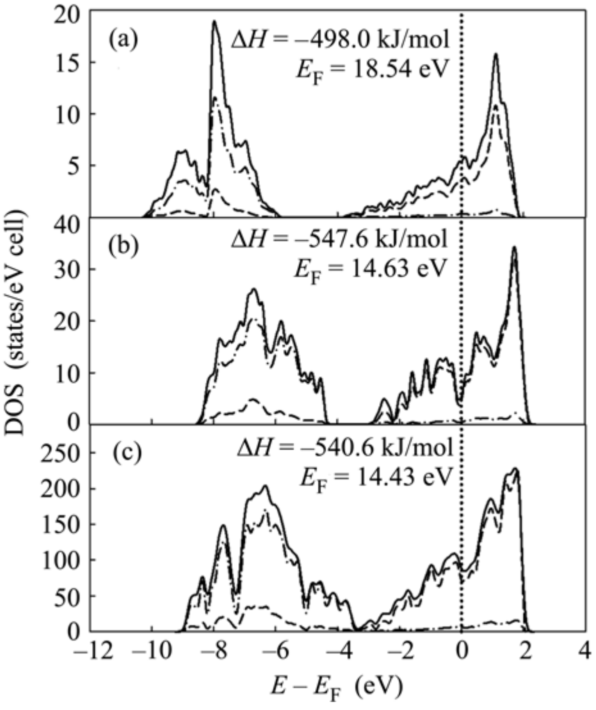

Fig. 4. Electron densities of states of titanium monoxide (a) without vacancies and with vacancies located according to the type of (b) monoclinic superstructure Ti_5O_5 and (c) cubic superstructure Ti_5O_5. The solid line shows the total density of states, the dotted line is the partial density of the $3d$ states of titanium, and the dash-dotted line presents the partial density of the $2p$ states of oxygen. The enthalpies of formation ΔH and Fermi energies E_F are given.

The existence of the p–d gap is the main discrepancy between the results of the theoretical [19–21] and experimental [24, 25] studies of the electronic structure of the different phases of titanium monoxide. The calculations of the electronic spectra of the ordered [19–21] and disordered [21, 24] phases unambiguously indicate its existence. At the same time, no p–d gap was found in the experimental spectra of titanium monoxide without vacancies [25], ordered monoclinic phase [25], and disordered cubic [24] phase. The results of this work vividly demonstrate that this discrepancy in the case of the disordered cubic phase can be explained by the existence of the short-range order, which was not taken into account earlier in the theoretical studies of the electronic structure. The solution of the discrepancy can also be proposed for other phases. According to [21], the samples of the vacancy-free titanium monoxide used for the experiment [25] contained a noticeable fraction of the residual vacancies. The appearance of the pair correlations between them could lead to the vanishing of the p–d gap. At the same time, the structure of the ordered phase could be misunderstood. In [25], it was attributed to the monoclinic phase Ti_5O_5 on the basis of the X-ray diffraction results. However, it was shown in [26] that the X-ray scattering spectrum can hardly distinguish this structure from the cubic ordered phase Ti_5O_5 [12]. It is seen in Fig. 4 that the latter has no p–d gap.

Let us turn now to the results of the calculation for the energy parameters of the different crystalline modifications. The enthalpies of the formation of titanium monoxide with the short-range order according to models 1 and 2 were much lower and somewhat higher, respectively, than the enthalpy of the formation of titanium monoxide with the completely disordered structure (Fig. 3). Thus, the short-range order according to model 1 is really preferable. According to the comparison of the results of this work with the results obtained in [23] in which the effect of the long-range order on the stability of titanium monoxide was studied, a decrease in the energy of the $B1$ basic lattice after the appearance of the short-range order is rather significant. It corresponds to the energy gain because of the ordering of vacancies according to the type of most stable monoclinic superstructure Ti_5O_5 to the long-range parameter $\eta = 0.7$.

