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Structure of the charge-density wave in $(TaSe_4)_2I$

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Abstract

$(TaSe_4)_2I$ is a quasi-one-dimensional (1D) electrical conductor. It exhibits a phase transition at $T_{CDW} = 263$ K towards a charge-density-wave (CDW) state at low temperatures. We report a full structure refinement of the incommensurately modulated structure in the CDW state at $T = 110$ K against synchrotron radiation, single-crystal x-ray diffraction data. At room temperature the crystal structure has tetragonal symmetry with space group $I422$. In the CDW state each main reflection in the x-ray scattering is surrounded by eight incommensurate satellites at $(\pm 0.064, \pm 0.064, \pm 0.151)$. The CDW state is found to comprise four domains, and it is characterized by one modulation wavevector. With respect to a $\sqrt{2} \times \sqrt{2} \times 1$ supercell it has the symmetry of the superspace group $F2(0, \beta, \gamma)$ with $\beta = 0.128$ and $\gamma = 0.151$. The first part of the modulation is found to be a transverse acoustic wave, involving amplitudes of similar magnitudes of about 0.13 Å on all atoms. The second part of the modulation involves displacements of the Ta atoms of about 0.03 Å, that are parallel to the 1D chains. These are interpreted as reflecting the CDW. A Landau free-energy model is developed, that shows that symmetry arguments allow the phase transition to be second order.

1. Introduction

$(TaSe_4)_2I$ is a quasi-one-dimensional (1D) metal, that belongs to the class of $(MX_4)_xY$ compounds (M = Ta, Nb; X = S, Se, Te; Y = I, Br, Cl; $x \geqslant 2$) [1]. A characteristic feature of these compounds is the presence of columns of composition MX_4 that are separated by chains of halogenide atoms. $(TaSe_4)_2I$ crystallizes in space group $I422$ with lattice parameters $a_0 = b_0 = 9.531$ Å and $c_0 = 12.824$ Å at room temperature (figures 1 and 2) [2]. The 1D electronic properties are presumably related to the 1D electron band formed by the $5d_z^2$ orbitals of the Ta atoms.

An anomaly in the temperature dependence of the electrical resistivity was interpreted as being due to the formation of a charge-density wave (CDW) below $T_{CDW} = 263$ K [3, 4].

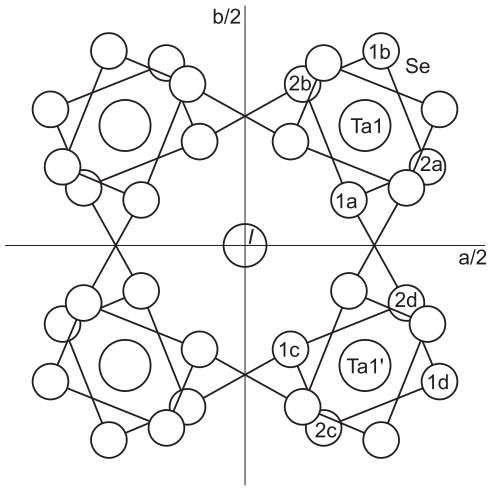

Figure 1. Projection of the basic structure of one unit cell onto the $(\vec{a}, \vec{b})$ plane. Shown are Ta1 atoms at $z = 0$, iodine atoms at $z = 0.15$, Se atoms at $z \approx -0.12$ (indicated by labels corresponding to table 3, later), and Se atoms at $z \approx 0.12$. Note that the axes of the F-centred unit cell are indicated.

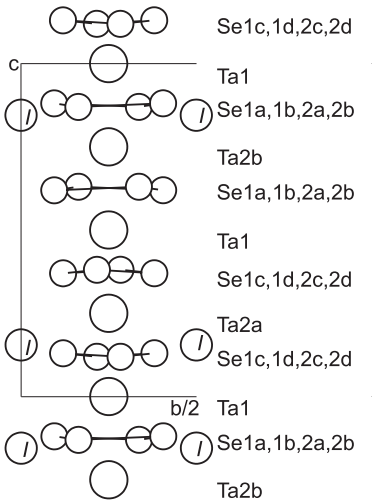

Figure 2. The structure of the $TaSe_4$ chain centred on $x = y = 0.25$. The labels of the atoms correspond to table 3, later.

