

Diffuse scattering and short-range order in uranium iodine phthalocyanine $[U_{1-x}Pc_2]I_{2-y}$ and the X-ray structure analysis of crystals with diffuse superstructure reflections

J. Krawczyk, A. Pietraszko, R. Kubiak and K. Łukaszewicz*

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland

Correspondence e-mail: kl@int.pan.wroc.pl

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Crystals of uranium iodine phthalocyanine present an example of a disordered commensurate modulated structure of the intergrowth type. The short-range order of both uranium ions and iodine chains $[I_3^-]_n$ has been analysed by Reverse Monte Carlo (RMC) simulation of X-ray diffuse scattering. The diffraction pattern of uranium iodine phthalocyanine contains diffuse superstructure reflections. In the routine crystal structure analysis diffuse superstructure reflections may be either omitted or measured and classified along with other Bragg reflections. The crystal structure of uranium iodine phthalocyanine is an example of such ambiguity. The crystal structures of two specimens of $[U_{1-x}Pc_2]I_{2-y}$ with slightly different composition have been published in the literature with different space groups and unit cells. We have shown that the structure of both specimens differs only in the degree of short-range order and is isostructural with $[YbPc_2]I_2$. We have also shown that while the omission of diffuse reflections results in the average crystal structure, the treatment of these reflections as normal Bragg reflections is incorrect and produces the structure averaged over a limited small range.

1. Introduction

Two crystal structures of iodine-doped uranium phthalocyanines have been published in the literature. Both are members of the family of tetragonal iodine-doped metal phthalocyanines. The crystal structure of $[UPc_2]I_{5/3}$ has been determined by Janczak & Kubiak (1999) in space group $P4/mcc$ with $a = 13.947$ and $c = 6.501$ Å (Fig. 1). The crystal structure of $[UPc_2]I_2$ determined by Janczak *et al.* (2000) in space group $P4/nnc$ with $a = 19.731$ and $c = 6.507$ Å is a superstructure of $[UPc_2]I_{5/3}$ (Fig. 2).

We have recently analysed the short-range order in iodine-doped ytterbium phthalocyanine $[YbPc_2]I_2$ by the Reverse Monte Carlo (RMC) simulation of diffuse superstructure reflections in the X-ray diffraction pattern of these crystals (Krawczyk *et al.*, 2002). It was interesting to perform similar studies for uranium iodine phthalocyanines and to explain the essential differences between $[UPc_2]I_{5/3}$ and $[UPc_2]I_2$. Preliminary measurements showed that the superstructure reflections of $[UPc_2]I_2$ were diffuse. Similar but more diffuse reflections were present in the X-ray diffraction pattern of $[UPc_2]I_{5/3}$. The [001] rotation patterns of $[UPc_2]I_{5/3}$ and $[UPc_2]I_2$ are presented in Figs. 3(a) and (b), respectively. The crystals were rotated by $\Delta\omega = 20^\circ$ over 50 s. Both rotation patterns revealed diffuse scattering in hkL layers, with L odd, indicating that the decision to regard diffuse reflections of

$[\text{UPc}_2]\text{I}_2$ as Bragg reflections was arbitrary and that it would be more correct to treat both structures in the same way.

This observation indicates a general problem of the X-ray crystal structure analysis when the superstructure reflections are not as sharp as those remaining. An automatic X-ray CCD diffractometer registers all diffuse reflections, but depending on the data reduction program the reflections with a certain degree of diffuseness may or may not be included in the set of Bragg reflections which may result in misleading and incorrect crystal structure determination.

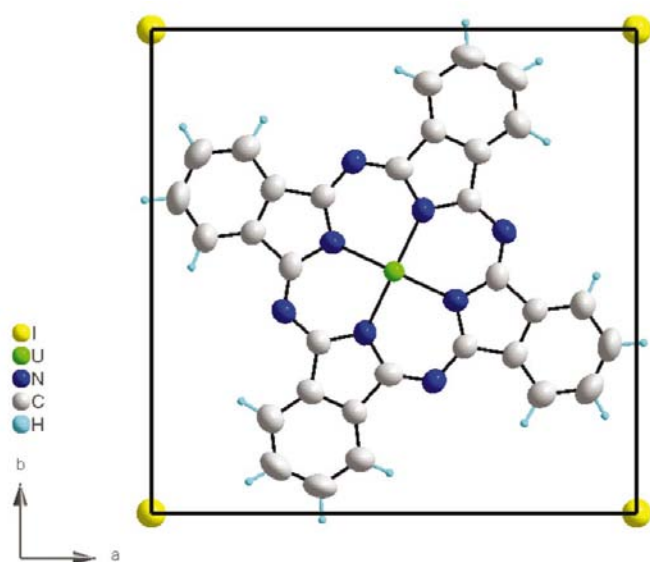


Figure 1
Crystal structure of $[\text{UPc}_2]\text{I}_{5/3}$ [UPcI(1)] in projection along $[001]$ according to Janczak & Kubiak (1999).

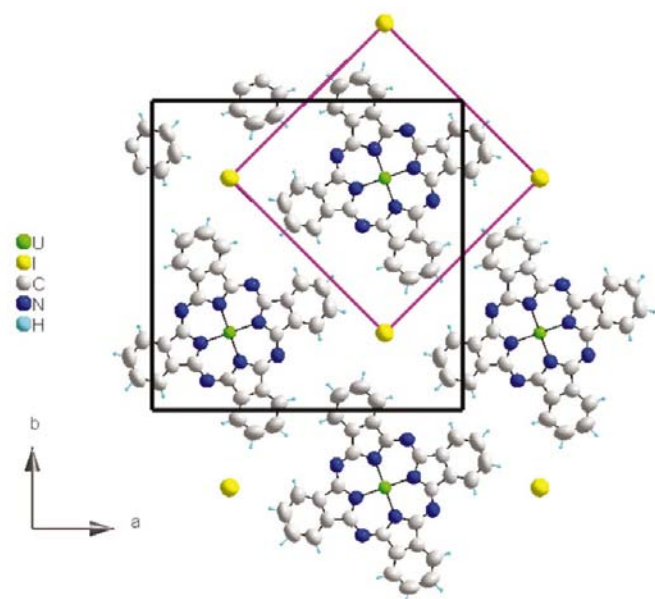


Figure 2
Crystal structure of $[\text{UPc}_2]\text{I}_2$ [UPcI(2')] in projection along $[001]$ according to Janczak *et al.* (2000).

