Физика твердого тела, 2012, том 54, вып. 3

05

Ferromagnetic and antiferromagnetic ordering in the wurtzite-type diluted magnetic semiconductors

© *Yu.E. Kitaev*[1,2], *P. Tronc*[2]

[1] Ioffe Physical Technical Institute, Russian Academy of Sciences,
St. Petersburg, Russia
[2] LPEM, Ecole Supérieure de Physique et de Chimie Industrielles,
Paris, France
E-mail: yu.kitaev@mail.ioffe.ru

(Received September 20, 2011)

We determined the magnetic symmetry groups (Shubnikov groups) of the wurtzite-type crystals doped with magnetic atoms periodically distributed at cation sites. The magnetic groups of doped crystals with ferro- or antiferromagnetic properties arise from the $P6_3mc$ (C_{6v}^4), $P3m1$ (C_{3v}^1), C_s^3 (Cm) or C_1^1 ($P1$) ordinary space groups. Those arising from the $P6_3mc$ or $P3m1$ group can present macroscopic ferromagnetic polarization only along the wurtzite symmetry axis whereas those arising from the C_s^3 (Cm) group can present ferromagnetic polarization only in the symmetry plane and those arising from the C_1^1 ($P1$) group can present polarization along any direction. Actual structures do not keep in general long-range order for magnetic atom distribution but the samples with macroscopic polarization should present local symmetries close to those listed above. Therefore, orientation of easy magnetization can provide information about the most frequent local symmetry.

The work was supported by the grant Egide ECO-NET 21344 WL du Ministère des Affaires Etrangères (France).

1. Introduction

After the pioneering work by Dietl et al. [1], a great amount of works has been devoted to Diluted Magnetic Semiconductors (DMSs) (for a review see [2,3]). Indeed, DMSs allow imagining electron devices where information is carried by electron spin instead of electric charge. Such a technique has been named spin electronics or spintronics. After Dietl, spins of magnetic atoms hosted in semiconductor lattice can align due to interaction with free-carrier spins, mainly hole spins.

Among the magnetic diluted semiconductors, the wurzite-type ones (GaN, ZnO etc) attract great attention. In the model, III–V semiconductors, as for example GaN, do not need to be *p*-doped since magnetic atoms themselves act as acceptors. On the contrary, II–VI semiconductors, as ZnO for example, cannot offer such a simple way for doping since magnetic atoms reside at Zn cation sites, therefore are isoelectronic with the replaced atoms. Later, another model has been proposed [2] where an important contribution to magnetic properties arises from grain boundaries. ZnO layers with magnetic atoms can be grown by various methods [2,3]. It seems reasonable to assume that the grain-boundary surface per unit volume in the crystal depends on the quality of the layer and should decrease when crystallographic quality is improved, for example by using MBE growth technique, even if this technique can also induce a columnar structure parallel to the wurtzite **c**-axis which is also the growth direction [4]. In addition, Raman experiments have revealed spectral lines indicating the presence of $ZnCo_2O_4$ or Co_3O_4 spinel structures in numerous samples. Such spinel crystals have a cubic structure and have generally antiferromagnetic properties [5–8]. Spinel structures have been observed also in ZnO samples with Mn or Fe atoms [8,9]. Last, theoretical considerations have lead to the idea that Zn vacancies in pure ZnO could behave as magnetic centers with a spin value equal to unity [10].

Distribution of magnetic atoms (Co, Ni, Mn,...) over cation sites in ZnO is a key point for studying possible intrinsic magnetic properties of crystals. The term intrinsic means that hereafter we do not take into account lattice defects as, for example, vacancies, interstitial atoms, grain boundaries, dislocations or inclusion of other crystal structures. To elucidate the relationship between the distribution of magnetic atoms and magnetic properties of samples, we propose hereafter an approach based on symmetry properties of wurtzite lattices with magnetic atoms. To make it possible to use the results of group theory, it is necessary to deal with periodic structures i. e., to assume that magnetic atoms are periodically distributed over cation sites of the wurtzite lattice. Obviously, such a distribution cannot fit completely actual structures. Indeed, the actual structures certainly do not keep long-range order for the magnetic-atom distribution but it seems reasonable to assume that at short range, i. e., few unit-cell lengths, the actual local-structure symmetry is not far from that of a periodic-structure symmetry. Thus, magnetic properties should depend on the involved region in the crystal. A clear anisotropy of magnetization properties with respect to the crystallographic axes has been put into evidence in MBE grown samples [4]. It demonstrates that some symmetry properties are kept in actual samples at least at short range. The symmetry properties should of course arise in part from wurtzite lattice symmetry of host ZnO crystals but also from magnetic-atom-distribution symmetry since the symmetry of doped crystals is the intersection of both. Note that, in a model with a random distribution of Co atoms over cation sites, Co–O–Co sequences should become more and more numerous when increasing the amount of magnetic atoms. This is consistent with the existence of different local symmetries in a given sample. In our model, we neglect possible lattice distorsions arising from the size of magnetic atoms as compared to that of Zn atoms.

The symmetry of magnetic crystals is described by the so-called black and white Shubnikov groups [11,12], whereas that of diamagnetic and non-magnetic crystal is described by grey Shubnikov groups and ordinary space groups, respectively. The tables of Shubnikov groups have been compiled by Litvin [13] but, to our knowledge, no results appeared in the literature for application of Shubnikov groups for the description of magnetic properties of the wurtzite-type materials.

Decreasing Co concentration makes it necessary to increase wurtzite unit-cell volume by an integer factor. This can be made using the retreval tools on the Bilbao Crystallographic Server [14,15]. One can construct the group-subgroup relationships between the parent wurtzite structure and the derivative structures obtained by various substitutions of atoms in the cation sublattice. Such an approach allows determining, for a given Co concentration, the possible magnetic structures with the direction of the magnetization.

