Apparently Complex High-Pressure Phase of Gallium as a Simple Modulated Structure

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The phase of gallium GaII, with symmetry $C222_1$ and 104 atoms per unit cell, has been recently reported as an example of *structural complexity* under high pressure. It is shown here that this phase is a simple modulated distortion of an average structure of $Fddd$ symmetry with all atoms structurally equivalent. The modulation can be described with only 4 parameters and satisfies symmetry properties described by a centrosymmetric superspace group. The structural distortion is dominated by a frozen transversal mode associated with a single irreducible representation of $Fddd$, with a wave vector on the line Q, at an edge of the Brillouin zone. The average structure can be related with an hcp configuration through simple sliding of hcp layers, reminiscent of the hcp-bcc Bürgers mechanism.

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High-pressure diffraction experiments have recently revealed a new class of apparently complex phases in rubidium (RbIII) [1], cesium (CsIII) [2], and gallium (GaII) [3]. They all display the same $C222_1$ symmetry and have, respectively, 52, 84, and 104 atoms in their conventional orthorhombic unit cell. The structures have been described as sequences of 8- and 10-atom xy layers stacked along the c axis [1–3]. Since the alkali elements Rb and Cs and the group-III element Ga have very different electronic configurations and valence, a general Hume-Rothery-type mechanism has been proposed as a unifying physical explanation for these phases with the bcc as reference structure [3,4]. On the other hand, a theoretical analysis of the structural mechanisms taking place at the high-pressure phase transitions of alkali metals [5] have shown that a better understanding of the displacive mechanism relating RbIII and CsIII to their neighboring structures, could be obtained by considering these structures as built of *four* buckled layers stacked along the b axis, each layer containing 13 atoms for RbIII, and 21 atoms for CsIII. In the present work we deepen on this alternative description for the particular case of GaII. We show that it yields a simple interpretation of the reported structure in terms of a displacive quasisinusoidal distortion of a simple average parent orthorhombic structure with a single symmetry-independent atom. The symmetry analysis of this modulation suggests that phase GaII could be related by a Peierls-like mechanism with the identified average parent structure.

The 104 atoms of the unit cell of GaII distribute into four layers, of 26 atoms each, around $y = 0$, $1/4$, $1/2$, and $3/4$. The two layers at $y = 1/2$ and $3/4$ are trivially related with the first two by the C centring. On the other hand, no space group operation relates the two atomic layers at $y = 0$ (layer 1) and $1/4$ (layer 2). This means that the rotational symmetry in the structure only connects atomic positions within the same layer. The similarity of the two layers is however remarkable. The projections on the plane xz of the two layers are shown in Fig. 1. In each layer two rows of 13 atoms can be distinguished with an approximate periodicity of $c/13$ along the c axis and a strong modulation along the a axis. It is immediate to obtain for each row of atoms

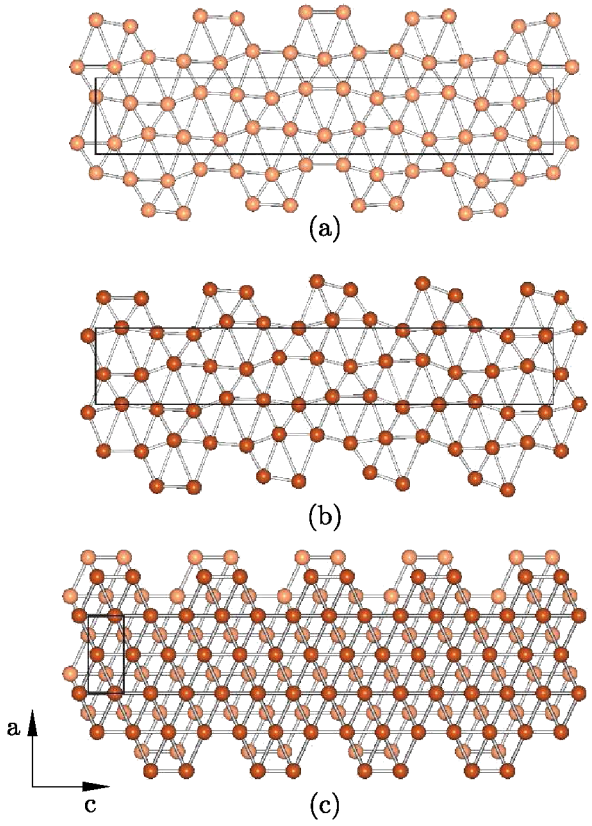

FIG. 1 (color online). xz projection of layer 1 (a), layer 2 (b), and both layers for the average structure (c).