2. Experimental

The crystals of uranium iodine phthalocyanine described by Janczak & Kubiak (1999) as $[\text{UPc}_2]\text{I}_{5/3}$ are denoted in this paper as UPcI(1) and those described by Janczak *et al.* (2000) as $[\text{UPc}_2]\text{I}_2$ we denote as UPcI(2). The crystals for this study were selected from the same batches as those used by Janczak & Kubiak (1999) and Janczak *et al.* (2000) for crystal structure determination. The crystals were obtained by the reaction of pure powdered uranium, 1,2-dicyanobenzene and iodine which were mixed and pressed into pellets. The pellets were heated to 513 K in evacuated glass ampoules for 4–5 h. Crystals of UPcI(1) were grown with a 1:6:2 molar proportion of uranium, 1,2-dicyanobenzene and iodine, and crystals of UPcI(2) with the molar proportion 1:8:2 (Janczak & Kubiak, 1999; Janczak *et al.*, 2000).

Lattice parameters and diffraction data were obtained with a KUMA diffraction KM4CCD four-circle diffractometer equipped with a CCD detector of 512×512 pixels. Graphite-monochromated Mo $K\alpha$ X-rays with $\lambda = 0.71073 \text{ \AA}$ were generated at 43 kV and 23 mA. A standard data collection was performed. The full set of X-ray diffraction data, 1769 frames,

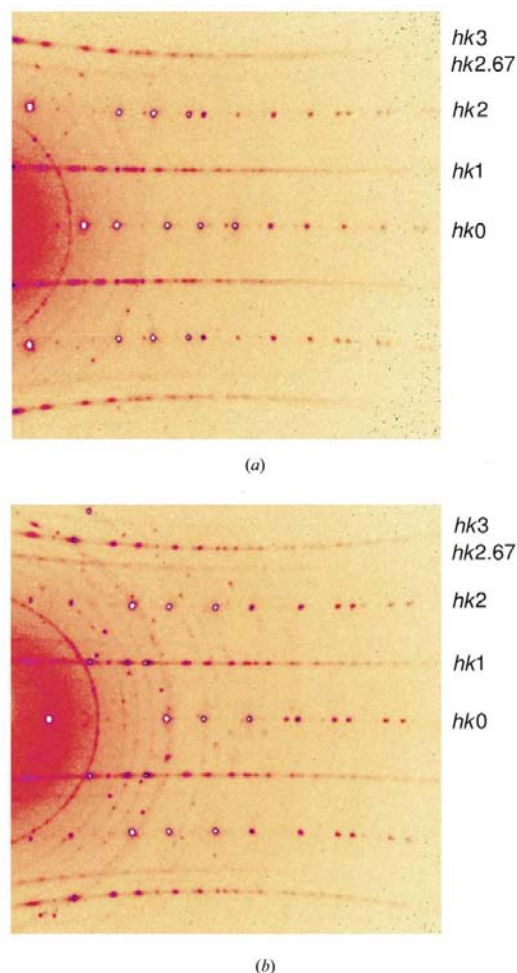


Figure 3
Rotation pattern $[001]$ of (a) UPcI(1) and (b) UPcI(2).

was collected over the range $3\text{--}96^\circ$ in 2θ in 10 runs with $\Delta\omega = 0.5^\circ$ and $t = 30$ s per frame.

3. Crystal structure of iodine-doped uranium phthalocyanine

Iodine-doped uranium phthalocyanine belongs to the family of tetragonal iodine-doped metal phthalocyanines $[\text{Me}_{1-x}\text{Pc}_2]\text{I}_{2-y}$, where Me is U, Yb, As, Bi, Ti or Sn. The crystal structures of $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})\text{Pc}]\text{I}_2$ have been determined by Janczak *et al.* (1999), $[\text{BiPc}_2]\text{I}_{1.5}$ by Janczak *et al.* (1998), $[\text{TiPc}_2]\text{I}_2$ and $[\text{SnPc}_2]\text{I}_2$ by Capobianchi *et al.* (1993).

The crystal structure of $[\text{Me}_{1-x}\text{Pc}_2]\text{I}_{2-y}$ consists of one-dimensional columnar stacks of $[\text{Me}_{1-x}\text{Pc}_2^{2/3+}]_n$ and linear iodine chains of $[\text{I}_3^-]_n$. The structure is disordered because in the average unit-cell metal atoms are located between phthalocyanine rings in the Wyckoff positions $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$ with occupancy 0.5. In a single columnar stack $\text{Me}_{1-x}\text{Pc}_2^{2/3+}$ metal atoms are ordered, but the neighboring stacks may

occur in two settings shifted by $\frac{1}{2}c$. The crystal structure is also commensurate modulated of the intergrowth type, similar to $[\text{YbPc}_2]\text{I}_2$ (Krawczyk *et al.*, 2002). The period c_I of iodine chains $[\text{I}_3^-]_n$ consisting of linear $(\text{I}-\text{I}-\text{I})^-$ anions is equal to $3/2$ of the lattice parameter c of the averaged unit cell. The modulation is disordered because iodine chains are arranged at random in three different settings with respect to the one-dimensional columnar stacks of $[\text{YbPc}_2^{2/3+}]_n$. The central I atoms may be located with equal probability at $z_{\text{I}1} = 0.25c, 0.75c$ or $1.25c$.

We have redetermined both crystal structures: UPcI(1) and UPcI(2) in the space group $P4/mcc$. By refining the occupancies of uranium and iodine we have obtained the chemical formulae $[\text{U}_{0.96}\text{Pc}_2]\text{I}_{1.74}$ and $[\text{U}_{0.97}\text{Pc}_2]\text{I}_{1.86}$ for UPcI(1) and UPcI(2), respectively. We have also redetermined the crystal structure of UPcI(2), denoted later as UPcI(2'), by including diffuse reflections along with the Bragg reflections in the refinement as a superstructure in space group $P4/nnc$ with a unit cell of doubled volume. The details of data collection and crystal structure refinement are presented in Table 1.¹ The crystal structures of UpcI(1) and UPcI(2) are isomorphic and do not essentially differ from the structure of $[\text{UPc}_2]\text{I}_{5/3}$ published by Janczak & Kubiak (1999), except for the non-stoichiometry owing to a deficit in uranium and iodine expressed by the non-integer occupancy determined in the refinement. There is a small deficit of uranium of 4 and 3% for UPcI(1) and UPcI(2), respectively. A much bigger deficit of iodine equals 13 and 7% for UPcI(1) and UPcI(2).