Thus, a model of the atomic structure with the short-range order in the distribution of vacancies has been proposed for the first time for the disordered phase of titanium monoxide, a representative of the class of strongly nonstoichiometric compounds with vacancies in both metal and nonmetal sublattices. The application of the supercell method made it possible to take into account the short-range order in the study of the electronic structure and the calculation of the total energy. The results of this work have demonstrated the importance of the inclusion of the short-range order both in theoretical studies of the structure and properties of similar compounds and for the correct interpretation of experimental data.

This work was supported by the Ural Branch of the Russian Academy of Sciences (project nos. RTsP P20, 12-M-23-2001, and 13-3-NP-532). All calculations were performed on the Uran supercomputer of the Institute of Mathematics and Mechanics, Ural Branch, Russian Academy of Sciences.

REFERENCES

1. A. I. Gusev and A. A. Rempel, *Nonstoichiometry, Disorder, and Order in Solids* (Ural Division, Russian Academy of Scineces, Yekaterinburg, 2001) [in Russian].
2. Y. Murata and N. Yukawa, J. Less-Common Met. **141**, 235 (1988).
3. P. Li and J. M. Howe, Acta Mater. **51**, 1261 (2003).
4. E. V. Shalaeva, B. V. Mitrofanov, and G. P. Shveikin, Phys. Status Solidi A **154**, 505 (1996).
5. P. S. Bell and M. H. Lewis, Phys. Status Solidi A **7**, 431 (1971).
6. J. R. Castles, J. M. Cowley, and A. E. C. Spargo, Acta Crystallogr. A **27**, 376 (1971).
7. M. D. Banus, T. B. Reed, and A. J. Strauss, Phys. Rev. B **5**, 2775 (1972).
8. D. Watanabe, J. R. Castles, A. Jostsons, and A. S. Marlin, Acta Crystallogr. **23**, 307 (1967).
9. D. Watanabe, O. Terasaki, A. Jostsons, and J. R. Castles, in *The Chemistry of Extended Defects in Non-Metallic Solids*, Ed. by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, 1970), p. 238.
10. A. A. Valeeva, A. A. Rempel, and A. I. Gusev, Inorg. Mater. **37**, 603 (2001).
11. A. Taylor and N. J. Doyle, in *The Chemistry of Extended Defects in Non-Metallic Solids*, Ed. by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, 1970), p. 523.
12. A. I. Gusev and A. A. Valeeva, JETP Lett. **96**, 364 (2012).
13. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
14. P. Giannozzi, S. Baroni, N. Bonini, et al., J. Phys.: Condens. Matter **21**, 395502 (2009).
15. A. A. Valeeva and A. A. Rempel, JETP Lett. **88**, 172 (2008).
16. M. G. Kostenko, A. A. Valeeva, and A. A. Rempel, Mendeleev Commun. **22**, 245 (2012).
17. M. G. Kostenko and A. A. Rempel, J. Exp. Theor. Phys. **115**, 999 (2012).
18. *International Tables for X-ray Crystallography*, Vol. 4, Ed. by J. A. Ibers and W. C. Hamilton (Kynoch, Birmingham, 1973), p. 71.
19. C. Leung, M. Weinert, P. B. Allen, and R. M. Wentzcovitch, Phys. Rev. B **54**, 7857 (1996).
20. J. Graciani, A. Marquez, and J. F. Sang, Phys. Rev. B **72**, 054117 (2005).
21. D. A. Andersson, P. A. Korzhavyi, and B. Johansson, Phys. Rev. B **71**, 144101-1 (2005).
22. M. G. Kostenko, A. V. Lukoyanov, V. P. Zhukov, and A. A. Rempel, JETP Lett. **95**, 647 (2012).
23. M. G. Kostenko, A. V. Lukoyanov, V. P. Zhukov, and A. A. Rempel, JETP Lett. **96**, 507 (2012).
24. M. A. Korotin, A. V. Efremov, E. Z. Kurmaev, and A. Muves, JETP Lett. **95**, 641 (2012).
25. S. Bartkowski, M. Neumann, E. Z. Kurmaev, et al., Phys. Rev. B **56**, 10656 (1997).
26. A. I. Gusev, J. Solid State Chem. **199**, 181 (2013).

Translated by L. Mosina