an average atomic position within a small unit cell having the same a and b parameters and $c_{\text{aver}} = c/13$. In the following this average unit cell is the reference basis used, if nothing on the contrary is indicated. The eight average atomic positions corresponding to eight 13-atom rows present in the $C222_1$ unit cell are (3/4, 0, 0), (1/4, 0, 1/2), (0, 1/4, 3/4), (1/2, 1/4, 1/4), plus those related by the C centring. These positions describe a structure with $Fddd$ symmetry in a nonconventional setting having the inversion center at (1/8, 1/8, 1/8) and the y and $-x$ axes interchanged. Its generators (besides the F centring translations) are $\{2x|0,0,0\}$, $\{2y|\frac{1}{2},0,0\}$, and $\{\bar{1}|\frac{1}{4},\frac{1}{4},\frac{1}{4}\}$. A single Wyckoff position $8a$ is occupied, all atoms being structurally equivalent. The average structure can be described as a set of two identical pseudohexagonal monatomic layers shifted by (1/4, 1/4, 3/4) plus the C translated ones. Taking this average structure as a reference, the atomic displacements in each of the 13 basic cells contained in the actual $C222_1$ structure can be described by a modulation function with a single modulation wave vector along the z axis.

The description of modulated structures (both commensurate and incommensurate) and their symmetry is the subject of the so-called superspace formalism (see [6] and references therein). For the purpose of this communication, we will limit ourselves to the most basic concepts of this approach. Once an average structure has been defined, the displacement, $\vec{u}_j = \vec{r}_j - \vec{r}_j^{\,o}$ of any atom at a position $\vec{r}_j$ with respect to its average reference $\vec{r}_j^{\,o} = \vec{r}_j^{\,b} + \vec{l}$ ($\vec{l}$ being a vector of the average lattice and $\vec{r}_j^{\,b}$ the average position within a unit cell) can be interpreted as the value of a vector function $\vec{u}_j(x_4)$, with period 1 associated to atom j of the average structure, particularized at the point $x_4 = \vec{q}.\vec{r}_j^{\,o}$ (mod. 1), $\vec{q}$ being the modulation wave vector. The parameter x_4 considered as a continuous variable is the so-called internal coordinate corresponding to the fourth dimension in the superspace formalism. In general, for a commensurate structure, as the case here, only a finite set of values of x_4 are to be considered. A modulated description makes then sense if the resulting extrapolated continuous modulation functions are smooth and simple, indicating some physical correlations of the atomic positions not described by the conventional space group. The modulation wave vector, when referred to the reciprocal cell of the average structure, must be of the form $\vec{q} = \frac{n}{13}\vec{c}^{\,*}_{\text{aver}}$ with n an integer. If a modulated description is reasonable and has a physical basis, the modulation will be dominated by the first harmonics of a particular choice of $\vec{q}$. For $\vec{q} = \frac{9}{13}\vec{c}^{\,*}_{\text{aver}}$ the modulation functions become indeed not only very simple, but have simple interrelations, as shown in Fig. 2. The atomic displacements along x of the row of 13 atoms in layer 1 associated with the average position (3/4, 0, 0) follow a simple pattern fitted with a function only containing a first and a third harmonic limited to cosine functions. The symmetry of the function with respect to $x = 0$ and 1/2 is forced by the $C222_1$ symmetry, but the simple smooth modulation describing the seven crystallographically independent points between $x_4 = 0$ and 1/2 (black points) is a signature of the relevance of a single modulation wave vector. Furthermore, only odd harmonics are significant. Similarly, the modulation function for the y displacements can be described by a first harmonic of sinus type, while the z modulation by a second harmonic, also of sinus type. Figure 2 also shows that the row of atoms in layer 2 with average position (1/2, 1/4, 1/4) and indicated by gray points follows exactly the same modulation functions, despite being space group independent from those in layer 1. It should be noted that consecutive points along x_4 in the previous Figures do not correspond to consecutive atoms along z in direct space. Hence, the simple underlying sinusoidal modulations are not evident in real space. The apparent larger point dispersion in Fig. 2(c) is due to the different scale of the figure. The displacement amplitudes