According to Janczak & Kubiak (1999) iodine ions (I_3^-) in $[\text{UPc}_2]\text{I}_{5/3}$ are polar. Janczak *et al.* (2000) report, however, non-polar I_3^- molecules in $[\text{UPc}_2]\text{I}_2$. In the present study we have refined both crystal structures UPcI(1) and UPcI(2) with polar iodine molecules I_3^- . Interatomic distances between the central and peripheral I atoms are 2.79 and 3.26 Å in both UPcI(1) and UPcI(2).

4. Short-range order of uranium in iodine-doped uranium phthalocyanine

X-ray diffraction patterns of iodine-doped uranium phthalocyanines UPcI(1) and UPcI(2) resemble the diffraction pattern of iodine-doped ytterbium phthalocyanine (Krawczyk *et al.*, 2002). They consist of hkL layers, with L even, containing Bragg reflections of the average structure. In the layers with L odd the Bragg reflections are weaker but they are accompanied by diffuse superstructure reflections, indicating the short-range order of uranium. The hkL layers with L a non-integer consist of very diffuse reflections [much more diffuse for UPcI(1)] due to the short-range order of iodine chains.

The localization of diffuse reflections due to the short-range order of U atoms and iodine chains in separate hkL layers allowed us to simplify the calculations by assuming that the

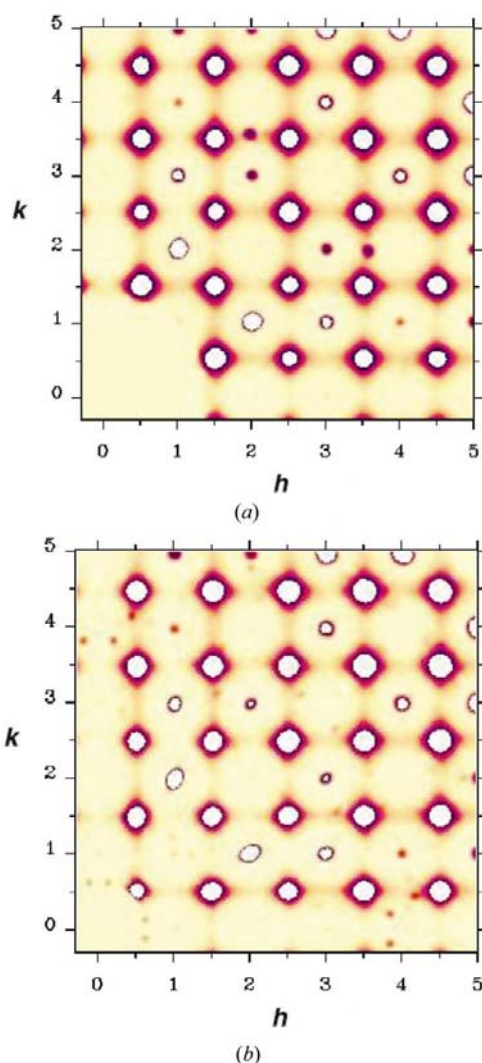


Figure 4
The layer $hk\bar{1}$ containing diffuse superstructure reflections reconstructed by the program *CrysAlis* (Meyer, 2002): (a) UPcI(1) and (b) UPcI(2).

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK0017). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₆₄ H ₃₂ I _{1.74} N ₁₆ U _{0.96}	C ₆₄ H ₃₂ I _{1.86} N ₁₆ U _{0.97}
<i>M_r</i>	1474.37	1491.98
Cell setting, space group	Tetragonal, <i>P4/mcc</i>	Tetragonal, <i>P4/mcc</i>
<i>a</i> , <i>c</i> (Å)	13.997 (2), 6.5230 (10)	13.995 (2), 6.5130 (10)
<i>V</i> (Å ³)	1278.0 (3)	1275.5 (3)
<i>Z</i>	1	1
<i>D_x</i> (Mg m ⁻³)	1.916	1.942
Radiation type	Mo <i>Kα</i>	Mo <i>Kα</i>
<i>μ</i> (mm ⁻¹)	4.16	4.28
Temperature (K)	293 (2)	293 (2)
Crystal form, colour	Irregular, black	Irregular, black
Crystal size (mm)	0.37 × 0.13 × 0.13	0.33 × 0.10 × 0.09
Data collection		
Diffractometer	KM4-CCD	KM4-CCD
Data collection method	Δω = 0.5°, <i>t</i> = 30 s per frame	Δω = 0.5°, <i>t</i> = 30 s per frame
Absorption correction	Numerical	Numerical
<i>T_{min}</i>	0.438	0.417
<i>T_{max}</i>	0.734	0.601
No. of measured, independent and observed parameters	15 699, 980, 867	16 555, 979, 894
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.064	0.064
θ _{max} (°)	29.6	29.6
Range of <i>h</i> , <i>k</i> , <i>l</i>	-18 ⇒ <i>h</i> ⇒ 19 -19 ⇒ <i>k</i> ⇒ 18 -7 ⇒ <i>l</i> ⇒ 8	-19 ⇒ <i>h</i> ⇒ 18 -18 ⇒ <i>k</i> ⇒ 19 -9 ⇒ <i>l</i> ⇒ 6
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.082, 1.20	0.039, 0.094, 1.17
No. of reflections	980	979
No. of parameters	78	78
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0313 <i>P</i>) ² + 0.9211 <i>P</i>], where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0424 <i>P</i>) ² + 1.1429 <i>P</i>], where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
(Δ/σ) _{max}	2.708	2.498
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.47, -0.50	0.49, -0.41
Extinction method	<i>SHELXL</i>	<i>SHELXL</i>
Extinction coefficient	0.0000 (8)	0.0000 (9)

Computer programs: *CrysAlis* (Meyer, 2002), *SHELXL97* (Sheldrick, 1997).

short-range order of uranium does not depend on the local arrangement of iodine chains and *vice versa*. From assumptions discussed in detail by Krawczyk *et al.* (2002), it follows that the short-range order and pair correlation coefficients of uranium in UPcI(1) and UPcI(2) may be studied and determined by the Reverse Monte Carlo (RMC) simulation of a single *hkL* layer with odd *L*, while the short-range order of iodine chains can be determined by RMC simulation of a single *hkL* layer with *L* a non-integer. The distributions of uranium and iodine chains could, therefore, be studied independently of each other.