Satellite reflections in x-ray scattering and electron diffraction were observed below T_{CDW} at positions defined by modulation wavevectors $(\pm 0.05, \pm 0.05, \pm 0.09)$ [5, 6], thus supporting the CDW interpretation of the phase transition. Further evidence for the low-dimensional electronic properties and a CDW state came from angle-resolved photoelectron spectroscopy (ARPES) [7, 8].

Each main reflection is, in principle, surrounded by eight satellite reflections in the x-ray diffraction. A major question then is whether the CDW state is a single-domain, multi-q or a multi-domain, single-q state. The correct description of the structure of the CDW state is a requirement for the development of theoretical models for the phase transition and for the

description of the physical properties of the CDW state. Tentatively assuming a four-domain, single-q state, Lee and co-workers reported a structure refinement on the measured intensities of six satellite reflections [9]. They determined an overall modulation parameter for all atoms, and they found a good agreement between measured and calculated intensities with a transverse displacement amplitude of 0.09 Å. Neutron scattering studies also indicated a multi-domain state, and a Landau free-energy model for the phase transition was proposed [10, 11]. Further scattering experiments indicated that the phase transition is not second order, despite the fact that the intensities of the satellite reflections grow continuously on decreasing the temperature below T_{CDW} [5, 12].

In the present contribution both the symmetry and the detailed atomic structure of the CDW state of $(TaSe_4)_2I$ are determined by means of single-crystal x-ray diffraction. It is found that the CDW state is a four-domain, single-q state with monoclinic symmetry. The major part of the modulation is a transverse wave with approximately equal amplitudes on all atoms of sizes of about 0.13 Å. A modulation of secondary size of the Ta atoms is found with displacements parallel to the 1D chains of magnitudes of about 0.03 Å. This modulation represents the CDW. An analysis of the relative phases of the displacements of different atoms, and of the interatomic distances, is used to characterize the phase transition and the CDW state. A Landau free-energy model is developed, that has the experimental structure as one of its solutions, and that shows that the symmetry allows the phase transition to be second order.

2. Experimental procedure

Single crystals of $(TaSe_4)_2I$ were grown by gas transport in evacuated quartz ampoules [2]. About 1 g of a stoichiometric mixture of the elements was used, with an excess of iodine, in order to account for the high vapour pressure of this element. A crystal of dimensions $0.02 \times 0.03 \times 2.0$ mm^3 was selected for the x-ray experiments.

At room temperature, x-ray scattering was measured on a Nonius-MACH3 four-circle diffractometer with a rotating-anode generator, and with Mo Kα radiation ($\lambda = 0.7107$ Å). The analysis confirmed the tetragonal structure ($R_F = 0.048$) with space group $I422$ and lattice parameters $a = b = 9.5235(8)$ Å and $c = 12.7720(12)$ Å [2].

X-ray scattering at low temperatures was measured at the Swiss–Norwegian beamline BM01 at the European Synchrotron Radiation Facility (ESRF), on a KUMA six-circle diffractometer operating in four-circle mode. The crystal was cooled with an Oxford Cryosystems nitrogen-gas-flow cryostat. The main problem was resolving the main reflection and the eight satellites around it. As the best compromise between optimal resolution and minimum absorption, we have chosen a wavelength of $\lambda = 1.2698(1)$ Å.

More than 20 single crystals of $(TaSe_4)_2I$ were tested, and the one with the narrowest reflections was selected for all experiments. Lattice constants were determined at three temperatures from the setting angles of 18 reflections (table 1). Deviations from tetragonal

Table 1. Lattice parameters of $(TaSe_4)_2I$ at selected temperatures (in Å). A tetragonal lattice was assumed with $a = b$ and $\alpha = \beta = \gamma = 90^\circ$.

