Structure of the two-dimensional incommensurate charge-density wave in $(\text{PO}_2)_4(\text{WO}_3)_8$ at 20 K

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The incommensurate charge-density waves (CDW's) in the $m=4$ phosphate bronze $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ have been studied by synchrotron-radiation x-ray scattering. The CDW is found to correspond to a $2-q$ state for all temperatures below the first phase transition at $T_{c1}=80$ K. The second phase transition at $T_{c2}=52$ K is found to involve the development of mixed second-order satellites within the primary CDW. The incommensurately modulated structure has been determined at $T=20$ K. The structure remains orthorhombic down to $T=20$ K. At 20 K the lattice parameters are $a=5.294(1)$ Å, $b=6.591(2)$ Å, and $c=17.415(16)$ Å. The two-dimensional CDW is characterized by the modulation wave vectors $\vec{q}^1=[0.330(2),0.292(2),0.000(2)]$ and $\vec{q}^2=(-0.330,0.292,0)$. The $(3+2)D$ superspace group was found as $P2_12_12_1(\alpha,\beta,0)(-\alpha,\beta,0)$. The primary CDW comprises the satellite reflections $(hklm_1m_2)$ with (m_1m_2) equal to $(\pm 1,0)$ and $(0,\pm 1)$. Below T_{c2} additional satellite reflections develop, that correspond to $(m_1m_2)=\pm(1,-1)$. Accordingly, harmonic modulation amplitudes $(1,0)$, $(0,1)$, and $(1,-1)$ were incorporated into the structure model. Refinement against 4970 observed reflection intensities resulted in a fit with $R=0.039$. The periodic lattice distortion shows that the CDW is located at the centers of the WO_3 slabs. The CDW is interpreted in terms of the formation of clusters of six tungsten atoms, that are linked together to form larger clusters of 12 to 18 atoms.

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I. INTRODUCTION

The monophosphate tungsten bronzes with pentagonal tunnels $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ comprise a homologous series of compounds with m equal to 4 or larger.¹ The interest in these compounds derives from their low-dimensional electronic properties, that are expressed in an anisotropic electrical conductivity as well as the formation of charge-density waves (CDW's).² Crystal structures are built of conducting slabs of WO_3 with a ReO_3 -type structure separated by layers containing the phosphate groups (Fig. 1). The thickness of the layers is proportional to m . Precisely m vertex-sharing WO_6 octahedra are found within a slab along a direction $[0vw]$ that makes an angle of approximately 30° with the $\vec{b}$ axis. The CDW properties depend on m too, whereby higher transition temperatures are found for compounds with larger m (for a recent review see Ref. 3).

The basic crystal structures of the various compounds $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ are known. Their electrical and magnetic properties as well as diffuse scattering phenomena related to the CDW have been studied extensively.⁴ However, structure determinations in the CDW state have largely evaded analysis. The analyses of the incommensurately modulated structures in the CDW state involve the superspace description.^{5,6} Applying this method, the sevenfold superstructure of $\text{P}_4\text{W}_{20}\text{O}_{68}$ ($m=10$) at room temperature was determined only recently,⁷ while for the $m=4$ compound the modulations corresponding to the q^1 -type CDW were reported by us.⁸ Detailed knowledge of the modulated structures may provide information about the location of the CDW and the mechanism of the Peierls transition. Furthermore, it will be the basis for accurate electronic structure calculations within the CDW state.

The $m=4$ compound $(\text{PO}_2)_4(\text{WO}_3)_8$ has CDW transitions at $T_{c1}=80$ K and $T_{c2}=52$ K.² Both transitions were

discovered by the observation of independent anomalies in the temperature dependence of the electrical resistivity.⁹ Above T_{c1} the x-ray scattering showed diffuse sheets of intensity in three different orientations.² They were attributed to one-dimensional (1D) CDW fluctuations on chains of vertex-sharing WO_6 octahedra that are present along $\vec{a} \pm \vec{b}$ and $\vec{a}$. The first transition was found to correspond to the condensation of part of the diffuse sheets into the so-called q^1 -type satellite reflections. At T_{c2} the remaining diffuse intensity condensed into the q^2 -type satellites. Band-structure calculations showed hidden 1D nesting of the Fermi surface of the quasi-two-dimensional electron bands, with three different wave vectors corresponding with the CDW wave vectors observed in the x-ray scattering.^{10,11} These observations resulted in a model of three independent CDW's that reside on the three different chains.^{2,7}

Recently we showed that at $T=20$ K the primary CDW is a $2-q$ state, and that the wave vector of the secondary CDW is a mixed second-order harmonic of the primary CDW.⁸ In the crystallographic literature, the $2-q$ state is denoted as a two-dimensional modulation, as precisely two wave vectors are needed to index all Bragg reflections with integers. A preliminary account was given of the structural modulations corresponding to the primary CDW only. Here we will present evidence that the primary CDW is a $2-q$ state for all temperatures $T < T_{c1}$. In particular we will show that the second CDW transition does not correspond to a lock-in transition of the primary CDW, but instead involves the development of higher harmonics within the primary CDW. We give the results of a superspace refinement of the incommensurately modulated structure of $(\text{PO}_2)_4(\text{WO}_3)_8$ at $T=20$ K, including satellite reflections and displacement functions corresponding to the secondary CDW. The analysis

FIG. 1. Projections of the basic structure of $(\text{PO}_2)_4(\text{WO}_3)_8$ along the three crystallographic directions. WO_6 octahedra are shown in dark grey for the W1 atoms and in light grey for the W2 atoms. Tetrahedra represent the PO_4 groups. (a) The projection along $\vec{a}$ clearly shows the WO_3 layers and the PO_4 tetrahedra with pentagonal tunnels. (b) The projection along $\vec{c}$ shows zig-zag chains of vertex-sharing W1 octahedra along $\vec{a}$, while chains of vertex-sharing tungsten octahedra with the repeat unit (W1-W1-W2) can be recognized parallel to $\vec{a} + \vec{b}$ as well as parallel to $-\vec{a} + \vec{b}$. (c) The projection along $\vec{b}$ most clearly shows that the structure is built of vertex-sharing octahedra and tetrahedra only.

of the structure shows that the CDW can be characterized by the formation of clusters on the WO_3 layers. The need for a new interpretation of the CDW transitions in the phosphate tungsten bronzes is discussed.