The layers *hk* $\bar{1}$ reconstructed by the program *CrysAlis* (Meyer, 2002) are presented in Figs. 4(*a*) and (*b*) for UPcI(1) and UPcI(2). They are one-pixel cross sections of the reciprocal lattice corrected for *L_p* factors and presented in *CrysAlis* format. The background was extracted. In both cases

the *hk* $\bar{1}$ reflections, with *h* + *k* odd, are diffuse, being more diffuse for UPcI(1). The RMC simulations of these layers were unsuccessful due to interactions with Bragg reflections.

In the RMC procedure we used the program *DISCUS* (Proffen & Neder, 1997). The *hk* $\bar{1}$ layers with removed Bragg reflections and small spots due to imperfections of the specimen are presented in the *DISCUS* format in Figs. 5(*a*) and (*b*) for UPcI(1) and UPcI(2), respectively. They were simulated by changing the distribution of U atoms in a set of 94 × 94 × 1 unit cells arranged in the (001) plane. Simulated *hk* $\bar{1}$ layers are shown in Figs. 6(*a*) and (*b*). It is convenient to show the agreement between measured and simulated data by comparison of the cross sections through the measured and simulated *hk* $\bar{1}$ layers at *k* = 1.5 (Figs. 7*a* and *b*). Distributions of U atoms in UPcI(1) and UPcI(2), in a fragment of the layer *x*, *y*, 0 ≥ *z* > 1 with the short-range order revealed by RMC, are shown in Figs. 8(*a*) and (*b*).

Pair correlation coefficients *c*(*uvw*) (Neder & Proffen, 1999) between pairs of sites occupied by U atoms and separated by *uvw* have been calculated as

$$c\langle uvw \rangle = (P\langle uvw \rangle - \theta^2)/\theta(1 - \theta), \quad (1)$$

where θ is the overall occupancy of uranium positions and *P*(*uvw*) is the joint probability that both sites separated by *uvw* are occupied by uranium at $z = \frac{1}{4}$, and

$$P\langle uvw \rangle = YY/(YY + VV + YV + VY),$$

where *YY* is the number of pairs of sites separated by *uvw* and occupied by uranium at $z = \frac{1}{4}$, *VV* is the corresponding number for U atoms at $z = 3/4$, while *YV* + *VY* is the number of pairs of sites occupied by uranium at different *z* values.

The distribution of correlation coefficients in a definite plane is called a correlation field (Neder & Proffen, 1999), which determines how these correlations extend within the crystal. Correlation fields of U atoms in the directions $\langle 100 \rangle$ and $\langle 110 \rangle$ for UPcI(1) and UPcI(2), respectively, are shown in Figs. 9(*a*) and (*b*). Correlations *c*(*uu0*) decay with increasing distance. In both crystals *c*(*uu0*) becomes zero at about *u* = 5.5, which is the measure of the range of order and the average radius of nanodomains. The correlations *c*(*u00*) show that in

spite of the similar size, the nanodomains of UPcI(2) are better ordered compared with UPcI(1).

5. Short-range order of iodine chains in iodine-doped uranium phthalocyanine

The iodine chains $[I_3^-]_n$ in UPcI(1) and UPcI(2) are distributed over three settings in a similar way as in iodine-doped ytterbium phthalocyanine (Krawczyk *et al.*, 2002). A deficit of iodine implies that iodine chains $[I_3^-]_n$ contain defects (vacancies or increased distances between neighboring I_3^- ions). The accuracy, however, of our experiment did not allow us to observe any effects of disorder within a single iodine chain. We have, therefore, assumed the order of single iodine chains as a sufficiently good approximation. A distribution of iodine chains over three settings with the short-range order was calculated by RMC simulation of $hk\bar{2}.6\bar{7}$ layers for UPcI(1) (Fig. 10*a*) and UPcI(2) (Fig. 10*b*). Even a rough comparison of these layers indicated greater disorder of iodine chains in UPcI(1). Simulated $hk\bar{2}.6\bar{7}$ layers are shown in Figs.

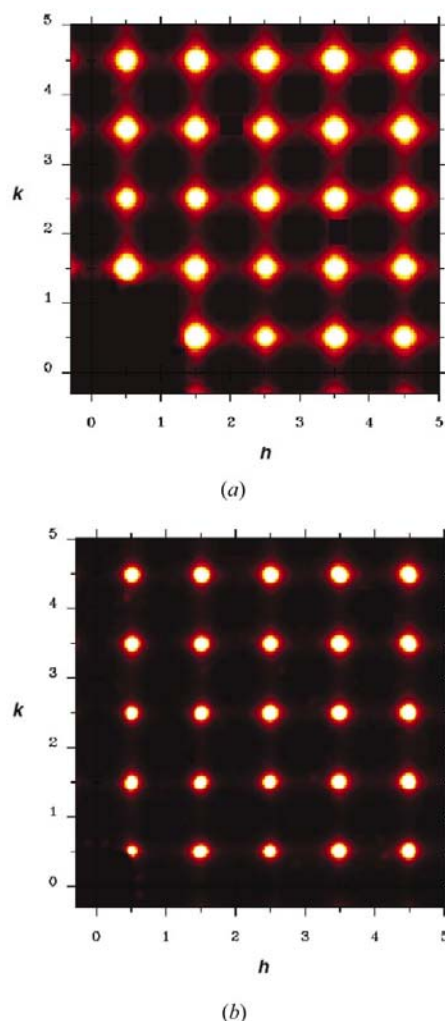


Figure 5
The layer $hk\bar{1}$ containing diffuse superstructure reflections (Bragg reflection are omitted): (a) UPcI(1) and (b) UPcI(2).