Temperature	a	c
295 K (Nonius)	9.5235(8)	12.7720(12)
295 K (KUMA)	9.5190(10)	12.762(7)
240 K (KUMA)	9.5086(12)	12.753(7)
120 K (KUMA)	9.4872(37)	12.742(4)

symmetry could not be found at any temperature. However, the widths of the reflections (600) and (060) had FWHM $= 0.08^\circ$ at $T = 295$ K and at $T = 240$ K, whereas these widths increased towards 0.23° at $T = 120$ K. The $(0, 0, 10)$ reflection remained narrow at all temperatures with FWHM $= 0.02^\circ$. These results are indicative of a small orthorhombic or monoclinic distortion that increases in size on further cooling below the CDW transition at $T_{CDW} = 263$ K. A splitting of the reflections was not observed, and it was not possible to determine the magnitudes of the lattice distortions.

At $T = 120$ K each main reflection was found to be surrounded by eight satellites at the expected positions $(\pm\alpha, \pm\alpha, \pm\gamma)$ [5]. The components of the modulation wavevectors were determined from the setting angles of the eight satellites around the main reflection (840). They were obtained as $\alpha = 0.0641(1)$ and $\gamma = 0.1510(1)$. These values are different from values reported in the literature, and they support previous observations that the precise values of the components of the modulation wavevectors are sample dependent [9]. These variations might be attributed to variations in purity and crystal quality of the samples.

In a first experiment the integrated intensities of the main reflections and all eight of the surrounding satellites were measured for a half-sphere ($l > 0$) with $32.7^\circ < \theta < 34^\circ$. Comparing equivalent reflections showed the intensities to obey tetragonal point symmetry. Alternatively, the intensities of the satellite reflections were used to determine the volume ratios of the domains for the different models. In all cases, equal occupancies of the domains were found (see section 3), which is compatible with a tetragonal appearance of the intensity distribution.

A further experiment that helped towards establishing the domain structure was the measurement of mixed higher-order satellites. As we discuss below, the mixed second-order satellites that need to be considered are $\vec{q}^1 + \vec{q}^2 = (0, 0, 2\gamma)$ and $\vec{q}^1 - \vec{q}^2 = (2\alpha, 2\alpha, 0)$. We have measured the integrated intensities of these satellites for the following values of the scattering angle: $19.3^\circ < \theta < 20.3^\circ$ and $22^\circ < \theta < 25^\circ$. Intensity was not found at any of these positions. This observation supports a multi-domain model, in which each of the four modulation wavevectors $(\pm\alpha, \pm\alpha, \gamma)$ occurs in a different domain.

In the final experiment the integrated intensities of the Bragg reflections were measured for $0^\circ < \theta < 40^\circ$. The main reflections at (h, k, l) together with one pair of satellites at $\pm(0.064, -0.064, -0.151)$ were measured in half a sphere ($l \leqslant 0$). This choice ensures that complete information on the scattered intensities from one domain is obtained, irrespective of the assumption on the symmetry. The data were corrected for the decay of the primary beam and for the remaining (but small) variations of the intensity control reflections. Finally, an absorption correction ($\mu = 467.8$ cm^{-1}) was applied using the shape of the crystal as determined from psi scans. A total of 4578 reflections were measured. These reduced to 1336 unique main reflections, all of which were classified as observed ($I > 2.5\sigma(I)$). Assuming two domains, each with a two-dimensional modulation, gave 2854 unique satellite reflections of which 2161 were observed (data set 1). Assuming four domains, each with a one-dimensional modulation, resulted in 2638 unique satellite reflections, of which 1983 were observed (data set 2). These data sets were used in the structure refinements.

