Symmetry and structure of multiferroic $Ba_2CoGe_2O_7$

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Crystal structure of $Ba_2CoGe_2O_7$ at room temperature (RT) and 90 K has been probed by single-crystal diffraction of x-ray synchrotron radiation. The space group (SG) found at both temperatures is well approximated by $P\text{-}42_1m$, in agreement with expectation for melilite-like compounds. The real structure of $Ba_2CoGe_2O_7$ is more distorted and has a lower symmetry, as follows from observation of a set of superstructure reflections violating 2_1 symmetry. Symmetry analysis based on the observed average-structure SG $P\text{-}42_1m$ revealed few possible candidates for the true structure that imposes different constraints on magnetic and polar properties.

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Multiferroic materials in which more than one order-parameter simultaneously appearing in a single phase have attracted extensive theoretical and experimental efforts. If an electric field controls the magnetism via magnetoelectric coupling, such process is much less dissipative in energy than the current control of magnetism in itinerant ferromagnets; thus multiferroics are interesting for potential use in spintronics and data storage. Ferroelectricity induced by magnetic ordering has been recently reported for a large number of structures[1] but understanding of mechanisms and symmetry requirements of the magnetically induced ferroelectricity is not yet complete.

Coupled electric and magnetic orderings were recently found in $Ba_2CoGe_2O_7$.[2] In this compound spontaneous electric polarization (EP) along the **c** direction of the unit cell occurs at the magnetic transition below 6.7 K in zero external field. The polarization changes the sign and increases nonlinearly if a magnetic field is applied along **c**. Notably, the temperature at which this polarization component appears increases with the field, while the temperature of magnetic phase transition is not that dependent on the magnetic field, as seen from the heat capacity data.[2] The other component of polarization, EPa (along the **a** direction), is enhanced at the magnetic transition temperature, and increases linearly with the field applied along the **c** direction.

On the contrary, in Ref. 3 no EPc is observed when a 5 T magnetic field is applied along **c** at any temperature between 2 and 12 K. However, a magnetic field being applied along [110] direction results in a polarization component EPc that is still observable at 11–12 K, that is, almost twice the temperature of magnetic ordering T_N. In agreement with Ref. 2, polarization along the **a** direction appears at T_N whatever the field that has been applied along **c**.

This unusual behavior, as well as a smooth rotation of the EP with the magnetic field rather than a sudden flip, is quite unique and cannot be explained by well-accepted spin-current model[4] or by an exchange striction mechanism[5] conventional for other multiferroics. A spin-dependent hybridization mechanism based on the metal-ligand *p-d* hybridization has been proposed in Ref. 3. Detailed theoretical investigation shows that the hybridization mechanism reproduces the experimental results from Ref. 3, as reported recently in Ref. 6. $Ba_2CoGe_2O_7$ is considered there as a prototype of the entire class of materials where an interplay between magnetism and ferroelectricity is based on the spin-dependent *p-d* hybridization. Alternatively, the theory proposed in Ref. 7 attributes unusual magnetoelectric behavior of the title compound to a spontaneous toroidal moment. Very recently, a theoretical analysis based solely on symmetry arguments has shown that the main features of the magnetoelectric behavior of $Ba_2CoGe_2O_7$ can be "predicted and understood without appealing to any particular atomic mechanism."[8]

Another interesting experimental finding in $Ba_2CoGe_2O_7$ is a giant directional dichroism of terahertz light in resonance with magnetic excitations.[9] A theory of magnetoelectric resonance, nonreciprocal directional dichroism, and a description of the electromagnon excitations in $Ba_2CoGe_2O_7$ are proposed in Ref. 10.

From the above short and uncompleted survey it is clear that symmetry information is essential to unravel the complex physics underlying magnetoelectric behavior of the title compound. However, a close inspection of the available information about the $Ba_2CoGe_2O_7$ compound reveals that no detailed structural study of $Ba_2CoGe_2O_7$ has been performed up to now. The only available structural information is given in Ref. 11 and is limited to the lattice parameters only, $a = b = 8.3836(3)$ Å and $c = 5.5510(3)$ Å, determined at room temperature with a laboratory x-ray powder diffractometer. On the basis of the observed powder pattern it has also been suggested that $Ba_2CoGe_2O_7$ is isostructural with melilite [$NaCaAlSi_2O_7$, $P\text{-}42_1m$ symmetry SG No. 113 (Ref. 12)]. Due to the lack of structural information on $Ba_2CoGe_2O_7$ in a number of studies (see Refs. 3 and 6 as examples), the mean structures of Co-åkermanite, $Ca_2CoSi_2O_7$ have been thought to be isostructural to that of $Ba_2CoGe_2O_7$. In order to perform density functional theory calculations and model cluster Hamiltonian analysis in Ref. 6, the Ca ions were