The present paper is organized as follows: in section 2 we model the decrease of Co concentration in the host lattice ZnO and determine the corresponding space groups; in section 3, the Shubnikov group construction is presented and the magnetic groups for wurtzite-type crystals are determined; in section 4 the restrictions imposed by site symmetry of magnetic atoms are derived, in section 5 possible configurations of magnetic moments are obtained. The results are discussed in section 6. Finally, section 7 contains a summary of results.

2. Modeling of $Zn_{1-x}Co_xO$ crystal symmetry

The set of space groups for the wurtzite-type structures depends on the distribution of magnetic impurities over the sites of the host lattice ZnO. The distribution of Co atoms among the cation sites in $Zn_{1-x}Co_xO$ remains still unknown. We can model all possible types of magnetic impurity orderings in the host lattice and analyze the corresponding magnetic groups using the following procedure.

First, we start from the virtual wurtzite-type structure with all Zn atoms being replaced by Co. Second, we decrease step-by-step the Co concentration in the host lattice to be as low as 0.1%.

This can be made using the retrieval tools on the Bilbao Crystallographic Server [14,15] within the procedure proposed by Megaw [16] and Bärnighausen [17]. Their procedure describes structural relationships between crystal structures based on symmetry relations between the structures' space groups. Starting from a highly symmetrical structure type (aristotype) and reducing the space-group symmetry less symmetric structure types (hettotypes) are obtained. In doing this, the splitting schemes of the occupied Wyckoff positions are taken into account. Such trees of group-subgroup relations are known also as the Bärnighausen trees [18,19].

We start from the parent wurtzite structure and obtain the derivative magnetic structures substituting atoms in the cation sublattice by magnetic impurity atoms. The main structure restriction imposed is that the positions of atoms in space do not change, i.e. they occupy the sites of the wurzite structure. As a result, we neglect all the derivative structures in the tree being the result of atomic displacements.

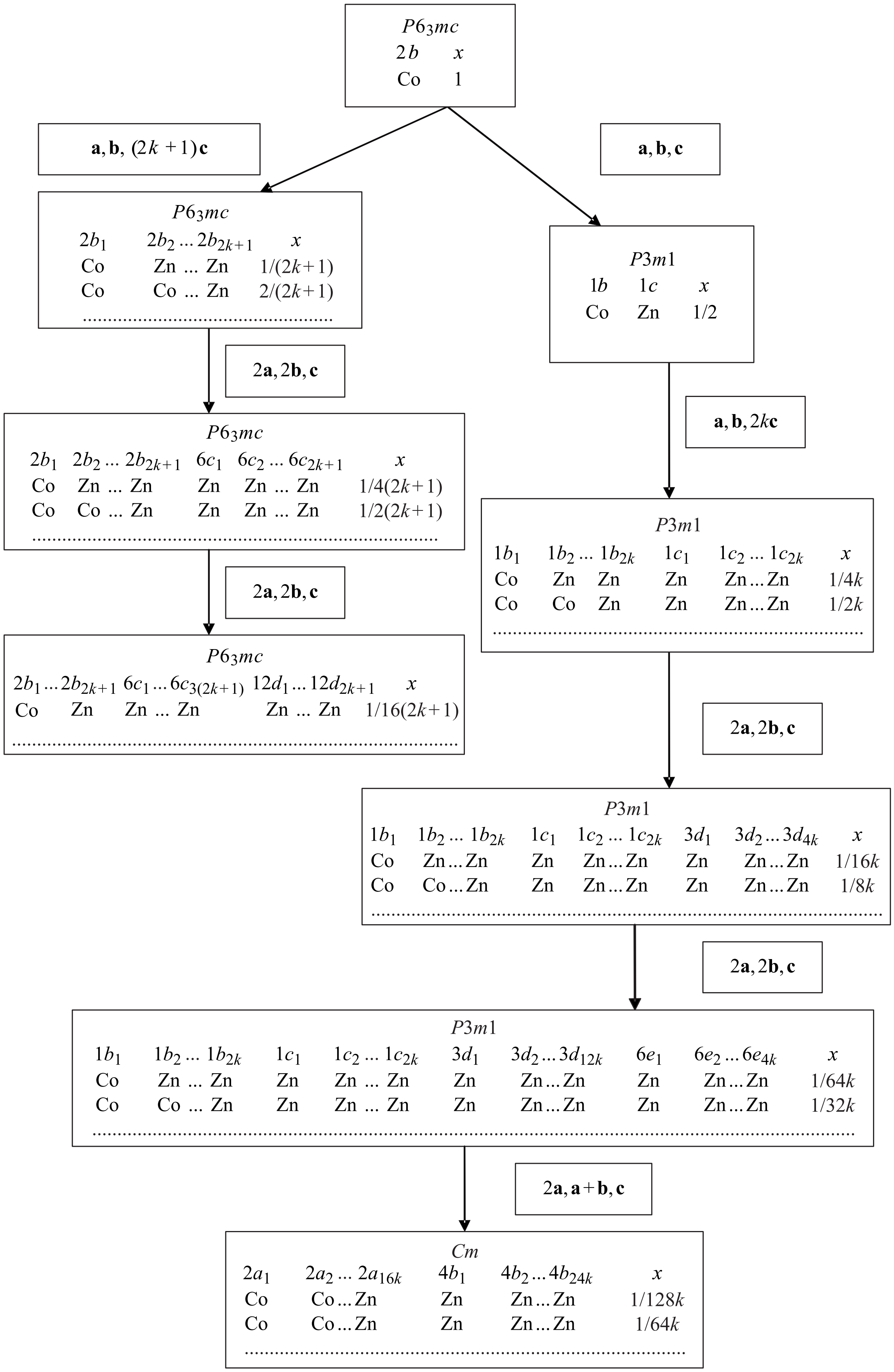
Using the MAXSUB program of the Bilbao Crystallographic Server we can find all possible maximal subgroups of the $P6_3mc$ (N 186) group. There are 4 maximal subgroups without multiplication of the unit cell $Cmc2_1$ (N 36), $P3m1$ (N 156), $P31c$ (N 159), and $P6_3$ (N 173) as well as one subgroup $P6_3cm$ (N 185) and 5 subgroups $P6_3mc$ (N 186) with the multiplication of the parent crystal unit cell along different directions. Thus, at the first step we obtain several branches of the group-subgroup relation tree. Repeating this procedure several times, we obtain structures with lower concentrations of impurity belonging to different branches of the tree and having different distributions of magnetic atoms.