II. EXPERIMENT

Crystals of $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ were kindly donated by D. Groult and Ph. Labbé.^{12,13} A bar-shaped crystal of dimensions $0.05 \times 0.05 \times 0.14 \text{ mm}^3$ was selected for the present experiment. X-ray diffraction with synchrotron radiation was performed at beamline D3 of Hasylab at DESY (Hamburg, Germany). Low temperatures were obtained with a closed-cycle He cryostat mounted on a four-circle Huber diffractometer. A wavelength of $\lambda = 0.5608 \text{ \AA}$ was chosen.

As reported earlier⁸ the lattice remained orthorhombic at $T = 20 \text{ K}$ with lattice parameters $a = 5.294(1) \text{ \AA}$, $b = 6.591(2) \text{ \AA}$, and $c = 17.415(16) \text{ \AA}$. The components of the modulation wave vectors corresponding to the first CDW were obtained from the positions of the satellite reflections as determined by Q scans along the three lattice directions. They are⁸

$$\vec{q}^1 = [0.330(2), 0.292(2), 0.000(2)], \quad (1a)$$

$$\vec{q}^2 = (-0.330, 0.292, 0.000). \quad (1b)$$

$\vec{q}^1$ and $\vec{q}^2$ are related to each other by the orthorhombic symmetry. The Bragg reflections corresponding to the secondary CDW were found at the positions of the mixed second-order satellite reflections of the primary CDW. They could be described by the wave vector $\vec{q}_1 - \vec{q}_2$

$= (0.660, 0, 0)$. Intensities could not be found at satellite positions defined by $\vec{q}_1 + \vec{q}_2 = (0, 0.584, 0)$.

Both ω scans and Q scans along the $\vec{c}^*$ direction showed that the positions relative to the main reflections of the satellite reflection $(-3.330, -5.292, 5.000)$ are independent of the temperature for $T \leq 70 \text{ K}$. For $T = 80 \text{ K}$ a definite assignment could not be obtained, while for $T = 90 \text{ K}$ scattered intensity was absent at the position of this satellite reflection. A ω scan at the position $(-1.340, -6.5)$ showed this $\vec{q}^1 - \vec{q}^2$ type of satellite to be absent at $T = 70 \text{ K}$. These observations are in agreement with the results of Foury and Pouget,² who showed that the $\vec{q}^1$ and $\vec{q}^2$ satellites are present below $T_{c1} = 80 \text{ K}$, and that the $\vec{q}^1 - \vec{q}^2$ appear below $T_{c2} = 52 \text{ K}$. Furthermore, our observations show that the modulation wave vectors are independent of the temperature. In particular it is found that the third component of $\vec{q}^1$ remains zero at all temperatures below $T_{c1} = 80 \text{ K}$. This implies that a possible lock-in transition of the third components of $\vec{q}^1$ and $\vec{q}^2$ can be excluded as the mechanism for the second CDW transition at $T_{c2} = 52 \text{ K}$.

A consequence of these observations is that all Bragg reflections can be indexed with five integers (h, k, l, m_1, m_2) according to

$$\vec{H} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m_1\vec{q}^1 + m_2\vec{q}^2. \quad (2)$$

Integrated intensities of Bragg reflections were collected in two runs. In the first experiment main reflections $(h, k, l, 0, 0)$ were measured together with the satellite reflections of the primary CDW defined by $(m_1, m_2) = (\pm 1, 0)$ or $(0, \pm 1)$. Integrated intensities were obtained from ω scans of width

TABLE I. The number of reflections and partial R factors for the five different refinements. Model 1: averaged structure, model 2: modulations according to the harmonics (0,1) and (1,0) on the atoms W1 and W2 only, model 3: modulations according to the harmonics (0,1) and (1,0) on all atoms, model 4: harmonics (0,1) and (1,0) on all atoms and harmonics (1,1) and (1,-1) on W1 and W2, and model 5: harmonics (0,1), (1,0), (1,1) and (1,-1) on all atoms.

Reflection group	Number of observed reflections	R values for model number									
		1		2		3		4		5	
		R	wR	R	wR	R	wR	R	wR	R	wR
All reflections	4970	3.45	4.93	3.92	4.95	3.84	4.94	3.88	4.95	3.97	4.94
Main reflections	1549	3.45	4.93	3.45	4.93	3.45	4.93	3.45	4.94	3.45	4.93
First-order satellites	3227			8.15	7.06	7.33	6.23	7.39	6.25	7.39	6.27
Second-order satellites	194							17.4	19.8	13.9	15.1

0.2° and 90 s per reflection. A total of 7670 reflections were measured in the range $8^\circ < 2\theta < 50^\circ$. The intensities were corrected for the variations of the intensity of the incoming beam and for Lorentz and polarization effects. Two intensity control reflections were measured every 60 min. The shape of the crystal was determined with the computer program HABITUS¹⁴ from a series of ψ scans collected on a laboratory diffractometer with Mo $K\alpha$ radiation. The crystal shape was then used to correct the synchrotron data for absorption effects ($\mu = 21.531 \text{ mm}^{-1}$) using the computer program ABSORB.¹⁵

In a second run main reflections were measured together with the satellites of the secondary CDW defined by $(m_1, m_2) = \pm(1, -1)$. A total of 2329 reflections were obtained in the range $8^\circ < 2\theta < 42^\circ$. The same type of corrections were applied to the intensity data as was done for the first data set. The 791 main reflections from the second run were also measured in the first run, and their intensities were used to bring the two data sets on the same scale ($R_{int} = 0.047$). Deviations from orthorhombic symmetry could not be found. The data were averaged in point symmetry 222, resulting in 9030 independent reflection data of which 4970 did have intensities larger than three times their standard deviations (criterion of observability). This data set was used for subsequent structure refinements.