simply substituted by Ba, and Si by Ge, in the structure of $Ca_2CoSi_2O_7$ published in 1993.[13] However, a number of more recent and more detailed studies on $Ca_2CoSi_2O_7$ (Refs. 14 and 15) question the structure proposed earlier and show that $Ca_2CoSi_2O_7$ at low temperature has a modulated commensurate phase described as a twinned orthorhombic structure with SG $P2_12_12$. In this superstructure CoO_4 tetrahedra are distorted and rotated to different degrees. The deformation of the basic crystal lattice and the corresponding symmetry changes were related to a misfit between the layers formed by CoO_4 and Si_2O_7 groups and interlayer cations (Ca).[15,16] Taking into account that the atomic radius for Ba is much larger than for Ca one should expect $Ba_2CoGe_2O_7$ not to be isostructural to $Ca_2CoSi_2O_7$, but rather be deformed and therefore have a different physical response, for example, within the Co-O hybridization model proposed in Ref. 3 and based on the geometrical measures of the structural arrangement. In terms of symmetry-constrained properties such deformations could imply a change of the space group. Even if no obvious symmetry changes have been noted, an isostructural deformation still may strongly affect physical properties; see the $(Ca_{1-x}Sr_x)_2$ $CoSi_2O_7$ mixed system as an example[17] where EP observed in the undoped $Ca_2CoSi_2O_7$ vanishes by adding Sr just at $x = 0.2$.

In order to fill the gap of structural information on $Ba_2CoGe_2O_7$ and provide reliable data for further experimental and theoretic research, we have collected single-crystal diffraction data on $Ba_2CoGe_2O_7$ at RT and 90 K with the help of synchrotron radiation.

A high-quality single crystal of $Ba_2CoGe_2O_7$ (6 mm in diameter and 15 mm in length) was grown using the floating zone method similar to those used in the previous studies.[3,9] A small needle-shaped crystal of about 60 × 150 μm was selected for the diffraction experiment.

Single-crystal diffraction measurements were performed at the KUMA6 diffractometer at BM01A station (Swiss-Norwegian Beam Lines, ESRF, Grenoble).[18] The data were collected at RT with a wavelength $\lambda = 0.698$ Å calibrated with a LaB6 NIST standard powder. An Oxford Cryostream 700+ cold nitrogen blower was used for the data collection at 90 K. The experimental frames were processed with the CRYSALIS software.[19] The same software was used for scaling, Lorentz, polarization, and absorption corrections. The crystal structure was refined using JANA2006.[20] The Becker-Coppens type 1 Gaussian isotropic extinction correction has been applied. The parameters for the quality of the data refinement are shown in Table I. Full results of the refinements including detailed structural parameters are deposited as crystallographic information files (CIF).[21]

TABLE I. Single-crystal diffraction experimental and refinement details for basic melilite structural model.

Parameters	293(2) K	90(1) K
a (Å)	8.3845(1)	8.3802(1),
c (Å)	5.5497(2)	5.5435(1)
V (Å^3)	390.14(2)	389.31(2)
No. of measured reflections	8239	12813
No. of independent reflections	623	628
No. of observed reflections	620	626
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	3.53	6.16
θ_{max} (°)	29.4	27.35
Wavelength (Å)	0.6980	0.6525
Refinement on F^2		
$R[F^2 2\sigma(F^2)]$,% $wR(F^2)$,% S	1.35, 4.07, 0.97	1.30, 3.90, 0.99
No. of refined parameters	36	36

Initially, the measured intensities of the Bragg reflections have been refined on the base of the melilite-type structure, proposed in Ref. 11, with tetragonal SG P-42$_1m$ (No. 113).[12] The results show that this model describes the structure with rather high accuracy for both temperatures. The melilite structure is composed of tetrahedral layers built up by CoO_4 and Ge_2O_7 groups and separated by intermediate layers of Ba cations as shown in Fig. 1.

Until now most numerical calculations for the title compound have been done without experimental information on the crystal structure but assuming a similarity with $Ca_2CoSi_2O_7$. Here we show the fractional atomic coordinates, and isotropic and anisotropic atomic displacement parameters (ADPs) of the crystal structure of $Ba_2CoGe_2O_7$ determined in P-42$_1m$ SG group at RT (Tables II and III); these data could serve as necessary experimental input for theoretical calculations.