However, among the maximal subgroups we should take into account only those ones for which $2b$ position of $P6_3mc$ (N 186) is splitted into several ones, i.e. we consider structures which can be obtained by various replacements of cations while keeping the positions of atoms being fixed.

Looking at the Wyckoff position splitting schemes, we find that among the above maximal subgroups only $P3m1$ (N 156) and $P6_3mc$ (N 186) with the multiplication of the unit cell correspond to a splitting of the $2b$ Wyckoff position occupied by cation atoms. Other maximal subgroups correspond either to structures with non-characteristic orbits or to structures formed by displacements of cations within the primitive unit cell. The complete group-subgroup relationship tree (Bärnighausen tree) for the wurtzite-type parent structure is shown in figure. Below, we shall consider separate branches in detail.

2.1. The $P6_3mc > P6_3mc \ldots > P6_3mc$ branch. To decrease uniformly the impurity concentration, we can consider, at the first step, the group - subgroup pair $P6_3mc$(N 186) $> P6_3mc$(N 186) with the transformation matrix (including the translation column part) which relates the coordinate system of the subgroup to that of the supergroup:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2k+1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$



Group-subgroup relationship tree (Bärnighausen tree) for the wurtzite-type parent structure

Table 1. Site symmetries of cation atoms in derivative structures

Derivative structure groups	Cation site symmetries
$P6_3mc$	$2b\,(3m)$, $6c\,(m)$
$P3m1$	$1b(3m)$, $1c(3m)$, $3d(m)$, $6e\,(1)$
Cm	$2a(m)$, $4b(1)$

Thus, we increase the unit cell along the z-direction. The $2b$ Wyckoff position of the group splits into $2b_1 + 2b_2 + \ldots + 2b_{2k+1}$ positions of the subgroup. Any combination of these positions could be occupied by Co atoms. If only one position is occupied, let $2b_1$, the resulting structure corresponds to $x = 1/(2k+1)$ concentration of Co atoms with $2(2k+1)$ cation atoms per primitive cell.

At the second step, we consider the group — subgroup pair $P6_3mc$(N 186) > $P6_3mc$(N 186) with the following transformation matrix

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

In this case, we double the unit cell both along x and y directions. The $2b_1 + 2b_2 + \ldots + 2b_{2k+1}$ Wyckoff positions of the group split into $2b_1 + 2b_2 + \ldots + 2b_{2k+1} + 6c_1 + 6c_2 + \ldots + 6c_{2k+1}$. At the next step, we double again the unit cell: the $2b_1 + 2b_2 + \ldots + 2b_{2k+1} + 6c_1 + 6c_2 + \ldots + 6c_{2k+1}$ positions split into $2b_1 + 2b_2 + \ldots + 2b_{2k+1} + 6c_1 + 6c_2 + \ldots + 6c_{2k+1} + 6c_{(2k+1)+1} + 6c_{(2k+1)+2} + \ldots + 6c_{3(2k+1)} + 12d_1 + 12d_2 + \ldots + 12d_{2k+1}$.

The $2b_1$ position being occupied by Co atoms, the resulting structure corresponds to $x = 1/16(2k+1)$ concentration of Co atoms.

Thus, the Co atoms in the $P6_3mc$ family can occupy $2b$ (site symmetry group $3m$), $6c\,(m)$ or $12d\,(1)$ positions. All possible site symmetries for magnetic impurities are presented in Table 1.

2.2. The $P6_3mc > P3m1 \ldots > P3m1 > Cm$ branch. Among the other maximal subgroups only $P3m1$ (N 156) corresponds to a splitting of the $2b$ Wyckoff position occupied by cation atoms. The remaining subgroups correspond either to structures with non-characteristic orbits or to structures formed by displacements of cations within the primitive unit cell.

For the group — subgroup pair $P6_3mc$(N 186) > $P3m1$(N 156), the transformation matrix is:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

Thus, the unit cell does not change along the z-direction. The $2b$ Wyckoff position of the group splits into $1b + 1c$ positions of the subgroup. Any of these positions, let $1b$, could be occupied by Co atoms. The structure corresponds to $x = 1/2$ concentration of Co atoms with 2 cation atoms per primitive cell.

At the second step, we consider the group — subgroup pair $P3m1$(N 156) > $P3m1$(N 156) with the following transformation matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2k \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

Thus, we increase the unit cell along the z direction. The $1b + 1c$ Wyckoff positions of the group split into $1b_1 + 1b_2 + \ldots 1b_{2k} + 1c_1 + 1c_2 + \ldots 1c_{2k}$ positions of the subgroup. Again, any of these positions, let $1b_1$, could be occupied by Co atoms. The resulting structure corresponds to $x = 1/4k$ concentration of Co atoms.

Next, the reduce the concentration of Co atoms within the xy-plane, we consider the group — subgroup pair $P3m1$(N 156) > $P3m1$(N 156) with the following transformation matrix

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

Hence, we double the unit cell both along x and y directions. The $1b_1 + 1b_2 + \ldots 1b_{2k} + 1c_1 + 1c_2 + \ldots 1c_{2k}$ Wyckoff positions of the group split into $1b_1 + 1b_2 + \ldots + 1b_{2k} + 1c_1 + 1c_2 + \ldots 1c_{2k} + 3d_1 + 3d_2 + \ldots 3d_{4k}$ positions of the subgroup. If the $1b_1$ position would be occupied by Co atoms, the resulting structure corresponds to $x = 1/8k$ concentration of Co atoms.