At room temperature $(\text{PO}_2)_4(\text{WO}_3)_8$ crystallizes in space group $P2_12_12_1$. The extinction conditions on the reflections measured at 20 K are in accordance with the $(3+2)D$ -superspace group⁵ $P2_12_12_1(\alpha, \beta, 0)(-\alpha, \beta, 0)$. This symmetry was confirmed by subsequent structure refinements (see below).

III. STRUCTURE DETERMINATION

In a first step the average structure was refined against the main reflections. The average structure was assumed to be isostructural to the structure at room temperature with space group $P2_12_12_1$.¹² With the coordinates of the atoms of the room-temperature structure as starting values, the refinement proceeded smoothly to an excellent fit with $R = 0.035$ (Table I). The atomic coordinates are close to those of a centrosymmetric structure with space group $Pm\bar{c}n$. However, the refinement in $Pm\bar{c}n$ gave a considerably worse fit to the dif-

fraction data with $R = 0.059$. The difference between the two models is that in $Pm\bar{c}n$ highly distorted WO_6 octahedra are aligned with the mirror planes, while in $P2_12_12_1$ the octahedra are tilted resulting in a more regular coordination of tungsten by oxygen. The less regular pattern of more regular octahedra is considered to be more stable than the regular pattern of distorted octahedra, and the atomic shifts towards the $P2_12_12_1$ space group are significant.¹³

The true structure at low temperatures is incommensurately modulated, and it is described within the superspace formalism.^{5,6} Atomic positions are given as the sum of their average positions and a shift due to the modulation, according to

$$\vec{x}^\mu = \vec{\bar{x}}^\mu + \vec{u}^\mu(\vec{\bar{x}}_4, \vec{\bar{x}}_5), \quad (3a)$$

$$\vec{\bar{x}}^\mu = \vec{L} + \vec{x}^{0\mu}, \quad (3b)$$

$$\vec{\bar{x}}_4 = t_1 + \vec{q}^1 \cdot \vec{\bar{x}}^\mu, \quad (3c)$$

$$\vec{\bar{x}}_5 = t_2 + \vec{q}^2 \cdot \vec{\bar{x}}^\mu, \quad (3d)$$

where $\vec{\bar{x}}^\mu$ are the coordinates of atom μ in the average structure with $\vec{L}$ a lattice vector and $\vec{x}^{0\mu}$ the average position in the unit cell. $\vec{x}^\mu$ is the true position. The modulation functions $\vec{u}^\mu(\vec{\bar{x}}_4, \vec{\bar{x}}_5)$ are periodic functions of their arguments with period 1. $(\vec{\bar{x}}_4, \vec{\bar{x}}_5)$ are the fourth and fifth coordinates in $(3+2)D$ superspace. The parameters (t_1, t_2) are the initial phases of the modulation functions. In superspace they can be varied arbitrarily, but for a particular representation of the structure in physical space they need to be given fixed values.

The modulation functions are described by a Fourier series. For the 2D modulations this is

$$u_\alpha^\mu(\vec{\bar{x}}_4, \vec{\bar{x}}_5) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} A_{n_1, n_2, \alpha}^\mu \sin(2\pi n_1 \vec{\bar{x}}_4 + 2\pi n_2 \vec{\bar{x}}_5) + B_{n_1, n_2, \alpha}^\mu \cos(2\pi n_1 \vec{\bar{x}}_4 + 2\pi n_2 \vec{\bar{x}}_5), \quad (4)$$

where $\alpha=x,y,z$. The pairs of integers (n_1, n_2) define the order of the harmonic. Only the terms (1,0), (0,1), and $(1\bar{1})$ have been used in the present analysis.

The symmetry of the modulated structure was given by the superspace group $P2_12_12_1(\alpha, \beta, 0)(-\alpha, \beta, 0)$. The symmetry elements are $(x_1, x_2, x_3, x_4, x_5)$, $(\frac{1}{2}+x_1, \frac{1}{2}-x_2, -x_3, -x_5, -x_4)$, $(-x_1, \frac{1}{2}+x_2, \frac{1}{2}-x_3, x_5, x_4)$, and $(\frac{1}{2}-x_1, -x_2, \frac{1}{2}+x_3, -x_4, -x_5)$. Because $P2_12_12_1$ does not have special positions, symmetry restrictions do not occur, neither on the average structure coordinates nor on the modulation functions.

The modulated structure is completely characterized when the average coordinates ($\vec{x}^0$), the temperature parameters (U_{ij}), and the modulation amplitudes ($A_{n_1, n_2, \alpha}, B_{n_1, n_2, \alpha}$) are given for each independent atom of the average structure. These parameters are determined and refined in the structural analysis. In general, for each observed order (m_1, m_2) of satellite reflections, some coefficients of the corresponding term in the Fourier series will have significant nonzero values. Therefore, in the present analysis, the infinite number of Fourier coefficients is reduced to the following 18 parameters for each atom: $A_{10, \alpha}, B_{10, \alpha}, A_{01, \alpha}, B_{01, \alpha}, A_{1\bar{1}, \alpha}$, and $B_{1\bar{1}, \alpha}$ ($\alpha=x,y,z$).

The modulation was determined in two major steps. First, the satellites belonging to the primary CDW were included into the refinement, and modulation amplitudes $A_{10, \alpha}, B_{10, \alpha}, A_{01, \alpha}, B_{01, \alpha}$ were introduced for the two independent tungsten atoms W1 and W2 (model 2). With arbitrary but small starting values for the modulation parameters the refinement proceeded to a good fit for both main reflections and first-order satellites (Table I). Subsequently, the modulation amplitudes for phosphor and oxygen were introduced, which lead to a further lowering of the R factor (model 3). The marginal influence of the modulations of phosphor and oxygen on the satellite intensities can be understood from the fact that tungsten dominates the scattering. The atomic number multiplied by the number of atoms in the formula unit shows that the relative contributions to the structure factor are W : O : P = 65 : 28 : 7. For increasing scattering angle this ratio will change in favor of tungsten, because its electrons are better localized than for the lighter elements. The effect is that standard deviations of the displacements of oxygen are obtained, that are up to 10 times larger than those of tungsten. Although the major modulation amplitudes are found on tungsten, the present refinements do not allow the conclusion that oxygen or phosphor do not participate in the CDW.