It is well known that many of the melilite-like compounds show incommensurate or commensurate modulated lock-in phases at low temperatures.[22] A close inspection of our data for $Ba_2CoGe_2O_7$ revealed the following: (a) No incommensurate reflections have been seen for the studied sample at both temperatures; (b) commensurate superstructure reflections of type (h,0,0), (0,k,0) with odd h and k, violating the systematic extinctions for the 2_1 symmetry element have been observed

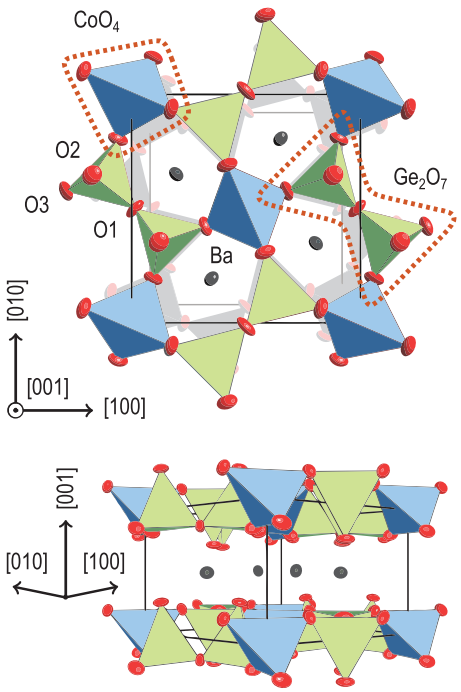

FIG. 1. (Color online) The average structure of $Ba_2CoGe_2O_7$ at RT. Positions of O and Ba atoms represented by ADP ellipsoids from Table III; top: projection onto the ab plane, bottom: perspective view.

TABLE II. The atomic position parameters of the average structure at RT (P-42$_1m$).

Ion	Wyckoff Positions	x	Y	z
Ba	4e	0.33477(2)	0.16523(2)	0.49262(4)
Co	2b	0	0	0
Ge	4e	0.14051(3)	0.35949(3)	0.03963(7)
O1	2c	0	0.5	0.1588(8)
O2	4e	0.1384(2)	0.3616(2)	0.7284(5)
O3	8f	0.0799(2)	0.1843(2)	0.1876(3)

(Fig. 2). These reflections are very weak yet observable up to $h, k = 13$ both at 90 K and RT. These observations allow us to conclude that the P-42$_1m$ structure indeed is only an approximate one, and the true symmetry of $Ba_2CoGe_2O_7$ should be lower.

Such reflections forbidden in P-42$_1m$ have been found already for other melilite-like compounds, e.g., $Ca_2CoSi_2O_7$.[14,16] In Ref. 16 a large number of the superstructure reflections was observed at 130 K and the P-4 tetragonal structure has been proposed being twinned with respect to the diagonal mirror plane $m_x y$. In Ref. 14 only two reflections, (9,0,0) and (27,0,0), are reported at 297 K. They were attributed to the multiple diffraction effect and were not considered for further structure determination the final structure model proposed in Ref. 14 is a twinned orthorhombic structure of $P2_12_12$ symmetry.

The large number of superstructure reflections we observe may serve as an argument that these Bragg reflections are not induced by multiple-scattering effects. This conclusion has been further confirmed in a separate experiment where one of these reflections, namely (–1,0,0) (see Fig. 2, right), was measured at different orientations corresponding to different Ψ angles. Abrupt changes in the integral intensity are expected for such scans (so-called Ψ scans) if multiple scattering took place. No trace of such response has been observed for our tests confirming structural origin of the observed reflections. We check also a number of other samples originating from the same large crystal and observe that the superstructure reflections can be found in all of them; however, their relative intensity is somewhat sample dependent. The latter observation suggests that the intensity of superstructure reflections could be affected by a twinning or domain structure seen before for the other melilites.[22]

The superstructure reflections appear at the **Q** vectors in the reciprocal space where the magnetic intensity in neutron