3. Domain structure and symmetry

Below T_{CDW} the diffraction pattern has a tetragonal appearance with eight satellites around each main reflection. An integer indexing $(h, k, l, m_1, m_2, m_3, m_4)$ of all Bragg reflections can be obtained by using four modulation wavevectors, according to

$$\vec{H} = h\vec{a} + k\vec{b} + l\vec{c} + m_1\vec{q}_t^{\,1} + m_2\vec{q}_t^{\,2} + m_3\vec{q}_t^{\,3} + m_4\vec{q}_t^{\,4} \tag{1}$$

with

$$\begin{aligned}\vec{q}_t^{\,1} &= (0.0641, 0.0641, 0.1510)\\ \vec{q}_t^{\,2} &= (-0.0641, -0.0641, 0.1510)\\ \vec{q}_t^{\,3} &= (0.0641, -0.0641, 0.1510)\\ \vec{q}_t^{\,4} &= (-0.0641, 0.0641, 0.1510).\end{aligned} \tag{2}$$

Assuming tetragonal symmetry, the CDW corresponds to a four-q state with modulation wavevectors as defined in equation (2).

A detailed analysis of this model was not performed, as we believe on the basis of all experimental information available that the true symmetry is less than tetragonal.

On the basis of the I-centred unit cell the symmetry can be reduced to orthorhombic $I222$. The four modulation wavevectors in equation (2) are made equivalent by the twofold axes, and the crystal would consist of two domains, each one with a four-q state. Because all waves are still present in a single domain, there seems to be no incentive for making this reduction in point symmetry, and this possibility was not considered further. Along the same lines, a monoclinic symmetry $I2$ is possible with a 2D modulation, which was not considered further either.

Alternatively, a reduction of the symmetry towards orthorhombic is obtained when the diagonal twofold axes of $I422$ are kept instead of the twofold axes along the $\vec{a}_t$- and $\vec{b}_t$-directions. The space group of the basic structure is then $F222$, and the lattice is described by a $\sqrt{2}a_t \times \sqrt{2}a_t \times c_t$ supercell that is F-centred (figure 1):

$$\vec{a} = -\vec{a}_t + \vec{b}_t \qquad \vec{b} = \vec{a}_t + \vec{b}_t \qquad \vec{c} = \vec{c}_t. \tag{3}$$

The transformed modulation wavevectors are

$$\begin{aligned}\vec{q}^{\,1} &= (0, 0.128, 0.151)\\ \vec{q}^{\,2} &= (0, -0.128, 0.151)\\ \vec{q}^{\,3} &= (-0.128, 0, 0.151)\\ \vec{q}^{\,4} &= (0.128, 0, 0.151).\end{aligned} \tag{4}$$

The transformed F-centred cell, the transformed modulation wavevectors, and the transformed reflection indices $(H, K, L, M_1, M_2, M_3, M_4)$ were used to describe the different orthorhombic, monoclinic, and triclinic models for which structure refinements were performed (equations (3) and (4)).

For a basic structure with the space group $F222$, $\vec{q}^{\,1}$ and $\vec{q}^{\,2}$ are equivalent by symmetry, whereas $\vec{q}^{\,3}$ or $\vec{q}^{\,4}$ cannot be obtained from $\vec{q}^{\,1}$ by any symmetry operator in $F222$. It follows that a two-q state defined by $\vec{q}^{\,1}$ and $\vec{q}^{\,2}$ is present in one domain, while the other domain has a two-q state generated by $\vec{q}^{\,3}$ and $\vec{q}^{\,4}$. The main reflections of the two domains are superimposed, but the eight satellite reflections around each main reflection split into two groups of four reflections, that are due to the two different domains. Corresponding satellite reflections were used to determine the volume fraction ratio of the two domains as 1.015(5). That is, each of the two domains occupies half the volume of the specimen.

There exist two (3 + 2)-dimensional superspace groups based on $F222$, that differ in the translation components along the fourth and fifth coordinates. The superspace group with zero translation components has the symbol $F222(0, \beta, \gamma)$. We have given the superspace group with non-zero translation components the tentative symbol $F222(0, \beta, \gamma)00s$, where s indicates a translational component of $\frac{1}{2}$.