In the second step, the mixed second-order satellites were added to the list of observed reflections, and the corresponding modulation amplitudes $A_{1\bar{1}, \alpha}$ and $B_{1\bar{1}, \alpha}$ were introduced for W1 and W2 atoms (model 4). Refinements resulted in a reasonable fit to the second-order satellites, while the fit to the first-order satellites remained good (Table I). Introduction of the corresponding modulation amplitudes for phosphor and oxygen lead to a lowering of the R factor for the second-order satellites. However, significantly nonzero values could not be obtained for these parameters, while large standard

TABLE II. Parameters of the basic structure of $(\text{PO}_2)_4(\text{WO}_3)_8$ after the refinement of model 4 with three modulation waves for W1 and W2 and two modulation waves for all other atoms. Given are the fractional coordinates of the atoms; standard deviations are given in parentheses.

Atom	x	y	z
W1	0.241 54(1)	0.411 29(1)	0.044 69(1)
W2	0.256 62(1)	0.247 02(1)	0.372 48(1)
P	0.225 91(7)	0.049 76(6)	0.187 85(2)
O1	0.958 21(18)	0.262 46(23)	0.005 20(7)
O2	0.245 50(20)	0.241 31(17)	0.139 15(7)
O3	0.269 60(18)	0.109 03(18)	0.272 18(7)
O4	0.980 67(17)	0.097 75(19)	0.401 88(6)
O5	0.471 86(21)	0.053 87(24)	0.412 75(7)
O6	0.441 52(17)	0.904 27(17)	0.163 99(6)
O7	0.974 32(17)	0.953 28(20)	0.179 02(7)
O8	0.242 88(20)	0.591 17(16)	0.958 28(6)

deviations and large correlation coefficients were found. The impossibility to determine the contribution of phosphor and oxygen displacements to the secondary CDW can be understood from the very few observed reflections that could be measured for the second-order satellites.

The comparison of the various refinements showed that model 4 is the best structure model that can be determined from our data. The average structure parameters, temperature factors, and modulation amplitudes for model 4 are summarized in Tables II–IV. Nonpositive definite temperature tensors were obtained for all refinements (models 1 through 5). They can be attributed to the very low temperature for which the scattering was measured, to the limited set of measured diffraction data, and to unknown geometrical factors preventing the computation of reliable corrections to the scattered intensities. Important is that the temperature parameters were not correlated with the modulation parameters. Thus the latter values can be considered reliable despite the negative temperature parameters.

IV. DISCUSSION

A. Symmetry and reliability of the model

The structure at room temperature as well as the average structure in the CDW state at $T=20$ K are acentric with space group $P2_12_12_1$. Deviations from a hypothetical, centrosymmetric structure with space group $Pm\bar{c}n$ are small but definite. For the present data, a structure model with $Pm\bar{c}n$ symmetry gave a fit with $R_F=0.059$ as opposed to the much better fit with the true structure at $R_F=0.035$ (Table I). The actual lower-symmetry results from rotations of the WO_3 octahedra out of the mirror planes, that have been considered to be essential to accommodate the strain within the WO_3 layers as introduced by the phosphate groups.³

In the hypothetical centrosymmetric structure, the tungsten atoms would be on mirror planes with $x=\frac{1}{4}$ (Table II). Symmetry restrictions for the modulation functions then are that $A_{0,1}^\alpha = A_{1,0}^\alpha$ and $B_{0,1}^\alpha = B_{1,0}^\alpha$ for $\alpha=x,y,z$. Inspection of

TABLE III. Temperature factors of $(\text{PO}_2)_4(\text{WO}_3)_8$ after the refinement of model 4, in $\text{\AA}^2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W1	−0.000 51 (3)	0.000 70 (3)	−0.001 23 (4)	−0.000 52 (2)	−0.000 49 (2)	0.000 14 (2)
W2	−0.000 72 (3)	0.000 90 (3)	−0.001 52 (4)	0.000 76 (2)	0.000 00 (2)	0.000 01 (2)
P	−0.002 26 (13)	0.001 37 (15)	−0.000 36 (16)	0.001 81 (14)	0.000 59 (11)	−0.002 32 (12)
O1	−0.000 91 (42)	0.012 28 (62)	0.003 93 (59)	−0.006 66 (45)	−0.000 16 (35)	0.011 30 (49)
O2	0.007 48 (49)	0.008 94 (62)	0.001 02 (60)	0.012 00 (53)	−0.001 15 (40)	−0.001 34 (40)
O3	0.002 51 (41)	0.008 05 (51)	−0.000 51 (51)	−0.000 08 (46)	−0.000 42 (34)	0.000 67 (41)
O4	0.000 17 (40)	−0.003 70 (51)	0.003 55 (53)	−0.000 18 (38)	0.003 92 (32)	−0.004 07 (42)
O5	0.014 31 (54)	0.009 69 (68)	−0.003 66 (54)	−0.005 49 (51)	0.001 28 (38)	−0.002 27 (51)
O6	−0.000 90 (37)	−0.003 64 (46)	0.003 81 (54)	0.000 80 (36)	0.001 49 (31)	0.000 16 (43)
O7	0.000 05 (39)	0.002 62 (54)	0.007 76 (58)	0.002 37 (38)	−0.000 91 (34)	−0.002 74 (47)
O8	0.004 74 (48)	0.002 21 (61)	0.008 50 (68)	−0.004 58 (49)	0.004 71 (39)	−0.001 24 (44)

Table IV shows that these restrictions are not fulfilled even approximately. For example, the amplitudes $A_{0,1}^x$ and $A_{1,0}^x$ of W1 have opposite signs instead of equal values as would be required by the mirror symmetry. Large deviations from the pseudoinversion symmetry are thus found for the modulation pattern.

The scattered intensity of $(\text{PO}_2)_4(\text{WO}_3)_8$ is dominated by the scattering of the tungsten atoms (Sec. III). This explains the relatively large standard deviations of the modulation parameters of the oxygen atoms, with values of about half the values of the displacements of the tungsten atoms (Table IV).