11(*a*) and (*b*) for UPcI(1) and UPcI(2). A comparison of cross sections through the measured and simulated $hk\bar{2}.6\bar{7}$ layers at $k = 1$ for UPcI(1) and UPcI(2), shown in Figs. 12(*a*) and (*b*), indicates that the simulation has been successful and reliable.

Figs. 13(*a*) and (*b*) show the distribution of iodine chains over three settings for UPcI(1) and UPcI(2), respectively. The chains of three different settings are marked in three colors. Contrary to uranium, the correlation coefficients $c\langle 100 \rangle$ for iodine chains (Figs. 14*a* and *b*) of the same setting are positive and the chains tend to form ribbons perpendicular to $\langle 010 \rangle$. The high value of the correlation coefficient $c\langle 200 \rangle$ for UPcI(2) means that every second parallel ribbon tends to have the same setting. Closer inspection of Fig. 13(*b*) reveals small regions with predominantly parallel orientation of ribbons, which may be regarded as clusters or nanodomains.

6. Ambiguity of the crystal structure analysis of crystals with diffuse superstructure reflections

The ambiguity of crystal structure determination depending on the inclusion or not of the diffuse reflections in the set of observed data deserves special consideration. In data collec-

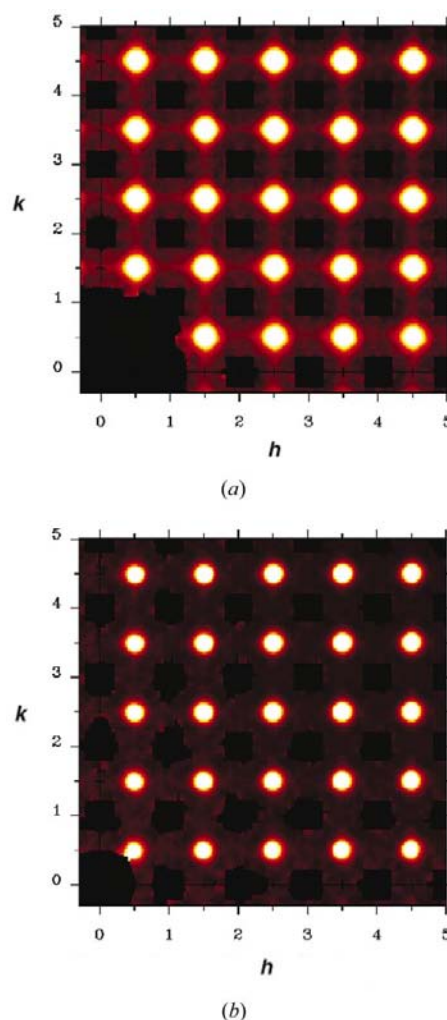


Figure 6
RMC simulated layers $hk\bar{1}$ of (a) UPcI(1) and (b) UPcI(2).

tion very diffuse reflections are usually omitted, but depending on data collection and reduction procedure the reflections with a certain degree of diffuseness may be either omitted or included into the set of Bragg reflections. The resulting ambiguity is related to the question of symmetry of disordered crystal structure.

It is customary to present a disordered crystal structure as an average structure with the space group resulting from the averaging. Diffuse superstructure reflections, however, provide information about the short-range order and the presence of nanodomains. With increasing correlation length the nanodomains grow in size and the reflections become less diffuse. Eventually, when the domains are sufficiently large the superstructure reflections become almost as sharp as the Bragg reflections, indicating an ordered superstructure with a unit cell of multiple volume and, usually, a new space group. In the intermediate cases when the superstructure reflections are still diffuse one can infer that the structure of a single nano-

domain is similar to that of a macroscopic domain in the ordered superstructure.

Diffuse superstructure reflections in the hkL layers, with L odd, in the diffraction pattern of tetragonal iodine-doped uranium phthalocyanine depend entirely on the ordering of U atoms. Omission of these reflections in the refinement procedure produces an averaged structure with space group $P4/mcc$ and a tetragonal unit cell with U atoms occupying at random Wyckoff positions $2(a)$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$) with occupancy 0.5. The inclusion of diffuse reflections in the refinement produces a superstructure tetragonal unit cell of doubled volume with space group $P4ccn$ with U atoms distributed over two Wyckoff positions: $2(a)$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and $2(b)$ ($\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$). In the general case the refinement results in different occupancies of U atoms in these two positions. Janczak *et al.* (2000) have determined the crystal structure of $[\text{UPc}_2]_2$ with the superstructure unit cell and occupancies of uranium in $2(a)$ and $2(b)$ positions equal to 0.167 and 0.833, respectively.

The crystal structure obtained by inclusion in the refinement of diffuse superstructure reflections presents an average

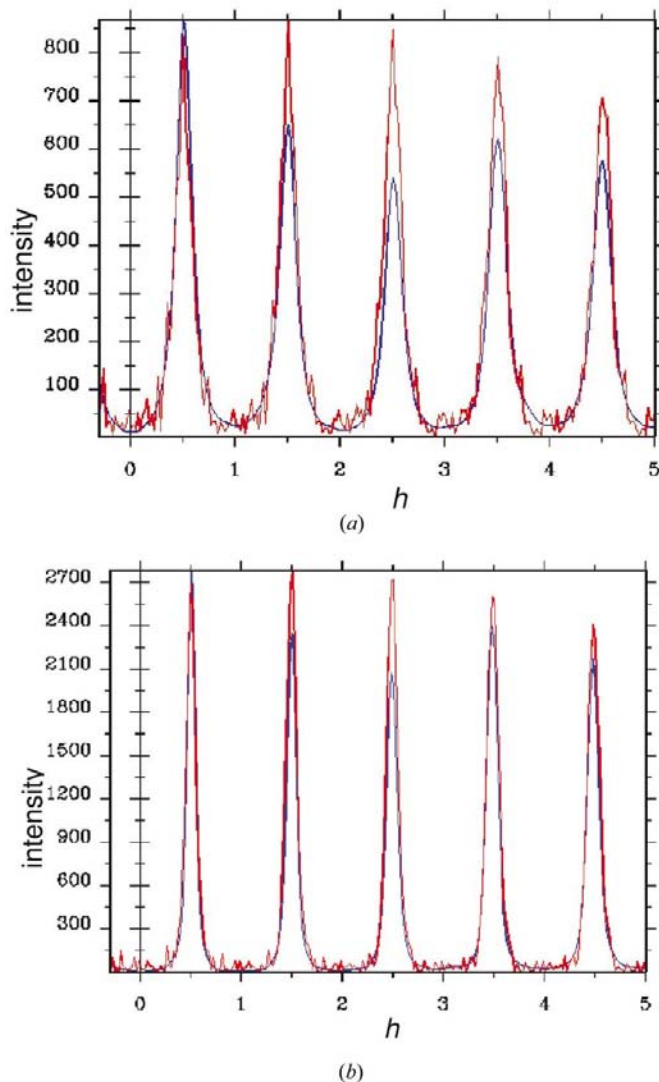


Figure 7
Cross section through the $hk\bar{1}$ layer at $k = 1.5$: (a) for UPcI(1) and (b) for UPcI(2). Measured: blue; simulated: red.