Monoclinic symmetry with a basic structure space group $F211$ (standard setting C2) results in four domains, each of which is modulated with one of the four modulation wavevectors. Again, the main reflections of all domains are superimposed, but now the eight satellite reflections around each main reflection split into four groups of two reflections $\pm\vec{q}$.

The volume fractions of the four domains now follow as 0.248(2), 0.247(2), 0.248(2), and 0.257(2). Within the accuracy of the experiment all domains occupy equal volumes. There is just one monoclinic superspace group, with the tentative symbol $F211(0, \beta, \gamma)$.

Further reduction of the symmetry towards triclinic leads to eight domains, and a one-q state again. Each satellite now has contributions of two domains, that cannot be further separated. The different possibilities for the symmetry of the CDW state are summarized in table 2.

Table 2. Characterization of the five possible symmetries of the CDW state of $(TaSe_4)_2I$. Given are the superspace group, the number of domains, the dimension of the modulation, and the reliability factors (R-values) of the main reflections and of the satellites for the best refinements within the different superspace groups.

Superspace group	Number of domains	Dimension of the modulation	R_F		wR_F^2	
			$m = 0$	$\|m\| = 1$	$m = 0$	$\|m\| = 1$
$P422(\alpha, \beta, \gamma)$	1	4	—	—	—	—
$F222(0, \beta, \gamma)$	2	2	0.085	0.099	0.092	0.090
$F222(0, \beta, \gamma)00s$	2	2	0.085	0.099	0.092	0.090
$F211(0, \beta, \gamma)$	4	1	0.090	0.082	0.096	0.080
$F1(0, \beta, \gamma)$	8	1	0.091	0.098	0.096	0.087

4. The modulated crystal structure

4.1. Structural parameters

The CDW is characterized by the presence of both a modulation of the electron density of the conduction band and a modulation of the positions of the atoms (periodic lattice distortion, PLD). The periods of the two modulations are equal, and they are given by the modulation wavevectors in equation (2). The structure of an incommensurately modulated crystal can be described by the superspace method [13], that is based on the indexing of the Bragg reflections with $3 + d$ integers. Depending on the assumption about the number of domains, $d = 1$, $d = 2$, or $d = 4$ is obtained for $(TaSe_4)_2I$. The symmetry is given by a $(3 + d)$-dimensional superspace group.

The positions of the atoms are given as the sum of a basic structure position and a shift due to the modulation, according to [14, 15]

$$\begin{aligned} \vec{x}^{\mu} &= \vec{\bar{x}}^{\mu} + \vec{u}^{\mu}(\bar{x}_4 \ldots, \bar{x}_{3+d}) \\ \vec{\bar{x}}^{\mu} &= \vec{L} + \vec{x}^{0\mu} \\ \bar{x}_{3+j} &= t_j + \vec{q}^{\,j} \cdot \vec{\bar{x}}^{\mu} \end{aligned} \tag{5}$$

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 $\vec{u}^{\mu}(\bar{x}_4, \bar{x}_{3+d})$ are periodic functions of their arguments with period 1. $\bar{x}_{3+j}$ for $j = 1, \ldots, d$ are the additional coordinates in $(3 + d)$-dimensional superspace. The parameters t_j with $j = 1, \ldots, d$ 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 Fourier series. For a two-dimensional modulation this is

$$u^{\mu}_{\alpha}(\bar{x}_4, \bar{x}_5) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} A^{\mu}_{n_1,n_2,\alpha} \sin(2\pi n_1 \bar{x}_4 + 2\pi n_2 \bar{x}_5) + B^{\mu}_{n_1,n_2,\alpha} \cos(2\pi n_1 \bar{x}_4 + 2\pi n_2 \bar{x}_5) \quad (6)$$

where $\alpha = x, y, z$. The pairs of integers (n_1, n_2) define the order of the harmonic. For both orthorhombic symmetries only the terms (1, 0) and (0, 1) have been used. For monoclinic and triclinic symmetries the modulation is one dimensional, and only the term with $n_1 = 1$ and $n_2 = 0$ was used.