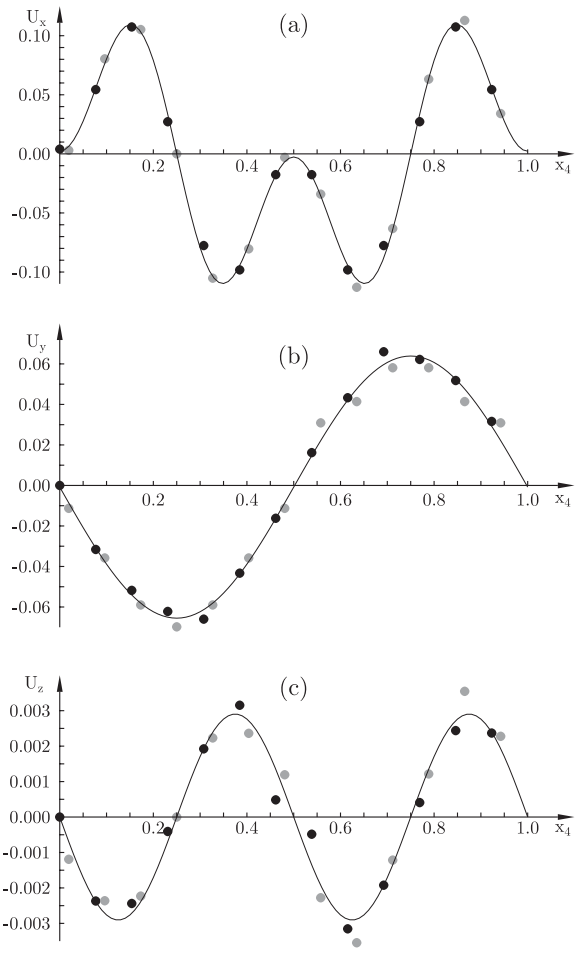

FIG. 2. Atomic displacements in relative units ($a = 5.976$ Å, $b = 8.576$ Å, $c = 35.758$ Å) along the x (a), y (b), and z (c) axis for the row of atoms at layer 1 with $\langle x\rangle = 3/4$ (black points) and the row of atoms in layer 2 with $\langle x\rangle = 1/2$ (gray points), as a function of the phase x_4, with $\vec{q} = \frac{9}{13}\vec{c}^{\,*}_{\text{aver}}$. The fitted functions are of the form: $u_x(x_4) = A\cos 2\pi x_4 + B\cos 6\pi x_4$, $u_y(x_4) = A\sin 2\pi x_4$, and $u_z(x_4) = A\sin 4\pi x_4$.

along z are about 5 times smaller than in the other two directions. For the second rows of atoms in both layers 1 and 2, a similar set of modulation functions can be obtained. As these atoms are related with those considered above by the $C222_1$ operations, they do not contain any additional independent structural parameter and their modulation functions are related with those described above. The set of the eight atomic modulation functions constructed in the way described above constitutes the structural modulation which relates the $Fddd$ average structure with the experimental 104-atom $C222_1$ structure. The symmetry constraints on the observed atomic modulations and the relations connecting them are uniquely described by a superspace group [6]. This superspace group can be labeled as $Fddd(00\gamma)0s0$ with $\gamma = 9/13$; its generators are listed in Table I. It corresponds to N. 70.2. in the list of [6], given here in a nonconventional setting. The reported $C222_1$ structure could also be described with the same modulation functions within lower superspace symmetries. However, in that case, the clear identity between the atomic modulations in layers 1 and 2 and the limitation of the x-component modulation to odd Fourier terms, would remain without any explanation.

The use of the superspace formalism in the case of commensurate modulated structures is nowadays a widespread technique and has demonstrated to be extremely efficient for interpreting all kind of superstructures [6–12]. According to the discussion above, the structure of GaII can be described with only 4 structural parameters, to be compared with the 38 parameters used in Ref. [3]. To our knowledge, this is one of the most extreme examples of the power of the superspace approach for describing a long period commensurate structure. The 3D conventional space group realized in a commensurate modulated structure depends on the value of the wave vector and on the global phase of the modulation [6,7]. The possible 3D space groups resulting from the superspace group $Fddd(00\gamma)0s0$ are listed in Table I. According to this table, the system would have a centrosymmetric space group $C112_1/d$ ($P2_1/c$ in conventional setting), just by shifting the modulation phase along x_4 a value of $1/104$. It is well known that long period commensurate modulated structures with very few harmonics in the modulation have diffraction patterns very weakly dependent on the modulation global phase [7], and therefore any of the space groups described by the same superspace group can be equally efficient for describing the experimental diffraction pattern. In other words, even if apparently commensurate, the experimental data can be equally well fitted for any value of the global phase of the modulation, and in practice the system can be considered incommensurate, with a "phason" degree of freedom proper of incommensurate structures [6,7]. In such situations the assignment of a 3D conventional space group becomes ambiguous. We could not have access to the experimental diffraction data set of [3], so we could not check directly if this is the case in GaII. We could, however, confirm its plausibility using an artificial dataset of intensities calculated from the published $C222_1$ structural model. The number of reflections and the limit of the modulus of their diffraction vectors were chosen in accordance with the experimental details of [3]. Using the program JANA [11] the fits of this data set with a global phase $t = 0$ (symmetry $C222_1$) and $t = 1/104$ (symmetry $C112_1/d$) were both excellent with equal agreement factors. Furthermore, even making a refinement in the "incommensurate mode", which means to use a structure factor formula proper of an incommensurate modulation vector, the agreement factor did not change significantly. This test suggests that GaII may be in practice an incommensurate modulated structure with a modulation vector approximately $(0, 0, 9/13)$ but no clear lock-in into this commensurate value.