At the next step, we double again the unit cell along x and y directions. $1b_1 + 1b_2 + \ldots 1b_{2k} + 1c_1 + 1c_2 + \ldots 1c_{2k}$ Wyckoff positions split into the $1b_1 + 1b_2 + \ldots 1b_{2k} + 1c_1 + 1c_2 + \ldots 1c_{2k} + 3d_1 + 3d_2 + \ldots 3d_{4k}$ ones while each $3d$ position splits into $3d_1 + 3d_2 + 6e$ positions.

Thus, the Co atoms in the $P3m1$ family can occupy $1b$ (site symmetry group $3m$), $1c$ $(3m)$, $3d$ (m) or $6e$ (1) positions.

The next step is the group — subgroup pair $P3m1$(N 156) > Cm(N 8) with the following transformation matrix

$$\begin{pmatrix} 2 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

Each $1b$ and $1c$ Wyckoff position of the group splits into $2a$ positions of the subgroup, each $3d$ positions splits into $2a + 4b$ and each $6e$ position into $4b_1 + 4b_2 + 4b_3$ positions.

Thus, the Co atoms in the Cm family can occupy $2a$ (site symmetry group m) or $4b$ (1) positions.

Even if all possible configurations in the (x, y) plane are not considered above, those that are considered involve the

Table 2. The set of magnetic groups for the space group $P6_3mc$

N_M	M	H	T	M_i		
186.1.1434	$P6_3mc$			$(1\|0, 0, 0)$	$(3_z\|0, 0, 0)$	$(3_z^{-1}\|0, 0, 0)$
				$(2_z\|0, 0, 1/2)$	$(6_z\|0, 0, 1/2)$	$(6_z^{-1}\|0, 0, 1/2)$
				$(m_x\|0, 0, 0)$	$(m_{xy}\|0, 0, 0)$	$(m_y\|0, 0, 0)$
				$(m_1\|0, 0, 1/2)$	$(m_2\|0, 0, 1/2)$	$(m_3\|0, 0, 1/2)$
186.2.1435	$P6_3mc1'$					
186.3.1436	$P6'_3m'c$	$P31c$	$(0, 0, 0; a, b, c)$	$(1\|0, 0, 0)$	$(3_z\|0, 0, 0)$	$(3_z^{-1}\|0, 0)$
				$(2_z\|0, 0, 1/2)'$	$(6_z\|0, 0, 1/2)'$	$(6_z^{-1}\|0, 0, 1/2)'$
				$(m_x\|0, 0, 0)'$	$(m_{xy}\|0, 0, 0)'$	$(m_y\|0, 0, 0)'$
				$(m_1\|0, 0, 1/2)$	$(m_2\|0, 0, 1/2)$	$(m_3\|0, 0, 1/2)$
186.4.1437	$P6'_3mc'$	$P3m1$	$(0, 0, 0; a, b, c)$	$(1\|0, 0, 0)$	$(3_z\|0, 0, 0)$	$(3_z^{-1}\|0, 0)$
				$(2_z\|0, 0, 1/2)'$	$(6_z\|0, 0, 1/2)'$	$(6_z^{-1}\|0, 0, 1/2)'$
				$(m_x\|0, 0, 0)$	$(m_{xy}\|0, 0, 0)$	$(m_y\|0, 0, 0)$
				$(m_1\|0, 0, 1/2)'$	$(m_2\|0, 0, 1/2)'$	$(m_3\|0, 0, 1/2)'$
186.5.1438	$P6_3m'c'$	$P6_3$	$(0, 0, 0; a, b, c)$	$(1\|0, 0, 0)$	$(3_z\|0, 0, 0)$	$(3_z^{-1}\|0, 0)$
				$(2_z\|0, 0, 1/2)$	$(6_z\|0, 0, 1/2)$	$(6_z^{-1}\|0, 0, 1/2)$
				$(m_x\|0, 0, 0)'$	$(m_{xy}\|0, 0, 0)'$	$(m_y\|0, 0, 0)'$
				$(m_1\|0, 0, 1/2)'$	$(m_2\|0, 0, 1/2)'$	$(m_3\|0, 0, 1/2)'$

Co-atom concentrations in the interval between maximal values and rather low ones. Besides, conclusions drawn in section 5 concerning magnetic properties including orientation of magnetization are provided for any possible ordinary space group [$P6_3mc(C_{6v}^4)$, $P3m1$ (C_{3v}^1), C_s^3 (Cm) or C_1^1 ($P1$) ordinary space group] and its associate magnetic groups. As a consequence, results concern any possible configuration type. To draw complete conclusion about a configuration that is not considered above, one has just to determine its ordinary and magnetic groups.

3. Magnetic groups for wurtzite-type structures

The symmetry of non-magnetic crystals is described by 230 space groups [20]. The space groups contain such symmetry operations as rotations, reflections and translations. However, the magnetic crystals possess the additional variable being the magnetic moment of atoms. If all the magnetic moments are collinear, i.e. they have only two values, the description of such crystals can be performed using 1191 black and white groups, or Shubnikov groups [11,12]. In these groups, an additional symmetry operation $1'$ is introduced, which change the colour of the atoms, or the direction of magnetic moments.

The magnetic group M is constructed from the ordinary one G in the following way

$$M = H + R(G - H),$$

where H is a subgroup of G of index 2, R is the operation of time inversion which inverts the direction of the magnetic moments.

The procedure of the construction of the irreducible representations of magnetic space groups has been developed in papers of Cracknell [21–24].

Each space group of the group-subgroup relationship tree (Bärnighausen tree) for the wurtzite-type parent structure generates a magnetic space group family.

According to the tables compiled by D. Litvin [13], for the space group of wurtzite, i.e. $P6_3mc$(N 186), the set of the magnetic space groups is given in Table 2.

In column 1 of Table 2, the numbers N_M of the magnetic groups are given where 186 is the number N of the ordinary space group from which the magnetic space group family is generated; $1, 2, 3, 4, 5$ are the numbers of the magnetic space groups belonging to the family; 1434–1438 are the numbers of the magnetic groups among 1651 magnetic groups.