4.2. Structure refinements

The different possibilities for the symmetry of the CDW state were tested by complete structure refinements of the incommensurately modulated structures.

In the case of orthorhombic, monoclinic, and triclinic symmetries the modulation is a two-q or one-q state, and the structure is described in two- or one-dimensional superspace. The problem of the twinning was accounted for by the following procedure. The basic structure coordinates, temperature factors, and the scale factor were refined against the main reflections only, using restrictions according to the space group $I422$. This approximation is based on the observation that the deviations from tetragonal symmetry originate in the modulation pattern, and that the basic or average structure will have $I422$ symmetry to a good approximation. In a second step the modulation parameters of the first-order harmonic were refined against the satellite reflections of one domain (equation (6)). The scale factor for these satellites was taken equal to the scale factor of the main reflections multiplied by the occupation fraction of one domain (equal to 0.5 or 0.25). The two refinements were alternated until convergence was achieved. The standard deviations that we report here are based on this block-type refinement.

Following this procedure, refinements were performed for structure models according to the four possible superspace groups. Good fits to the data of comparable qualities were obtained for all symmetries (table 2), and the R-value cannot be used to select the correct structure model. The similarities of the different refinements go beyond those of the R-factors. The modulation amplitudes of the two orthorhombic symmetries have equal values, while they are half the size of the corresponding amplitudes in the monoclinic and triclinic symmetries. However, the structure models are completely different, because the monoclinic and triclinic structures are one-q states, while both orthorhombic structures are two-q states. The difference between the two orthorhombic structure models is in the phase relation between the two waves. Only the triclinic structure model appeared to correspond to a small deviation from the structure with monoclinic symmetry, and this is the reason that we have discarded the triclinic symmetry.

The selection of the correct structure model amongst the two orthorhombic symmetries and the monoclinic symmetry must be made on the basis of information other than refinement R-values. The observed broadening of the reflections below T_{CDW} indicates a lowering of the lattice symmetry, and either orthorhombic or monoclinic would be possible. The absence of mixed higher-order satellites is in accordance with only one wave being present in each domain, and the orthorhombic symmetries can be discarded. In this respect it is noted that both in our experiments with a scintillation detector as well as in experiments performed by Favre-Nicolin using imaging plates [16,17] the mixed higher-order satellites were not observed. Furthermore, Lorenzo *et al* [10] found unequal intensities for satellite reflections that were related by the diagonal twofold axes, indicating that they have studied a crystal with monoclinic symmetry and domains with unequal occupations.

Finally, it is noted that the monoclinic structure gives a better fit to the satellite reflections than the orthorhombic structures do (table 2). All these observations lead to the conclusion that the true modulated structure in the CDW state has monoclinic symmetry $F211(0, 0.128, 0.151)$. The structural parameters are given in the tables 3, 4, and 5. All coordinates are given with respect to the F-centred unit cell and the modulation wavevector $\vec{q}^1$ (equations (3) and (4)).

Table 3. Fractional atomic coordinates of the basic structure parameters for the final refinement of the modulated structure with monoclinic symmetry (model 3, space group $F2$, a-axis unique). Standard deviations are given in parentheses. Numbers without standard deviations are fixed by symmetry.

Atom	x^0	y^0	z^0
I1	0	0	0.15495(4)
Ta1	0.25	0.25	0
Ta2a	0.25	0.25	0.25
Ta2b	0.25	−0.25	0.25
Se1a	0.21645(2)	0.09475(2)	0.88064(2)
Se1b	−0.21645( )	−0.09475( )	0.88064( )
Se1c	0.09475( )	−0.21645( )	0.88064( )
Se1d	−0.09475( )	0.21645( )	0.88064( )
Se2a	0.38012(2)	0.16377(2)	0.87003(2)
Se2b	−0.38012( )	−0.16377( )	0.87003( )
Se2c	0.16377( )	−0.38012( )	0.87003( )
Se2d	−0.16377( )	0.38012( )	0.87003( )

Table 4. Temperature parameters of the atoms for the final refinement of the modulated structure with monoclinic symmetry (model 3, space group $F2$, a-axis unique). The parameters for the atoms that are not shown follow by symmetry. Standard deviations are given in parentheses.