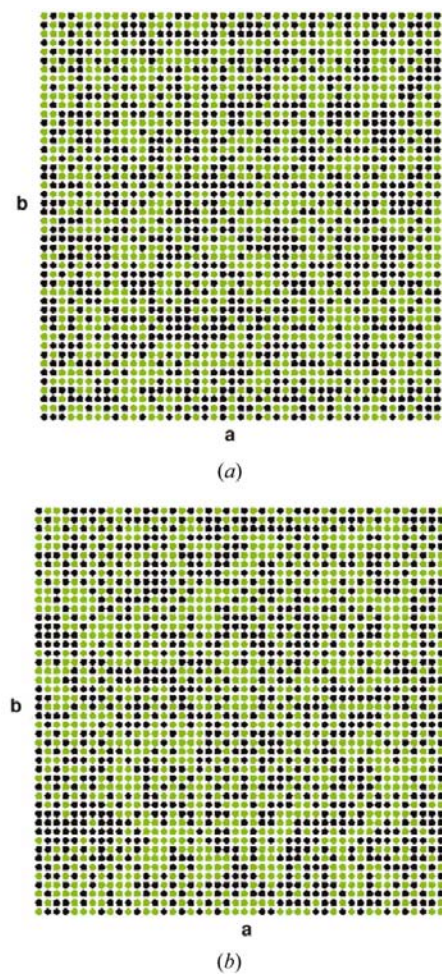


Figure 8
Distribution of U atoms in the layer $x, y, 0 \leq z < 1$ with the short-range order revealed by RMC. Empty circles: U at $z = \frac{1}{4}$; full circles: U at $z = \frac{3}{4}$ (a) in UPcI(1) and (b) in UPcI(2).

structure. However, contrary to the averaging over an infinite volume if the diffuse reflections are neglected, the averaging in this case occurs over a limited volume depending on the coherence length of the X-rays and the mosaic spread of the crystal specimen.

Non-equal occupancies of $2(a)$ and $2(b)$ Wyckoff positions obtained by the inclusion of diffuse reflections in the refinement of the crystal structure are related to the intermediate case extending from the disordered crystal structure with short-range order up to an almost perfectly ordered superstructure. The reversal of the occupancies of the $2(a)$ and $2(b)$ Wyckoff positions (0.167 and 0.833) \Rightarrow (0.833 and 0.1670) is immaterial; it does not change the absolute values of calculated structure factors $|F_c|$, only reversing the signs of the calculated structure factors of the superstructure reflections. Equal occupancies of $2(a)$ and $2(b)$ Wyckoff positions means complete disorder resulting in the disappearance of super-

structure reflections. Full occupancy of one position and zero of another indicates a completely ordered superstructure.

7. Conclusions

The diffraction patterns of superstructure crystals contain additional reflections requiring multiplication of the unit cell. If superstructure reflections are diffuse, an ambiguity may arise because in the routine crystal structure analysis diffuse superstructure reflections may be either omitted or measured and classified along with Bragg reflections. The crystal structure of uranium iodine phthalocyanine is an example of such an ambiguity. The crystal structures of two specimens of $[U_{1-x}Pc_2]I_{2-y}$ with slightly different composition have been published in the literature with different space groups and unit cells (Janczak & Kubiak, 1999; Janczak *et al.*, 2000). We have shown that the crystal structures of both specimens differ only in the degree of short-range order and are isostructural with ytterbium iodine phthalocyanine. We have also shown that while the omission of diffuse reflections results in the average crystal structure, the treatment of these reflections as normal

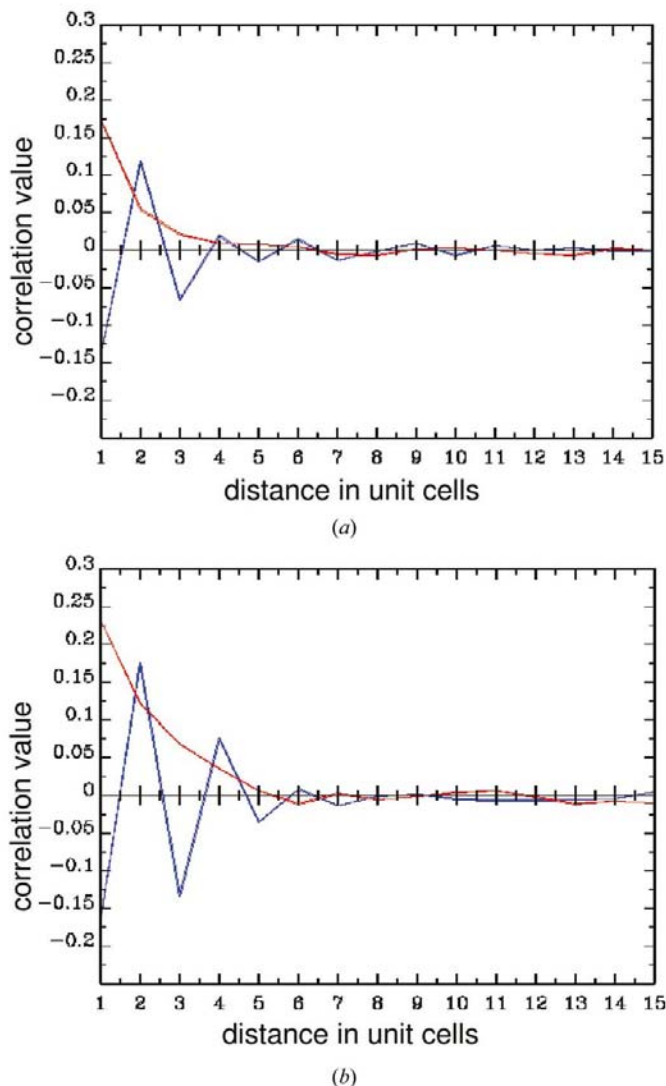


Figure 9 Correlation field for U atoms (a) in UPcI(1) and (b) in UPcI(2). $c(u00)$: blue; $c(uu0)$: red.