Note that one group from each family (here 186.1.1434) concides with the ordinary group, one group (here 186.2.1435) is a so-called grey group (contains all elements of the ordinary group plus all these elements multiplied by the operation R which reverses the magnetic moments), the other groups (here 186.3.1436, 186.4.1437 and 186.5.1438) are so-called black-white magnetic groups (each one contains the elements of the subgroup of index 2 plus the rest of the elements multiplied by R).

In column 2, the symbols of the magnetic groups M are given; in column 3, the symbols of the subgroups H of index 2 are presented; in column 4, the shift of new origin and new translation vectors T (for all groups in question the origin does not shift and unit cell does not change) are given and in column 5 are listed all the elements M_i of the magnetic group with the anti-unitary ones multiplied by R denoted by prime.

The ordinary space group describes the symmetry of a nonmagnetic phase, the grey group corresponds to

Table 3. The set of magnetic groups for the space group $P3m1$

N_M	M	H	T	M_i		
156.1.1279	$P3m1$			$(1\|0, 0, 0)$ $(m_x\|0, 0, 0), 0)$	$(3_z\|0, 0, 0), 0)$ $(m_{xy}\|0, 0, 0)$	$(3z^{-1}\|0, 0, 0)$ $(m_y\|0, 0)$
156.2.1280	$P3m11'$					
156.3.1281	$P3m'1$	$P3$	$(0, 0, 0; a, b, c)$	$(1\|0, 0, 0)$ $(m_x\|0, 0, 0)'$	$(3_z\|0, 0, 0)$ $(m_{xy}\|0, 0, 0)'$	$(3_z^{-1}\|0, 0, 0)$ $(m_y\|0, 0, 0)'$
156.4.1282	$P_{2c}3m1$	$P3m1$	$(0, 0, 0; a, b, 2c)$	$(1\|0, 0, 0)$ $(m_x\|0, 0, 0)$	$(3_z\|0, 0, 0)$ $(m_{xy}\|0, 0, 0)$	$(3_z^{-1}\|0, 0, 0)$ $(m_y\|0, 0, 0)$
156.5.1283	$P_{2c}3m'1$	$P31c$	$(0, 0, 0; a, b, 2c)$	$(1\|0, 0, 0)$ $(m_x\|0, 0, 0)'$	$(3_z\|0, 0, 0)$ $(m_{xy}\|0, 0, 0)'$	$(3_z^{-1}\|0, 0, 0)$ $(m_y\|0, 0, 0)'$

Table 4. The set of magnetic groups for the space group Cm

N_M	M	H	T	M_i	
8.1.38	Cm			$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)$
8.2.39	$Cm1'$				
8.3.40	$C1m'1$	$P1$	$(0, 0, 0; b, \{a+b\}/2, c)$	$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)'$
8.4.41	$C_{2c}1m1$	Cm	$(0, 0, 0; a, b, 2c)$	$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)$
8.5.42	C_P1m1	Pm	$(0, 0, 0; a, b, c)$	$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)$
8.6.43	$C_{2c}1m'1$	Cc	$(0, 0, 0; a, b, 2c)$	$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)'$
8.7.44	$C_P1m'1$	Pc	$(0, 1/4, 0; c, -b, a)$	$(1\|0, 0, 0)$	$(m_y\|0, 0, 0)'$

a paramagnetic phase whereas magnetic groups describe different ferromagnetic or antiferromagnetic phases.

For the space groups $P3m1$(N 156) and Cm(N 8), the sets of the magnetic space groups are given in Tables 3 and 4, respectively.

4. Site symmetry of magnetic impurity

The site symmetry of magnetic atoms imposes restrictions on possible orientations of magnetic moments. It should be noted that within the Shubnikov approach, we limit ourselves by the admissible magnetic structures, i. e. those which are compatible with the corresponding Shubnikov group symmetry.

We can formulate the following rule: for a given site symmetry group, only those orientations of the magnetic moments are allowed which are left invariant under the action of both unitary and antiunitary elements of the group.

The magnetic moment being the axial vector, for unitary elements, the mirror reflections (m) leave invariant the magnetic moments oriented perpendicular to the symmetry plane whereas changing the sign of the magnetic moments lying in the plane. The rotations act on the axial vectors like on polar vectors. For the corresponding antiunitary elements, the axial vectors additionally change a sign under the operation of time inversion. The magnetic moments **M** allowed by the impurity site symmetry are given in Table 5. In tables [13], all possible components of allowed magnetic moments at the site of Wyckoff position orbits for the magnetic groups are given. Below, we summarize the results for all possible magnetic space groups generated by $P6_3mc$, $P3m1$ and Cm ordinary groups.

Table 5. Magnetic moments **M** in the wurzite-type diluted magnetic semiconductors allowed by site symmetry

Site symmetry of magnetic impurity	Allowed **M**
$3m$	0
$3m'$	parallel to **c**-axis
m	perpendicular to symmetry plane
m'	parallel to symmetry plane
1	arbitrary

5. Magnetic moment ordering

5.1. Group $P6_3mc$(N 186) family. As noted above, Co impurity in this family can occupy Wyckoff positions $2b$, $6c$, and $12d$. The 3-fold rotation axes are unitary elements in all Shubnikov groups related to the group $P6_3mc$(N 186) whereas mirror planes enter either like unitary or anti-unitary elements in different Shubnikov groups. Consider the procedure of obtaining the maximal allowed magnetic moment configuration for the impurity atoms occupying the sites of the two-point orbit $2b$