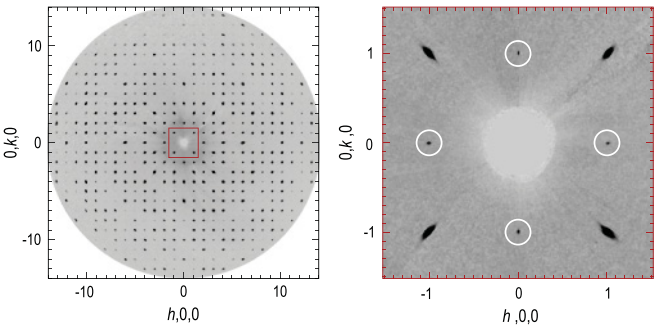

FIG. 2. (Color online) The $hk0$ layer calculated from two-dimensional detector images measured at 90 K; left: whole data set, right: magnified selected part with superstructure reflections noted by circles.

diffraction occurs below $T_N = 6.7$ K.[23] Moreover, a clearly visible forbidden peak (100) at 10 K, when no magnetic order is assumed, is shown in the inset of Fig. 1 in Ref. 23 and is attributed to multiple scattering. Our data indicate a possibility that this intensity could also have a structural origin; the structural contribution could be distinguished from multiple-scattering effects with help of Ψ scans. Careful study of nuclear and magnetic contributions to the total intensity of the forbidden reflections in the P-42$_1m$ SG should be therefore considered in the future investigations of the magnetic structure.

We have tried to account for the superstructure reflections in the structure solution and refinement using various low-symmetry models, but these efforts gave no improvement comparing with the high-symmetry approximant. This is generally expected as superstructure Bragg reflections have relatively low intensity, they are relatively low in number, and their intensities are corrupted by an unresolved twinning pattern. Resolution of possible twinning could be done in a complimentary crystallographic study with higher angular resolution. Here we propose a symmetry analysis enumerating possible structures compatible with the observed extinctions. Since no additional reflections indicating change of translational symmetry have been seen, we limit our consideration to the Γ point of the Brillouin zone. Sorting out irreducible representations (IRs in Table IV) at the Γ point, one readily finds[24] that only six SGs with lower symmetry are expected for the parent P-42$_1m$ symmetry; they are listed in Table IV. Only those allowing for observed superstructure reflections have to be considered, thus the number of the possible structures with the higher-symmetry SGs reduces to two: tetragonal P-4 (No. 81)[12] and orthorhombic $Cmm2$ (No. 35).[12] As mentioned

TABLE III. The ADP of the average structure at RT (P-42$_1m$).

Ion	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}/U_{eqv}
Ba	0.0131(1)	U_{11}	0.0123(2)	0.0027(1)	−0.0008(1)	$-U_{13}$	0.0128(1)
Co	0.0109(2)	U_{11}	0.0126(6)	0	0	0	0.0114(2)
Ge	0.0104(1)	U_{11}	0.0096(3)	0.0005(2)	−0.0002(1)	$-U_{13}$	0.0101(1)
O1	0.0188(2)	U_{11}	0.012(3)	0.008(2)	0	0	0.017(1)
O2	0.0201(1)	U_{11}	0.010(2)	0.004(2)	0.001(1)	$-U_{13}$	0.017(1)
O3	0.0219(2)	0.0129(1)	0.015(2)	−0.005(1)	−0.004(1)	0	0.016(1)

TABLE IV. Isotropy subgroups for the $P\text{-}42_1m$ SG (No. 113).

IR	SG	No	$(h,0,0)/(0,k,0)$, $h\neq 2n$, $k\neq 2n$
Γ2	$P2_12_12$	18	Not allowed
Γ3	$Cmm2$	35	Allowed
Γ4	P-4	81	Allowed
Γ5	$P2_1$	4	Not allowed
	Cm	8	Allowed
	$P1$	1	Allowed

above the low intensity of superstructure reflections does not permit a unique choice between these two solutions using structural refinement. We therefore have to attract restrains that follow from the other (even macroscopic) measurements.

It is well worth it to stress that, due to the small diffraction intensity of the superstructure reflections, corresponding structural deformation is also expected to be small and all the conclusions obtained for the high-symmetry approximant, $P\text{-}42_1m$, are largely valid.[8] Neutron diffraction has evidenced that magnetic structure is aniferromagnetic with two Co ions having their spins aligned in the ab plane.[23] Symmetry analysis results in a set of Shubnikov groups listed in Ref. 8 that would correspond to such antiferromagnetism, allowing also for a weak ferromagnetism. Notably, for spins aligned along [110], the magnetic space group is $Cm'm2'$ and that is just one of our solutions complimented by the time reversal. Also, at variance with P-4, $Cmm2$ is a polar space group, and corresponding yet unsolved crystal structure should be compatible with the polarization observed in $Ba_2CoGe_2O_7$ under magnetic field well above the temperature of antiferromagnetic ordering (experimental observation not addressed yet in previously proposed microscopic models based on $P\text{-}42_1m$ symmetry). However, the final choice of the structural solution has to be done on the basis of more detailed crystallographic study aiming in particular to solve the twinning problem.