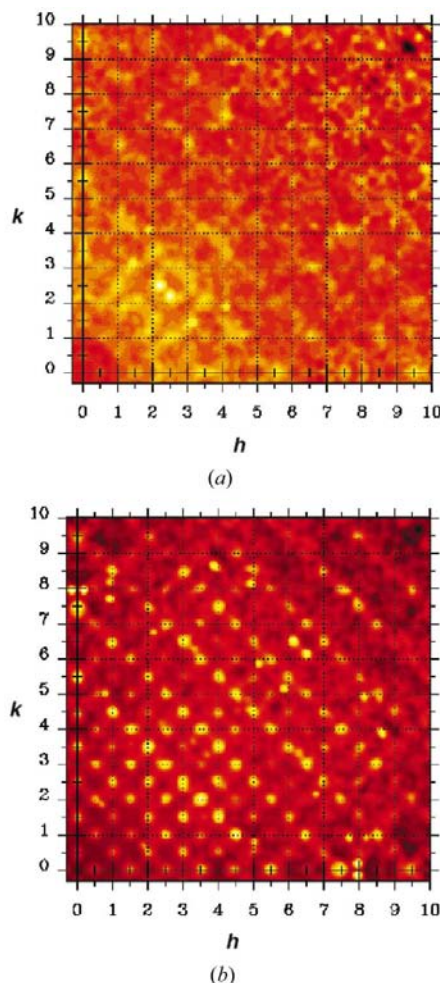


Figure 10 The layer $hk2.67$ (a) in UPcI(1) and (b) in UPcI(2).

Bragg reflections is incorrect and produces a disordered structure averaged over a limited small range.

The space group of the average structure of uranium iodine phthalocyanine (with long-range averaging) is $P4/mcc$. The short-range order of U atoms results, however, in small ordered regions which may be regarded as superstructure anti-phase nanodomains with a tetragonal unit cell: $a' = a2^{1/2} \approx 19.7 \text{ \AA}$, and space group $P4/nnc$. The space-group symmetry of nanodomains $P4/nnc$ is a subgroup of $P4/mcc$. With an increasing degree of order the nanodomains grow in size and eventually the crystal structure is to be treated as an ordered structure with domains. The intermediate cases with a medium-order range may be ambiguous in relation to the space-group symmetry.

The crystals of uranium iodine phthalocyanine present an interesting example of a disordered commensurate modulated structure of the intergrowth type. Both U atoms and iodine chains are disordered, but the short-range ordering of the U atoms is independent of the ordering of the iodine chains and results in different nanodomains. Contrary to uranium, the iodine chains of the same setting tend to form ribbons running along $[001]$ and perpendicular to $\langle 010 \rangle$ (Figs. 12*a* and *b*).

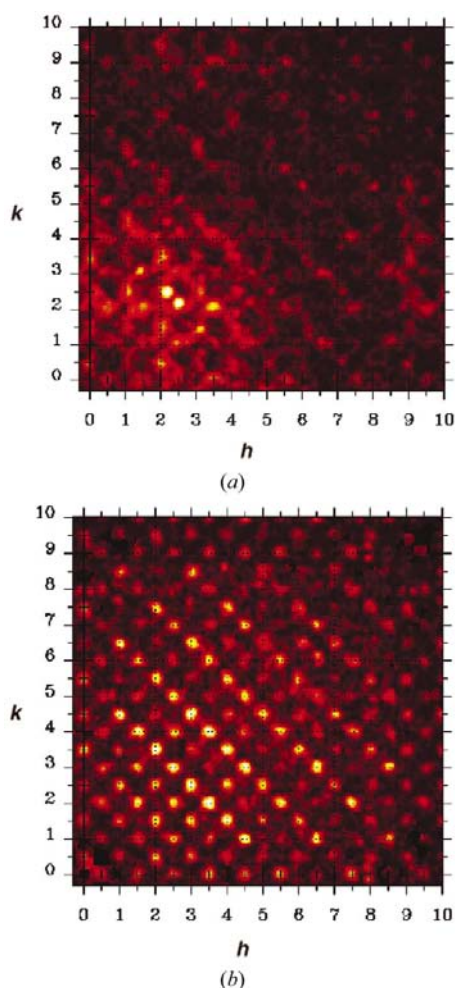


Figure 11
RMC simulated layer $hk\overline{2.67}$ (a) in UPcI(1) and (b) in UPcI(2).

Closer inspection reveals small regions (clusters or small nanodomains) with ribbons of different settings which are predominantly parallel and result in the local orthorhombic symmetry. The clusters of locally ordered iodine ribbons are much smaller and apparently independent of the nanodomains connected with the ordering of U atoms.

The deficit of uranium is small and nearly the same in crystals UPcI(1) and UPcI(2). The deficit of iodine is much larger and is twice as large in UPcI(1) as in UPcI(2). A larger deficit of iodine probably results in considerable disorder of iodine chains distributed over three settings in both crystals, especially in UPcI(1). The origin of disorder in iodine-doped tetragonal metal phthalocyanines, as well as the chemical and physical implications, remain out of the scope of the present paper. Complicated disorder observed in these materials may result in interesting physical properties, but the small size and