Because the modulation parameters of the oxygen atoms are all smaller than 1.5 times their standard deviations, the refinements do allow the conclusion that the major part of the modulation is on tungsten. However, nonzero oxygen displacements cannot be excluded. On the contrary, based on the comparison with modulations in other CDW crystals,¹⁶ one would expect the oxygen displacements to have values up to about half the displacements of the tungsten atoms. The second CDW is even smaller than the first one with only a few observable reflections. It turned out to be impossible to refine modulation parameters for oxygen atoms for the cor-

TABLE IV. Modulation amplitudes of the independent atoms according to Eq. (4) in $\text{\AA}$ along the lattice axes, for the refinement of model 4. Standard deviations in the last digits are in parentheses. The phase of the modulation wave was fixed by $B_{10}^z = B_{01}^z$ for W1.

Atom	(n_1, n_2)	A_{n_1, n_2}^x	B_{n_1, n_2}^x	A_{n_1, n_2}^y	B_{n_1, n_2}^y	A_{n_1, n_2}^z	B_{n_1, n_2}^z
W1	(1,0)	−0.0138 (2)	0.0113 (2)	−0.0002 (4)	0.0077 (4)	−0.0012 (5)	0.0038
	(0,1)	0.0142 (2)	−0.0072 (2)	−0.0053 (4)	0.0126 (3)	−0.0065 (4)	0.0038 (2)
	(1,−1)	−0.0033 (5)	−0.0042 (7)	−0.0041 (6)	0.0045 (2)	−0.0025 (8)	0.0020 (6)
W2	(1,0)	0.0043 (2)	0.0019 (2)	0.0091 (4)	0.0050 (4)	−0.0015 (4)	−0.0037 (5)
	(0,1)	−0.0028 (3)	−0.0016 (3)	0.0089 (4)	0.0049 (4)	−0.0008 (4)	−0.0043 (4)
	(1,−1)	0.0008 (5)	−0.0004 (10)	−0.0003 (9)	−0.0002 (7)	−0.0004 (11)	−0.0001 (9)
P	(1,0)	0.0027 (11)	−0.0048 (12)	0.0019 (19)	0.0011 (21)	0.0011 (20)	−0.0051 (19)
	(0,1)	−0.0022 (12)	0.0047 (11)	0.0021 (19)	0.0001 (20)	0.0025 (18)	−0.0010 (20)
O1	(1,0)	0.0010 (45)	0.0038 (32)	0.0021 (53)	−0.0026 (61)	0.0024 (55)	−0.0028 (54)
	(0,1)	0.0042 (46)	0.0023 (31)	0.0030 (55)	−0.0029 (58)	−0.0027 (58)	−0.0029 (56)
O2	(1,0)	−0.0045 (58)	−0.0075 (58)	0.0009 (91)	−0.0035 (99)	−0.0133 (91)	−0.0025 (95)
	(0,1)	−0.0080 (56)	0.0027 (58)	0.0096 (87)	0.0016 (93)	0.0084 (86)	−0.0069 (91)
O3	(1,0)	0.0024 (39)	−0.0069 (41)	0.0079 (67)	0.0095 (65)	−0.0011 (60)	−0.0115 (66)
	(0,1)	−0.0017 (42)	0.0033 (37)	−0.0022 (72)	0.0027 (62)	0.0052 (59)	0.0015 (67)
O4	(1,0)	0.0069 (39)	0.0000 (38)	0.0005 (47)	0.0012 (48)	−0.0060 (53)	0.0001 (56)
	(0,1)	−0.0007 (38)	0.0059 (40)	−0.0011 (48)	0.0029 (48)	0.0011 (56)	−0.0018 (55)
O5	(1,0)	0.0058 (47)	−0.0014 (47)	0.0006 (59)	0.0069 (59)	0.0011 (60)	0.0002 (57)
	(0,1)	−0.0013 (48)	0.0034 (49)	−0.0003 (64)	0.0048 (63)	0.0013 (62)	−0.0033 (60)
O6	(1,0)	0.0003 (36)	−0.0023 (36)	0.0048 (45)	0.0053 (46)	0.0023 (50)	0.0004 (51)
	(0,1)	−0.0054 (35)	0.0033 (36)	0.0038 (45)	0.0042 (46)	0.0054 (51)	−0.0009 (51)
O7	(1,0)	0.0025 (36)	0.0000 (37)	0.0078 (49)	0.0051 (50)	0.0029 (56)	0.0020 (56)
	(0,1)	0.0016 (36)	0.0038 (37)	0.0048 (50)	−0.0001 (51)	−0.0025 (55)	0.0001 (54)
O8	(1,0)	−0.0026 (53)	0.0054 (48)	0.0155 (82)	−0.0049 (73)	0.0017 (95)	0.0029 (111)
	(0,1)	−0.0026 (50)	0.0010 (46)	−0.0106 (85)	0.0079 (78)	0.0014 (102)	0.0088 (113)

FIG. 2. Distance between W1a and W2f as a function of (t_1, t_2) for (a) the complete modulation functions, and (b) the (1,0) and (0,1) harmonics only. For a definition of the atoms see Fig. 4 and Table V. Contours of constant distance are drawn at intervals of $0.0015 \text{ \AA}$. Solid lines represent distances larger than average, while broken lines represent distances shorter than average. The thick solid line parallel to t_2 defines the region where both distances W1a-W2f and W1d-W2h are shorter than average. The almost quadratic regions with the dots at their centers represent the part of (t_1, t_2) space that define the existence regions of the clusters of six tungsten atoms.

responding harmonic, and only tungsten modulations for the $(1, -1)$ harmonic are considered. A similar observation was made for the modulated structure of the $m=10$ phosphate bronze, for which modulations of the phosphor and oxygen atoms were not included into the structure model at all.⁷ Because reliable values for the oxygen and phosphor modulations could not be determined, the analysis of the displacements is restricted to those of the tungsten atoms.