The above description of GaII lets emerge a hidden simplicity of the underlying physics, quite different from the mechanism proposed previously [3,4], where the bcc structure was used as reference. GaII can be considered the result of the stabilization of a $Fddd$ eight-atom structure through the additional freezing of a distorting mode of transversal character with wave vector $\vec{q} = (0, 0, 9/13)$ at the symmetry line Λ (out of the first Brillouin zone). An equivalent wave vector is $(1, 1, 4/13)$, lying along the symmetry line Q on a Brillouin zone edge [13,14]. The observed superspace group defines the transformation properties of this mode and they correspond to a single irreducible representation of $Fddd$, namely Q_3 in the notation of [15]. This frozen primary mode includes similar amplitudes for the x and y components but $\pi/2$ shifted, so that a helicoidal distortion along z results. A strong second mode, polarized along x, with wave vector $3\vec{q}$ and the same symmetry, significantly corrects that primary distortion. A remarkable feature of the transversal modulation is its large amplitude, with values of the order of 0.5 Å. The quasisinusoidal character of the modulation despite such large amplitudes suggests that the stabiliza-

TABLE I. List of generators of the $Fddd(00\gamma)0s0$ superspace group and resulting 3D groups for rational $\vec{q} = \frac{r}{s}\vec{c}^*_{\text{aver}}$ modulation wave vectors and t global phase.

Generators:	$\{m_x\|\frac{1}{4},\frac{1}{4},\frac{1}{4},0\}$	$\{m_y\|\frac{1}{4},\frac{1}{4},\frac{3}{4},\frac{1}{2}\}$	$\{m_z\|\frac{1}{4},\frac{1}{4},\frac{3}{4},\frac{1}{2}\}$
$r = 4N$	$t = 0(\text{mod.}\frac{1}{2s})$ $F2/d11$	$t = \frac{1}{4}(\text{mod.}\frac{1}{2s})$ $Fd2d$	$t =$ arbitrary $Fd11$
$r = 4N + 2$	$t = 0(\text{mod.}\frac{1}{2s})$ $F2dd$	$t = \frac{1}{4}(\text{mod.}\frac{1}{2s})$ $F12/d1$	$t =$ arbitrary $F1d1$
$r =$ odd	$t = 0(\text{mod.}\frac{1}{4s})$ $C222_1$	$t = \frac{1}{8s}(\text{mod.}\frac{1}{4s})$ $C112_1/d$	$t =$ arbitrary $C112_1$

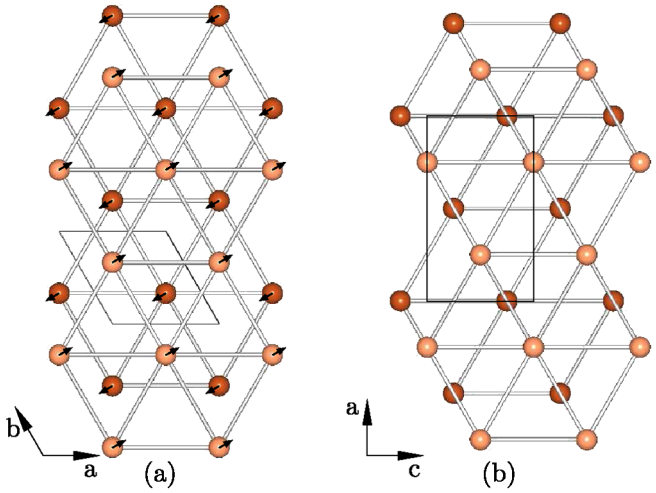

FIG. 3 (color online). (a) Scheme of two consecutive hexagonal layers of the hcp structure, indicating the sliding direction which yields the *Fddd* average structure of GaII. (b) Scheme of the configuration observed for the first two layers of the *Fddd* average structure of GaII, idealized with the hexagonal metrics.

tion of the distortion is achieved through some Peierls-like mechanism and Fermi surface nesting properties.