To summarize, present single-crystal diffraction study of $Ba_2CoGe_2O_7$ at RT and 90 K has revealed the following. First, melilite tetragonal crystal structure ($P\text{-}42_1m$), widely accepted for the title compound, is indeed a rather good approximation. We also report here the structural parameters characteristic for this average structure; the reported structural parameters may serve as a solid experimental basis to be compared with theoretical calculations. In contrast to $Ca_2CoSi_2O_7$, often used in the theoretical models as being isostructural to $Ba_2CoGe_2O_7$, no incommensurate or modulated structures have been observed in the studied samples.

Second, we have observed a set of superstructure reflections commensurate with the tetragonal cell and violating the 2_1 axis. Enumeration of the possible subgroups led us to the conclusion that the real structure has lower than $P\text{-}42_1m$ symmetry and most probably corresponds to the $Cmm2$ space group. The twinning and domain formation are also possible, in agreement with the previous reports on melilite-type compounds; this issue should be addressed in future structural studies. In these circumstances more detailed structural investigation (also regarding magnetic structure) on $Ba_2CoGe_2O_7$ at low temperatures (close to 6.7 K) should be performed taking into account the results presented here.

We would like to conclude on observed symmetry and possible mechanisms of multiferroic response. As has been recently shown, careful symmetry consideration could help rationalize numerous experimental observations without any microscopic model.[8] Symmetry is just self-consistent and a very condensed representation of many experimental data; correspondingly it does not decide whether a certain microscopic model is right or wrong, but rather defines constrains bracketing a class of potentially correct models.

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[1] T. Kimura *et al.*, Nature **426**, 55 (2003); Y. Tokura, Science **312**, 1481 (2006); S.-W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).
[2] H. T. Yi *et al.*, Appl. Phys. Lett. **92**, 212904 (2008).
[3] H. Murakawa *et al.*, Phys. Rev. Lett. **105**, 137202 (2010).
[4] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).
[5] T. Arima *et al.*, Phys. Rev. Lett. **96**, 097202 (2006).
[6] K. Yamauchi, P. Barone, and S. Picozzi, Phys. Rev. B **84**, 165137 (2011).
[7] P. Toledano, D. D Khalyavin, and L. C. Chapon, Phys. Rev. B **84**, 094421 (2011).
[8] J. M. Perez-Mato and J. L. Ribeiro, Acta Crystallogr. A **67**, 264 (2011).
[9] I. Kézsmárki *et al.*, Phys. Rev. Lett. **106**, 57403 (2011).
[10] S. Miyahara and N. Furukawa, J. Phys. Soc. Jpn. **80**, 073708 (2011).
[11] H. F. McMurdie *et al.*, Powder Diffr. **1**, 64 (1986).
[12] *International Tables for Crystallography*, edited by T. Hahn (Springer, Dordrecht, 2006), Vol. A.
[13] K. Hagiya and M. Ohmasa, Acta Crystallogr. B **49**, 172 (1993).
[14] K. Hagiya *et al.*, Acta Crystallogr. B **57**, 271 (2001).
[15] Z. H. Jia, A. K. Schaper, W. Massa, W. Treutmann, and H. Rager, Acta Crystallogr. B **62**, 547 (2006).
[16] M. Riester, H. Böhm, and V. Petriček, Z. Kristallogr. **215**, 102 (2000).
[17] M. Akaki *et al.*, J. Phys.: Conf. Ser. **200**, 012003 (2010).
[18] Instrument web: [http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM01/bm01-a/crystal.htm].
[19] CRYSALIS software version171.34.31, Agilent Technology, 2010.
[20] V. Petriček, M. Dusek, and L. Palatinus (Institute of Physics, Praha, Czech Republic, 2006).
[21] ICSD, CSD-No. 423350, 423351; [www.fiz-karlsruhe.de].
[22] Z. H. Jia, Ph.D. thesis, University of Marburg, Germany, 2005.
[23] A. Zheludev *et al.*, Phys. Rev. B **68**, 024428 (2003).
[24] H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1989), pp. 1–120.