B. Atomic clusters

It has been established that the CDW in $(\text{PO}_2)_4(\text{WO}_3)_8$ is two dimensional at 20 K.⁸ The secondary CDW that develops below $T_{c2}=52 \text{ K}$ was shown to correspond to the mixed higher harmonic $\vec{q}^1 - \vec{q}^2$ of the primary CDW. The present observation that the third components of both modulation wave vectors are zero below T_{c1} shows that the second CDW transition is not related to a lock-in transition of the primary CDW. One interpretation is that the CDW is a $2-q$ state in its entire range of existence. The other possibility would be that for $T_{c2} < T < T_{c1}$ there is a $1q$ CDW. Then the symmetry would necessarily be reduced to monoclinic, and domains would be present, in order to explain the observed q^1 and q^2 satellite reflections. However, we did not observe split reflections, that would result from the two orientations of the monoclinic symmetry, while the reflections were very sharp [full width at half maximum = 0.001° (Ref. 8)]. Therefore a monoclinic distortion, and consequently the single- q state, is highly unlikely. We conclude that most likely the CDW is a $2-q$ state for all temperatures below T_{c1} .

The largest modulations are found on the tungsten atoms, and this is taken as an indication that the CDW originates in low-dimensional electron bands residing on these tungsten atoms. A remarkable feature is that the modulation is very small. The largest displacement is $0.04 \text{ \AA}$ of the W1 atoms.

The W2 atoms are displaced up to $0.02 \text{ \AA}$ out of their average positions. The second CDW [that is, the $(1, -1)$ harmonics of the modulation functions] is almost exclusively located on the W1 atoms. These observations suggest that the CDW is concentrated at the centers of the layers on the W1 atoms, in agreement with theoretical predictions.¹⁷

In transition-metal dichalcogenides the $2q$ CDW's have been found to correspond to the formation of clusters of metal atoms within the layers supporting the low-dimensional electron bands.¹⁸ For the incommensurate CDW in $1T \text{ TaS}_2$ this interpretation could be confirmed with so-called t plots of the distances between the metal atoms.¹⁹ Here we will employ t plots of distances between tungsten atoms to derive the clusters that correspond to the $2q$ CDW in $(\text{PO}_2)_4(\text{WO}_3)_8$.

Distances between atoms in incommensurately modulated structures are defined in the same way as they are for periodic structures. Special to incommensurate structures is that the positions of the atoms relative to the unit cell depend on the unit cell, i.e. on $\vec{L}$ in Eq. (3). Distances between atoms will depend on $\vec{L}$ accordingly. Instead of producing a table of the infinite number of different distance values as they are obtained for the different sets of integers (l_1, l_2, l_3) , the distance between any pair of atoms can be considered as a continuous function of (t_1, t_2) [Eq. (3)].⁶ Because the modulation functions are periodic, all information about distances occurring anywhere in the structure then is contained in the interval defined by $0 \leq t_1 < 1$ and $0 \leq t_2 < 1$. For 2D modulations these so-called t plots can be displayed by contour lines of equal distance on a grid defined by t_1 and t_2 axes.

As an example consider the distance between the atoms W1a and W2f (Fig. 2). For the atom W1a we obtain $\vec{q}^1 \cdot \vec{x}^0 = 0.200$ and $\vec{q}^2 \cdot \vec{x}^0 = 0.040$, while for W2f $\vec{q}^1 \cdot \vec{x}^0 = 0.463$ and $\vec{q}^2 \cdot \vec{x}^0 = -0.027$. For $(t_1, t_2) = (0, 0)$ these val-

FIG. 3. Distance between W1d and W2h as a function of (t_1, t_2) for (a) the complete modulation functions, and (b) the (1,0) and (0,1) harmonics only. For a definition of the atoms see Fig. 4 and Table V. Contours of constant distance are drawn at intervals of 0.0015 Å. Solid lines represent distances larger than average, while broken lines represent distances shorter than average.

ues are the respective values of $\bar{x}_4$ and $\bar{x}_5$, and the distance between these two atoms is displayed in the t plot at the point defined by $t_1=0$ and $t_2=0$. The distance between this pair of atoms in another unit cell defined by the lattice translation $\vec{n}$ can be computed by substitution of the new coordinates into Eq. (3). Alternatively, this distance occurs in Fig. 2 at the point $(t_1, t_2) = [-\vec{q}^1 \cdot \vec{n} \pmod{1}, -\vec{q}^2 \cdot \vec{n} \pmod{1}]$. For example, for $\vec{n} = (1, 0, 0)$ one obtains $(t_1, t_2) = (0.670, 0.330)$. The relative area in (t_1, t_2) space that corresponds to distances less than average is equal to the fraction of this particular type of contact that has distances less than average in the real structure. From Fig. 2 it follows that about half the distances between W1a and W2f are smaller than average, and they can be part of a cluster. The other half is larger than average, and they represent boundaries between clusters.

A property of the t plots is that different distances can be compared directly, thus showing the local structure as a function of (t_1, t_2) . For example, compare the t plot of the distance between W1a and W2f with the t plot for W1d and W2h (Figs. 2 and 3). For both pairs of atoms minimum separation occurs at $t_1 \approx 0.7$, while maximum separation is obtained for $t_1 \approx 0.3$. To a large extent the regions where the distances are less than average coincide in (t_1, t_2) space for the two atom pairs. The remaining area in (t_1, t_2) space contains mainly points where both distances are larger than average as well as a small misfit area, where one distance is less and the other larger than average. This implies that the variations of these two bonds are correlated. Either both bonds are shorter than average, and the four atoms W1a, W1d, W2f, and W2h form a cluster, or both bonds are larger than average, and the corresponding part in the structure will be a boundary between clusters.