Table 6. Allowed magnetic moments **M** in the $P6_3mc$ family

Shubnikov magnetic group	Impurity Wyckoff position and site symmetry	Allowed **M** components $[uvw]$ at the sites of the orbit	Type of ordering
$P6_3'm'c$	$2b(3m'.)$	$[0, 0, w](z)$; $[0, 0, -w](z+1/2)$	Antiferromagnetic along the z-axis (atoms with antiparallel moments in the planes z and $z+1/2$)
	$6c(.m'.)$	$[u, -u, w]$, $[u, 2u, w]$, $[-2u, -u, w](z)$; $[u, -u, -w]$, $[u, 2u, -w]$, $[-2u, -u, -w](z+1/2)$	$u=0$: antiferromagnetic along the z-axis (atoms with antiparallel moments in the planes z and $z+1/2$) $u \neq 0$: umbrella-type structure (according to classification of [25])
$P6_3'mc'$	$2b(3m.)$	$[0, 0, 0](z)$; $[0, 0, 0](z+1/2)$	No magnetic structure
	$6c(.m.)$	$[u, u, 0]$, $[-u, 0, 0]$, $[0, -u, 0](z)$; $[u, u, 0]$, $[-u, 0, 0]$, $[0, -u, 0](z+1/2)$	Hexagonal-type structure
$P6_3m'c'$	$2b(3m'.)$	$[0, 0, w](z)$; $[0, 0, w](z+1/2)$	Ferromagnetic along the z-axis
	$6c(.m'.)$	$[u, -u, w]$, $[u, 2u, w]$, $[-2u, -u.w](z)$; $[-u, u, w]$, $[-u, -2u, w]$, $[2u, u, w](z+1/2)$	$u=0$ Ferromagnetic along the z-axis $u \neq 0$ Umbrella-type structure

Table 7. Allowed magnetic moments **M** in the $P3m1$ family

Shubnikov magnetic group	Impurity Wyckoff position and site symmetry	Allowed **M** components $[uvw]$ at the sites of the orbit	Type of ordering
$P3m'1$	$1b(3m'.)$ $1c(3m'.)$ $3d(.m'.)$	$[0, 0, w]$ $[0, 0, w]$ $[u, -u, w]$, $[u, 2u, w]$, $[-2u, -u, w]$	Ferromagnetic along the z-axis Ferromagnetic along the z-axis $u=0$: ferromagnetic along the z-axis $u \neq 0$: umbrella-type structure
$P_{2c}3m1$	$2b(3m.)$	$[0, 0, 0](z)$; $[0, 0, 0](z+1)$	No magnetic structure
	$2c(3m.)$	$[0, 0, 0](z)$; $[0, 0, 0](z+1)$	No magnetic structure
	$6d(.m.)$	$[u, u, 0]$, $[-u, 0, 0]$, $[0, -u, 0](z)$; $[-u, -u, 0]$, $[u, 0, 0]$, $[0, u, 0](z+1)$	Trigonal-type structure (atoms with antiparallel moments in the planes z and $z+1$)
$P_{2c}3m'1$	$2b(3m'.)$	$[0, 0, w](z)$; $[0, 0, -w](z+1)$	Antiferromagnetic along the z-axis (atoms with antiparallel moments in the planes z and $z+1$)
	$2c(3m'.)$	$[0, 0, w](z)$; $[0, 0, -w](z+1)$	Antiferromagnetic along the z-axis (atoms with antiparallel moments in the planes z and $z+1$)
	$6d(.m'.)$	$[u, -u, w]$, $[u, 2u, w]$, $[-2u, -u, w](z)$; $[-u, u, -w]$, $[-u, -2u, -w]$, $[2u, u, -w](z+1)$	$u=0$: antiferromagnetic along the z-axis (atoms with antiparallel moments in the planes z and $z+1$) $u \neq 0$ Umbrella-type structure (atoms with antiparallel moments in the planes z and $z+1$)

$(1/3, 2/3, z)(2/3, 1/3, z+1/2)$. The site symmetry group $3m$ contains only mirror planes intersecting along the z-axis and 3-fold rotation axes parallel to the z-axis. Thus, the site symmetry of the magnetic impurity at the $2b$ sites allows the orientation of the magnetic moments only along the z-axis because the 3-fold rotation axes do not leave invariant the magnetic moments along x and y axes.

In the magnetic group 186.3.1436 $P6_3'm'c$, the elements $(1|0, 0, 0)$, $(3_z|0, 0, 0)$, $(3_z^{-1}|0, 0, 0)$ and $(m_x|0, 0, 0)'$, $(m_{xy}|0, 0, 0)'$, and $(m_y|0, 0, 0)'$ enter the site symmetry group and do not change M whereas $(m_1|0, 0, 1/2)$, $(m_2|0, 0, 1/2)$, $(m_3|0, 0, 1/2)$ and $(2_z|0, 0, 1/2)'$, $(6_z|0, 0, 1/2)'$, $(6_z^{-1}|0, 0, 1/2)'$ transform the magnetic moment **M** of the atom occupy-

Table 8. Allowed magnetic moments **M** in the the Cm family

Shubnikov magnetic group	Impurity Wyckoff position and site symmetry	Allowed **M** components $[uvw]$ at the sites of the orbit	Type of ordering
$C1m'1$	$2a(.m'.)$	$[u, 0, w](0, 0, 0)$, $[u, 0, w](1/2, 1/2, 0)$	Ferromagnetic within the xz-plane
$C_{2c}1m1$	$4a(.m.)$	$[0, v, 0](z)$, $[0, -v, 0](z + 1)$	Antiferromagnetic along the y-axis (atoms with antiparallel moments in the planes z and $z + 1$)
C_P1m1	$2a(.m.)$	$[0, v, 0](0, 0, 0)$, $[0, -v, 0](1/2, 1/2, 0)$	Antiferromagnetic along the y-axis [atoms with antiparallel moments shifted by $(1/2, 1/2, 0)$]
$C_{2c}1m'1$	$4a(.m'.)$	$[u, 0, w](z)$, $[-u, 0, -w](z + 1)$	Antiferromagnetic within the xz- plane (atoms with antiparallel moments in the planes z and $z + 1$)
$C_P1m'1$	$2a(.m'.)$	$[u, 0, w](0, 0, 0)$, $[-u, 0, -w](1/2, 1/2, 0)$	Antiferromagnetic within the xz-plane [atoms with antiparallel moments shifted by $(1/2, 1/2, 0)$]

ing $(1/3, 2/3, z)$ position into $-\mathbf{M}$ of the atom at $(2/3, 1/3, z + 1/2)$. In this case, two magnetic impurity atoms occupying different sites of the two-point orbit $(1/3, 2/3, z)(2/3, 1/3, z + 1/2)$ are with opposite magnetic moments. Thus, this group describes the antiferromagnetic state.