It is also interesting that the average *Fddd* structure of GaII [see Fig. 1(c)] can be related with the hcp structure by means of a simple sliding of the hcp layers as in the so-called Bürger's mechanism for the hcp-bcc transformation. The direction of the sliding is however different and involves a set of four consecutive layers. Pairs of consecutive layers have relative shifts given by $(1/6, 1/12, 0)_{\mathrm{hcp}}$, while each of these pairs of layers is shifted with respect to its consecutive one by $(1/2, 0, 0)_{\mathrm{hcp}}$. Figure 3 shows how the relative sliding of two hcp consecutive layers along the direction $(2, 1, 0)_{\mathrm{hcp}}$ produces the configuration of the *Fddd* average structure. The same *Fddd* configuration detected here for GaII as average structure, has also been observed, but as exact symmetry, in some specific elements, namely, Pu [16], Am [17] and Cm [18], where the layers are also pseudohexagonal.

Although having the same orthorhombic space group, the structure of GaII is quite different from those reported for CsIII [1] and RbIII [2]. These two phases have also a large number of atoms per conventional unit cell (84 and 52, respectively), and they can also be divided into 4 layers stacked along the y axis [5]. But their average y coordinates are 1/8, 3/8, 5/8 and 7/8. This means a rather different situation, with the two layers being symmetry related within the space group $C222_1$, in contrast with the case of GaII. Indeed, phases CsIII and RbIII can also be interpreted as modulated structures, but of composite character. Layers at $y = 1/8$ and 3/8 form two subsystems with different average structures that modulate each other. The two subsystems are monoclinic with monoatomic lattices and are related by symmetry operations of an orthorhombic superspace group. The modulations are also in this case smooth, simple, and describable by a few parameters. Their amplitudes are much smaller than in GaII. Phases CsIII and RbIII can be considered very peculiar examples of commensurate composites with symmetry interrelated subsystems. A detailed study of these two phases from this perspective will be presented elsewhere. In conclusion, the large unit cell phases GaII, RbIII, and CsIII are far from being examples of *structural complexity* in the sense initially assumed.

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[1] R. J. Nelmes, M. I. McMahon, J. S. Loveday, and S. Rekhi, Phys. Rev. Lett. **88**, 155503 (2002).
[2] M. I. McMahon, R. J. Nelmes, and S. Rekhi, Phys. Rev. Lett. **87**, 255502 (2001).
[3] O. Degtyareva, M. I. McMahon, D. R. Allan, and R. J. Nelmes, Phys. Rev. Lett. **93**, 205502 (2004).
[4] G. J. Ackland and I. R. Macleod, New J. Phys. **6**, 138 (2004).
[5] H. Katzke and P. Tolédano, Phys. Rev. B **71**, 184101 (2005).
[6] T. Janssen, A. Janner, A. Looijenga-Vos, and P. M. de Wolf, in *International Tables for Crystallography C*, edited by A. J. C. Wilson (Kluwer Academic, Dordrecht, 1992), p. 797.
[7] J. M. Perez-Mato, in *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. Perez-Mato, F. J. Zúñiga, and G. Madariaga (World Scientific, Singapore, 1992), p. 117.
[8] F. Parisi, Acta Crystallogr. Sect. A **50**, 574 (1994).
[9] S. van Smaalen, Crystallography Reviews **4**, 79 (1995).
[10] K. E. Stitzer, J. Darriet, and H. C. zur Loye, Curr. Opin. Solid State Mater. Sci. **5**, 535 (2001).
[11] V. Petricek and M. Dusek, *JANA 2000* (Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, 2000).
[12] V. Petricek and M. Dusek, Z. Kristallogr. **219**, 692 (2004).
[13] M. I. Aroyo, A. Kirov, C. Capillas, J. M. Perez-Mato, and H. Wondratschek, Acta Crystallogr. Sect. A **62**, 115 (2006).
[14] Bilbao Crystall. Server: http://www.cryst.ehu.es.
[15] H. T. Stokes and D. M. Hatch, ISOTROPY, stokes.byu.edu/isotropy.html (2002).
[16] W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr. **8**, 431 (1955).
[17] S. Heathman, R. G. Haire, T. le Bihan, A. Lindbaum, K. Litfin, Y. Méresse, and H. Libotte, Phys. Rev. Lett. **85**, 2961 (2000).
[18] S. Heathman, R. G. Haire, T. le Bihan, A. Lindbaum, M. Idiri, P. Normile, S. Li, R. Ahuja, B. Johansson, and G. H. Lander, Science **309**, 110 (2005).