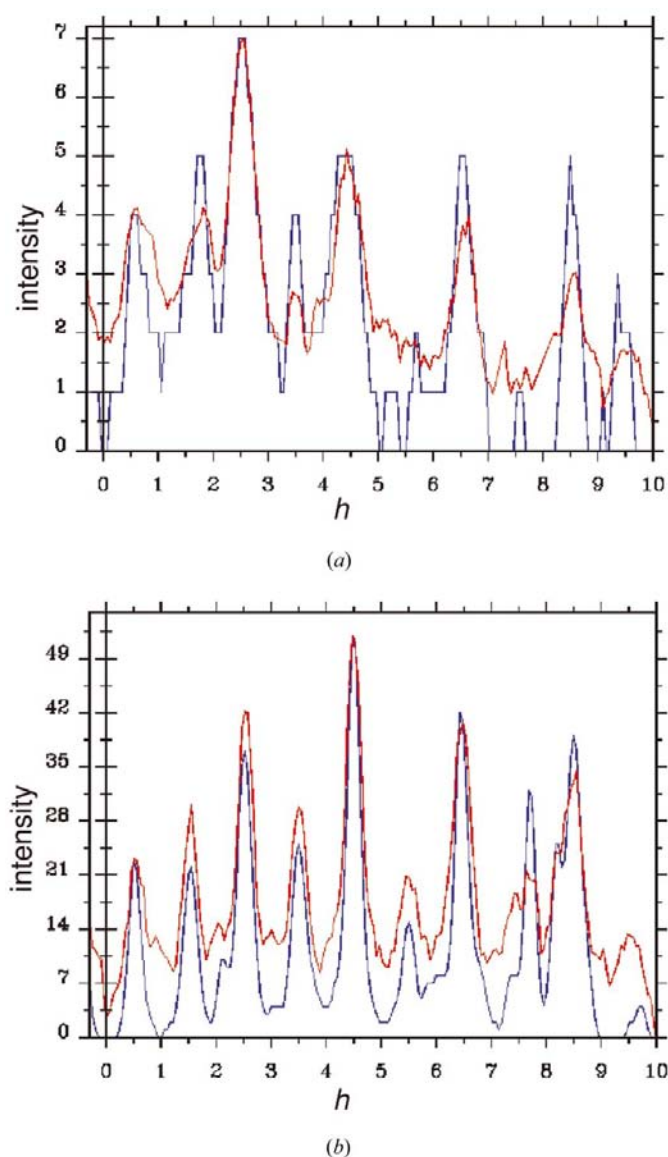


Figure 12
Cross section through the layer $hk\overline{2.67}$ at $k = 1$ (a) for UPcI(1) and (b) for UPcI(2). Measured: blue; simulated: red.

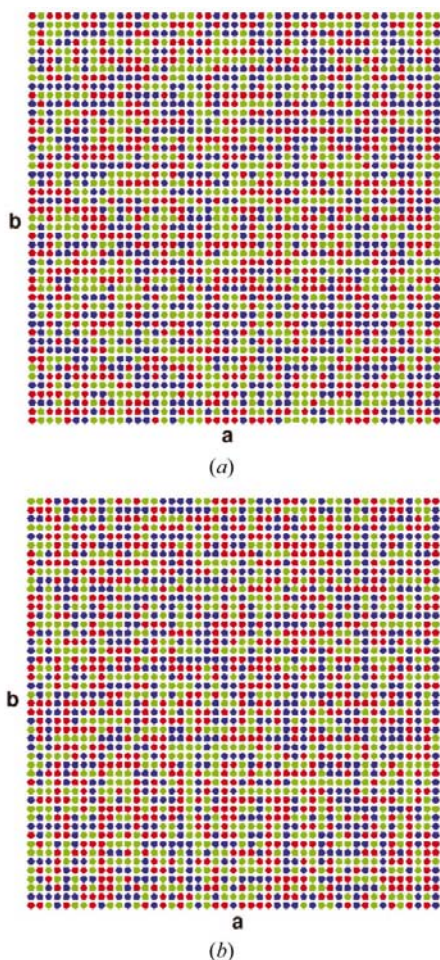


Figure 13
Distribution of iodine chains over three settings revealed by RMC and marked by three colours: (a) in UPcI(1) and (b) in UPcI(2).

insufficient quality of the crystals has not allowed us so far to undertake a proper study.

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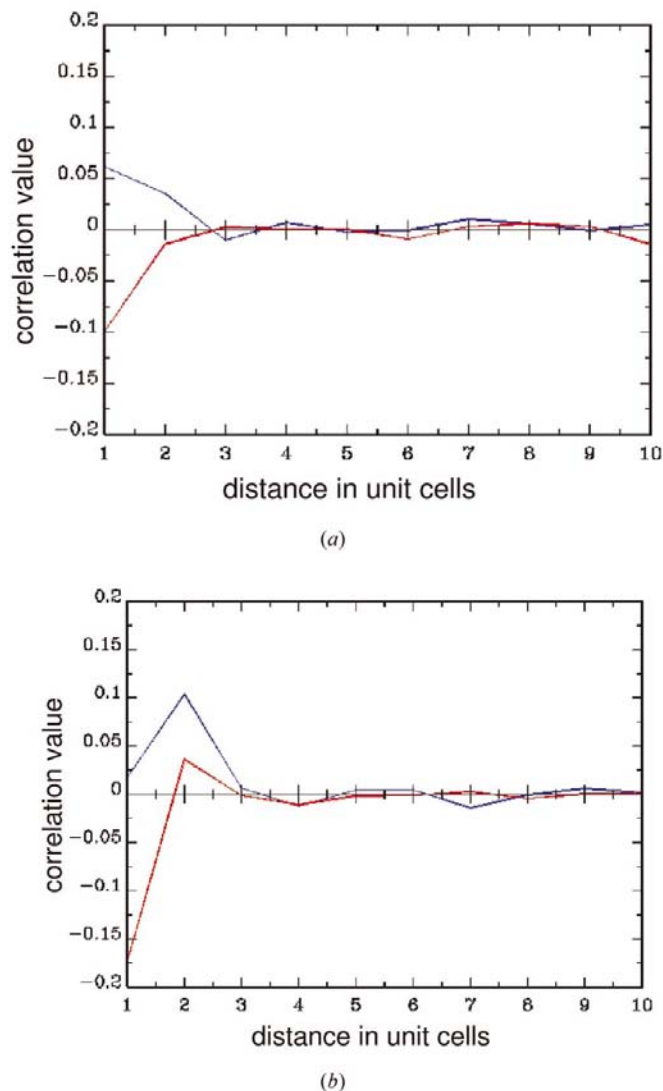


Figure 14
Correlation field for iodine chains: (a) in UPcI(1) and (b) in UPcI(2). $c(u00)$: blue; $c(uu0)$: red.

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