In the magnetic group 186.4.1437 $P6_3'mc'$, the symmetry operations $(1|0, 0, 0)$, $(3_z|0, 0, 0)$, $(3_z^{-1}|0, 0, 0)$ and $(m_x|0, 0, 0)$, $(m_{xy}|0, 0, 0)$, and $(m_y|0, 0, 0)$ enter the site symmetry group. Mirror reflections transform **M** into $-\mathbf{M}$. Therefore, the site symmetry allows only $\mathbf{M} = 0$, i.e. no magnetic structure corresponds to this group.

In the magnetic group 186.5.1438 $P6_3m'c'$, the mirror and glide reflections are anti-unitary elements. Therefore they do not change the direction of the magnetic moment oriented along the z- axis. The elements $(m_x|0, 0, 0)'$, $(m_{xy}|0, 0, 0)'$, and $(m_y|0, 0, 0)'$ enter into the site symmetry group whereas $(m_1|0, 0, 1/2)'$, $(m_2|0, 0, 1/2)'$, $(m_3|0, 0, 1/2)'$ transform one point from the two-point orbit $(1/3, 2/3, z)$ into another $(2/3, 1/3, z + 1/2)$. The rest of elements $(1|0, 0, 0)$, $(3_z|0, 0, 0)$, $(3_z^{-1}|0, 0, 0)$, $(2_z|0, 0, 1/2)$, $(6_z|0, 0, 1/2)$ $(6_z^{-1}|0, 0, 1/2)$ are elements of the unitary subgroup. The $(1|0, 0, 0)$, $(3_z|0, 0, 0)$, $(3_z^{-1}|0, 0, 0)$ enter into the site symmetry group whereas $(2_z|0, 0, 1/2)$, $(6_z|0, 0, 1/2)$, $(6_z^{-1}|0, 0, 1/2)$ transform one point into another in the orbit. They also do not change **M**. Thus, this group describes the ferromagnetic phase.

In Table 6, we summarize the results for all possible site symmetries of magnetic impurities in the $P6_3mc$ family.

The site symmetry of the $12d$ position is 1. Therefore, any orientation of the magnetic moment is allowed by site symmetry. No ferro- or antiferromagnetic ordering is for this case. The orientation and ordering of magnetic moments for general positions are given in tables [13].

5.2. Group $P3m1$ (N 156) family. In this family, Co impurities can occupy Wyckoff positions $1b$, $1c$, and $3d$. The allowed magnetic structures for this family are presented in Table 7. The site symmetry of the $3d$ position is 1. As noted above, no ferro- or antiferromagnetic ordering is for this case. The orientation and ordering of magnetic moments for general positions are given in tables [13].

5.3. Group Cm (N 8) family. In this family, Co impurities can occupy Wyckoff positions $2a$ and $4b$. The allowed magnetic structures for this family are presented in table 8 except for atoms at $4b$ position with the site symmetry 1.

In Table 8, the results are given for the Cm group with the standard setting (i.e. with the m_y mirror plane). The results for the equivalent orientations of the Cm subgroups with respect to the parent group $P6_3mc$ (i.e. with m_x and m_{xy} mirror planes) are obtained by the permutation of the corresponding axes.

6. Discussion

In the DMSs, the mean distance between first-neighbour magnetic atoms is generally too large to allow spin-spin interaction to be sufficently strong to align their spins. According to the Dietl model, spin orientation is mediated by carrier spins which align due to the applied magnetic field. Thus, ferro- or antiferromagnetic states of the structure are induced by the magnetic field and magnetization orientation should depend on the field. DMSs with a high symmetry ($P6_3mc$ or $P3m1$) can in some cases allow orientation but only along the growth direction whereas DMSs with a low symmetry (Cm) can in some cases allow orientation either perpendicular to or within the symmetry plane. Knowledge of distribution of magnetic atoms over the cation sites of the lattice would be the key point to determine the magnetic properties of actual structures. Unfortunately, such a knowledge cannot be easily provided by experiments. Information about cohesive energy of various possible distributions would help in determining actual structures but would not be sufficient since in general growth methods do not provide structures at complete thermodynamical equilibrium at the growth temperature. Nevertheless, it seems reasonable to assume that local lattice structures with a high symmetry are less probable that those with a low one. Indeed, the local structures with the $P6_3mc$ symmetry involve a six-fold screw axis parallel to the growth direction that is probably not kept in DMSs since it would induce a rather long-range order in the structure. Besides, the structures with the $P3m1$ symmetry assign a symmetrical role to the three symmetry planes intersecting locally that is certainly a very restricting condition. On the contrary, local structures with the Cm symmetry imply existence of a single symmetry plane and hence seem much more probable. One can also imagine existence of local structures without any symmetry. Concerning the later case, it should be stressed that it does not fit the results for $Zn_{1-x}Co_xO$ structures with a low amount of cobalt ($x = 0.003-0.005$) grown by plasma-assisted MBE. Indeed, it has been experimentally shown [4] that the (x, y) layer plane is an „easy plane" for ferromagnetism. This result suggests strongly that the Co atoms are not distributed at random but, on the contrary, that the local symmetry is Cm since it is the only symmetry that can induce such an orientation of ferromagnetism (the direction of magnetization lies within the symmetry plane, see section 5.3). Note that it would be interesting to measure magnetization with rotating the sample around the growth direction. One can expect an identical effect from the three symmetry planes at the scale of the whole sample hence a three-fold periodic behaviour for magnetization and, may be, even a six-fold one if glide planes remain active.