A more complete picture of the clusters is obtained by considering the variations of several other bonds around this central cluster. Figure 4 shows the same projection of one

layer of WO_3 of the basic structure as Fig. 1(b), but now with individual atoms and bonds displayed. Tungsten atoms are numbered 1 and 2 according to W1 and W2 in Table II, and symmetry operators are indicated by letters (Table V). It appears that there is a single type of short distance between pairs of W1 atoms (Fig. 5), whereas there are three symme-

FIG. 4. Projection of one layer of WO_3 onto the $\vec{a}, \vec{b}$ plane similar to Fig. 1(b), but now showing the individual atoms. Large and medium sized circles represent W1 and W2 atoms, respectively. Small circles represent oxygen. Phosphor is not shown. Different tungsten atoms are indicated by a letter defining a symmetry operation applied to the coordinates of W1 or W2. See Table V for the definition of symmetry operators. Both the unit cell and the fundamental cluster unit are indicated by thick lines.

TABLE V. Atoms and symmetry operators used in distance calculations of $(\text{PO}_2)_4(\text{WO}_3)_8$. The fractional coordinates of the basic structure, the values of $\bar{x}_4$ and $\bar{x}_5$ in the section $(t_1, t_2) = (0, 0)$, and the symmetry operator as it applies to the coordinates in Tables II and IV are given for each atom. More atoms follow by the application of translations to atoms given in this table.

Atom	x^0	y^0	z^0	$\vec{q}^1 \cdot \vec{x}^0$	$\vec{q}^2 \cdot \vec{x}^0$	Symmetry operation
W1a	0.241 54	0.411 29	0.044 69	0.200	0.040	<i>a</i> : $(x_1, x_2, x_3, x_4, x_5)$
W1b	-0.258 46	0.088 71	-0.044 69	-0.059	0.111	<i>b</i> : $(-0.5+x_1, 0.5-x_2, -x_3, -x_5, -x_4)$
W1c	0.741 54	0.088 71	-0.044 69	0.271	-0.219	<i>c</i> : $(0.5+x_1, 0.5-x_2, -x_3, -x_5, -x_4)$
W1d	0.741 54	1.088 71	-0.044 69	0.563	0.073	<i>d</i> : $(0.5+x_1, 1.5-x_2, -x_3, -x_5, -x_4)$
W1e	1.241 54	1.411 29	0.044 69	0.822	0.002	<i>e</i> : $(1+x_1, 1+x_2, x_3, x_4, x_5)$
W1m	1.241 54	0.411 29	0.044 69	0.530	-0.290	<i>m</i> : $(1+x_1, x_2, x_3, x_4, x_5)$
W2f	0.743 38	0.747 02	0.127 52	0.463	-0.027	<i>f</i> : $(1-x_1, 0.5+x_2, 0.5-x_3, x_5, x_4)$
W2g	-0.256 62	0.747 02	0.127 52	0.133	0.303	<i>g</i> : $(-x_1, 0.5+x_2, 0.5-x_3, x_5, x_4)$
W2h	0.243 38	0.752 98	-0.127 52	0.300	0.140	<i>h</i> : $(0.5-x_1, 1-x_2, 0.5+x_3, -x_4, -x_5)$
W2k	-0.256 62	-0.252 98	0.127 52	-0.159	0.011	<i>k</i> : $(-x_1, -0.5+x_2, 0.5-x_3, x_5, x_4)$
W2l	-0.756 62	-0.247 02	-0.127 52	-0.322	0.178	<i>l</i> : $(-0.5-x_1, -x_2, 0.5+x_3, -x_4, -x_5)$

try independent types of short distances between W1 and W2 (Figs. 2, 3, and 6). Short distances between W2 atoms are not present. The largest variations occur for the pairs W1a-W2f and W1d-W2h (Table VI). The pair W1a-W2h has the smallest variation, while the variation of the distance between W1 atoms is slightly larger.

Within the WO_3 layer quasi-one-dimensional features can be recognized as zigzag chains of vertex-sharing octahedra of the W1 atoms occurring parallel to $\vec{a}$. Chains of vertex-sharing tungsten octahedra with the repeat unit (W1-W1-W2) are found parallel to $\vec{a} + \vec{b}$ as well as parallel to $-\vec{a} + \vec{b}$. These features have been considered to carry electron bands with a 1D character as they are responsible for the CDW's with $\vec{q}^1 - \vec{q}^2$, $\vec{q}^1$, and $\vec{q}^2$, respectively.^{3,11}

Consider the chains parallel to $\vec{a} + \vec{b}$. As discussed in detail by Canadell and Whangbo,¹¹ every repeat unit contains two pathways of tungsten-to-tungsten contacts. In Fig. 4

these are W1d-W2f-W1a-W1b and W1d-W2h-W1a-W1d. Figure 6 shows that the contacts W2h-W1a and W1d-W2f have a small variation only, and the contacts of this type can be considered to be present through all of the structure. It was shown above, that the two contacts W2f-W1a and W1d-W2h are simultaneously shorter than average and simultaneously larger than average. These bondsthus appear to define sites where the chain is broken (both bonds are large) and sites where the four atoms come together (both contacts are short), thus forming a part of a cluster of tungsten atoms.

To explore the sizes and shapes of the clusters, the t plots of contact distances between atoms around W1a, W1d, W2f, and W2h need to be superimposed with those of W1a-W2f and W1d-W2h. Figure 7 shows the t plot of the distance between W1a and W2g. It is equivalent with the t plot of W1d-W2h by a screw axis. Superposition of all three t plots shows regions centered on $(t_1, t_2) = (0.6, 0.8)$ and of

FIG. 5. Distance between W1a and W1b as a function of (t_1, t_2) for (a) the complete modulation functions, and (b) the (1,0) and (0,1) harmonics only. For a definition of the atoms see Fig. 4 and Table V. Contours of constant distance are drawn at intervals of 0.0015 Å. Solid lines represent distances larger than average, while broken lines represent distances shorter than average.