In any symmetry group antiferromagnetic phase(s) can exist. It is well known that spinel structures as Co_3O_4 or $ZnCo_2O_4$ for example are antiferromagnetic materials. It suggests that DMSs with a high amount of magnetic atoms can present antiferromagnetic properties. Indeed, stoichiometric phases correspond in general to the maximal cohesive energy value for their chemical composition and therefore should be actually achieved during the growth process through phase separation. Note that, even in a model with a random distribution of Co atoms, the percentage of sequences such as Co–O–Co should increase with the amount of cobalt. On the contrary, for a very low amount of cobalt, Lande-factor values calculated for the samples of [4], suggest that magnetic atoms are diluted in the ZnO matrix, keeping the possible existence a priori of ferro- and antiferromagnetic local structures with the Cm symmetry. Since it is the ferromagnetic phase that is actually achieved, one can conclude that the magnetic moments lie within the symmetry plane and that their direction presents a small angle with the layer plane since the magnetization value is much larger within the plane than along the growth direction.

Last, the columnar structure of the samples probably weakens the symmetry properties at least in the layer plane since the columns are parallel to the growth direction. The effect is probably weaker in the samples of [4] since the column diameter is large, i. e., of the order of $1\,\mu$m. In addition, according to the model proposed by Straumal et al. [3], the effect of grain boundaries should also be weaker making the magnetization to arise mainly from intrinsic properties of the ZnO lattice itself and from distribution of magnetic atoms over cation sites.

7. Conclusion

To model the wurtzite-type diluted magnetic semiconductors with decreasing the magnetic impurity atom concentration, we have applied the procedure of constructing the group-subgroup relationship tree starting from the parent wurtzite structure. The derivative structures correspond to various distributions of the magnetic impurities over the cation sublattice sites of the host lattice. The type of magnetic ordering is shown to depend on the symmetry group of the magnetic semiconductor and site symmetry of impurities. Within this procedure, we derived all possible magnetic groups and corresponding magnetic structures for different distributions of the magnetic impurities over the cation sublattice sites of the host lattice. Allowed orientation of the magnetic moments depends on the site symmetry of the impurities.

For the derivative structures with $P6_3mc$ and $P3m1$ symmetry, ferro- and antiferromagnetic ordering is allowed for magnetic moments oriented along the hexagonal c-axis. Ferro- and antiferromagnetic ordering in the plane perpendicular to the hexagonal c-axis can be realized only in the derivative structures with low symmetry Cm. In this case, the magnetic moments can align along any direction in the symmetry plane of the wurtzite structure.

References

[1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand. Science **287**, 1019 (2000).

[2] W. Prellier, A. Fouchet, B. Mercey. J. Phys.: Condens. Matter **15**, R1583 (2003).

[3] B.B. Straumal, A.A. Mazilkin, S.G. Protasova, A.A. Myatiev, P.B. Straumal, G. Schutz, P.A. van Aken, E. Goering, B. Baretzky. Phys. Rev. B **79**, 205 206 (2009).

[4] P. Sati, R. Hayn, R. Kuzian, S. Regnier, S. Schafer, A. Stepanov, C. Morhain, C. Deparis, M. Laugt, M. Goiran, Z. Golacki. Phys. Rev. Lett. **96**, 017 203 (2006).

[5] Y. Liu, J.L. MacManus-Driscoll. Appl. Phys. Lett. **94**, 022 503 (2009).

[6] J.-J. Li, W.-C. Hao, H.-Z. Xu, T.-M. Wang. J. Appl. Phys. **105**, 053 907 (2009).

[7] M. Schumm, M. Koerdel, J.F. Morhange, Z. Golacki, K. Grasza, P. Skupinski, W. Szuszkiewicz, H. Zhou, V. Malik, H. Kalt, C. Klingshirn, J. Geurts. J. Phys.: Conf. Series **92**, 012 149 (2007).

[8] R.Y. Sato-Berru, A. Vasquez-Olmos, A.L. Fernandez-Osorio, S. Sotres-Martinez. J. Raman Spectrosc. **38**, 1073 (2007).

[9] J.B. Wang, H.M. Zhong, Z.F. Li, W. Lu. J. Appl. Phys. **97**, 086 105 (2005).

[10] T. Chanier, I. Opahle, M. Sargolzaei, R. Hayn, M. Lannoo. Phys. Rev. Lett. **100**, 026 405 (2008).

[11] A.V. Shubnikov, N.V. Belov. Colored symmetry. Pergamon Press, Oxford (1964).
[12] A.V. Shubnikov, V.A. Koptsik. Symmetry in Science and Art. Plenum Press, New York (1974).
[13] D.B. Litvin. Acta Crystalogr. Section A: Found. Crystallogr. **57**, 729 (2001); Magnetic Space Group Types: http://www.bk.psu.edu/faculty/litvin/Download.html.
[14] M.I. Aroyo, A. Kirov, C. Capillas, J.M. Perez-Mato, A. Wondratschek. Acta Crystallogr. Section A: Found. Crystallogr. **62**, 115 (2006); www. cryst.ehu.es
[15] M.I. Aroyo, J.M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov, A. Wondratschek. Z. Kristallogr. **221**, 15 (2006).
[16] International tables for crystallography. Vol. A: Space group symmetry. Ed. Th. Hahn. Springer, Dordrecht (2006).
[17] A.P. Cracknell. Progr.Theor.Phys. **33**, 812 (1965).
[18] A.P. Cracknell. Progr.Theor.Phys. **35**, 196 (1966).
[19] A.P. Cracknell. Progr.Theor.Phys. **36**, 648 (1966).
[20] A.P. Cracknell. Progr.Theor.Phys. **38**, 1252 (1967).
[21] H. Megaw. Crystal Structures: a Working Approach. W.B. Saunders, Philadelphia (1973).
[22] H. Bärnighausen. MATCH Commun. Mat. Chem. **9**, 139 (1980).
[23] E. Koch. Acta Crystalogr. Section A: Found. Crystallogr. **40**, 593 (1984).
[24] O. Bock, U. Muller. Acta Crystalogr. Section B: Struct. Science **58**, 594 (2002).
[25] A. Wills. J. Phys. IV France **11**, Pr9-133 (2001).