FIG. 6. Distance between W1a and W2h as a function of (t_1, t_2) for (a) the complete modulation functions, and (b) the (1,0) and (0,1) harmonics only. For a definition of the atoms see Fig. 4 and Table V. Contours of constant distance are drawn at intervals of 0.0015 Å. Solid lines represent distances larger than average, while broken lines represent distances shorter than average.

diameter 0.36 (Fig. 2), where all three contacts are smaller than average. For these t values clusters exist that involve at least the six atoms W1a, W1d, W1s, W2f, W2h, and W2g. The superposition of the t plots of other distances shows this cluster of six tungsten atoms to be the fundamental building unit of clusters in $(\text{PO}_2)_4(\text{WO}_3)_8$. They are linked by contacts between W1 and W1 that are shorter than 3.732 Å (Fig. 5) to form larger clusters of 12 tungsten atoms. A small fraction of the distances between W1m and W2f is shorter than average at the t values of the existence domain of the fundamental cluster (Fig. 2), resulting in still larger clusters containing between 16 and 18 tungsten atoms.

C. Nature of the CDW

The cluster picture for the CDW state of $(\text{PO}_2)_4(\text{WO}_3)_8$ is similar to the characteristics of the CDW state of the transition-metal dichalcogenides. In the latter compounds 1D nestings of the Fermi surfaces of the average crystal structures are found with three differently oriented wave vectors.²⁰ Yet, the CDW state itself is characterized by a 2D modulation and the formation of clusters of Ta atoms.¹⁸ For $(\text{PO}_2)_4(\text{WO}_3)_8$ hidden 1D nesting of the Fermi surface by

three differently oriented wave vectors was proposed by Whangbo *et al.*^{10,11} Completely analogous to the dichalcogenides, the CDW appears to be two dimensional and it is characterized by the formation of clusters of W atoms on the layers of WO_3 .

The effect of the secondary CDW on the structure can again be analyzed by t plots. The t plots of the contact distances computed without the second harmonic modulation parameters are much more symmetrical than for the real low-temperature modulation (Figs. 2, 3, 5, and 6). On introduction of the second harmonic, the variation of the distances increases for all four independent contacts. Accordingly, distances between tungsten atoms within the clusters are shorter with the second harmonic included, and the clusters will be

FIG. 7. Distance between W1a and W2g as a function of (t_1, t_2) . For a definition of the atoms see Fig. 4 and Table V. Contours of constant distance are drawn at intervals of 0.0015 Å. Solid lines represent distances larger than average, while broken lines represent distances shorter than average.

TABLE VI. Distances between selected pairs of atoms. See Fig. 4 and Table V for the definition of the atoms. Given are the average distance, the distances of minimum and maximum separation, and the total variation. All values are in Å.

Atom	Atom	Average distance	Minimum distance	Maximum distance	Variation
W1a	W2f	3.747	3.732	3.759	0.027
W1d	W2h	3.733	3.719	3.755	0.036
W1a	W1b	3.735	3.727	3.743	0.016
W1a	W2h	3.751	3.745	3.755	0.010
W1a	W2g	3.733	3.719	3.755	0.036

more stable when the secondary CDW is present. Secondly, the regions of short contacts and the regions of large distances are deformed by the presence of the second harmonic, with the probable effect that clusters can be formed more favorably by matching one short contact with a small distance for a neighboring contact.

This picture is different from previous interpretations of the CDW state and the CDW phase transitions (e.g., see Refs. 2 and 7). There it was assumed that the different chains support independent CDW's that develop at the successive phase transitions. We have shown⁸ that the wave vector of the secondary CDW is related to the wave vectors of the primary CDW by $\vec{q} = \vec{q}^1 - \vec{q}^2$. Presently, we have shown that the secondary CDW corresponds to the development of a higher harmonic in the primary CDW. Its effects will include an energy gain due to the additional nesting of the Fermi surface and an energy gain due to a favorable modification of the lattice strain (see preceding paragraph). It is stressed that our interpretation is in full accordance with the concept of hidden nesting.¹⁰ However, we propose that the 1D nesting features of the Fermi surface do not necessarily require independent CDW's on 1D chains in the structure. For the higher-symmetric transition-metal chalcogenides, 1D nesting of the Fermi surfaces was also found, but it was never suggested that this should be related to 1D features of the crystal structures. Both for the phosphate bronzes and the transition-metal chalcogenides the shapes of the Fermi surfaces result from the 2D character of the electronic bands, and all atoms of the conducting slabs participate in forming the shapes of these bands.

A reconsideration of the components of the q vectors of the CDW's in the $m=6$ compound² shows that most likely they will have a similar relationship as we have presently determined for the $m=4$ compound. To establish this relationship experiments towards determining the third components of the q vectors are necessary for the $m=6$ compound. Assuming these third components to be zero, the primary CDW in the $m=6$ compound is a mixed second-order harmonic of the secondary CDW that develops at low temperatures.

V. CONCLUSIONS

We have determined the incommensurately modulated structure in the double CDW state of $(\text{PO}_2)_4(\text{WO}_3)_8$ at $T=20$ K. Our study of the temperature dependence of the components of the CDW wave vectors and of the periodic lattice distortion corresponding to the CDW at low temperatures showed that the CDWs have the following characteristics.

The CDW originates in low-dimensional electron bands on the tungsten atoms of the WO_3 layers. There is a tendency for the CDW to concentrate at the centers of the layers (W1 type of atoms).

The CDW represents a $2-q$ state throughout the whole temperature range of its existence. The second CDW transition at $T_{c2}=52$ K is not a lock-in transition, but it corresponds to the development of a higher harmonic $\vec{q}^1 - \vec{q}^2$ of the CDW that is present below $T_{c1}=80$ K. Its effect is to further stabilize the clusters of W atoms.

The CDW corresponds to the formation of clusters of six tungsten atoms that are linked together to form superclusters of 12 to 18 atoms.

The finding of clusters of tungsten atoms stresses the 2D character of the CDW. It shows the great similarities between CDW formation in the phosphate tungsten bronze $m=4$ and the transition-metal dichalcogenides. In the latter compounds clusters of metal atoms have been found as the characteristic feature of the CDW, and phase transitions have been observed characterized by the development of higher-order harmonics in an already present CDW.¹⁸⁻²⁰ The present characterization of the CDW in the phosphate tungsten bronzes is opposed to previous interpretations of the CDW as a collection of 1D CDW's residing on different chains of vertex-sharing WO_6 octahedra.^{2,7,11} The present findings call for a different theoretical interpretation of CDW formation in this class of compounds.

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