Atom	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
I1	0.0310(2)	0.0310( )	0.0452(3)	0	0	0
Ta1	0.0028(1)	0.0028( )	−0.0090(2)	0.0037(1)	0	0
Ta2a	0.0051(2)	0.0049(2)	−0.0101(2)	0	0	0
Se1a	0.0044(2)	0.0051(1)	−0.0012(2)	0.0012(1)	−0.0003(1)	0.0006(1)
Se2a	0.0035(2)	0.0042(1)	−0.0010(2)	−0.0015(1)	0.0001(1)	0.0003(1)

The problem with all of the refinements was that some temperature factors were not positive definite. They can be ascribed to a non-perfect absorption correction. The important point is that these problems are independent of the symmetry that was used for the refinement, and that they were independent of whether the average structure or modulated structures were refined. The selection of the symmetry and the determination of the values of the modulation parameters should therefore still be accurate.

5. Discussion

5.1. Description of the structure

The crystal structure of $(TaSe_4)_2I$ in its CDW state has been determined to be a one-q state with monoclinic symmetry and four orientational domains. The sudden broadening of the Bragg reflections below T_{CDW} clearly shows that the lattice symmetry is lower than tetragonal. The

Table 5. Modulation parameters for the independent atoms for the final refinement of the modulated structure with monoclinic symmetry (model 3, space group $F2$, a-axis unique). Values are in ångströms according to equation (6). Standard deviations are given in parentheses. Numbers without standard deviations are fixed by symmetry.

Atom	A_n^x (Å)	A_n^y (Å)	A_n^z (Å)	B_n^x (Å)	B_n^y (Å)	B_n^z (Å)
I1	−0.0041(8)	−0.0098(4)	0.0017(6)	0.1389(7)	0.0000(4)	−0.0002(7)
Ta1	−0.0001(5)	−0.0098(2)	−0.0008(4)	0.1345(7)	0.0016(2)	0.0276(3)
Ta2a	0	−0.0100(3)	−0.0252(5)	0.1327(9)	0	0
Ta2b	0	−0.0099(3)	0.0235(5)	0.1322(9)	0	0
Se1a	−0.0014(11)	−0.0166(4)	−0.0013(5)	0.1222(13)	−0.0001(4)	0.0064(5)
Se1b	0.0060(11)	−0.0042(4)	0.0038(5)	0.1418(13)	−0.0013(4)	0.0090(5)
Se1c	0.0181(11)	−0.0123(4)	−0.0084(6)	0.1274(12)	−0.0018(4)	−0.0077(6)
Se1d	−0.0224(10)	−0.0095(4)	0.0098(6)	0.1411(13)	0.0012(4)	−0.0075(6)
Se2a	0.0040(10)	−0.0097(4)	0.0129(6)	0.1153(11)	0.0040(4)	−0.0002(6)
Se2b	−0.0020(10)	−0.0104(4)	0.0013(6)	0.1500(12)	−0.0026(4)	0.0009(6)
Se2c	0.0028(10)	−0.0081(4)	−0.0100(6)	0.1126(11)	−0.0073(4)	−0.0032(6)
Se2d	0.0027(11)	−0.0105(4)	−0.0004(6)	0.1446(12)	0.0047(4)	0.0000(6)

absence of mixed higher-order satellites in the x-ray diffraction was used as evidence for the symmetry being monoclinic as opposed to orthorhombic. Although some doubt might still exist concerning this conclusion, it is noticed that all available experimental information (present results and references [10, 16, 17]) agrees with monoclinic symmetry and does not give any evidence for orthorhombic symmetry.

The principal part of the modulation is found to be a displacement along $\vec{a}$. All atoms have about the same amplitude of about 0.13 Å and the same phase (table 5). This finding explains why reference [9] obtained a good fit to a data set of six satellite reflections, using one overall modulation parameter for all atoms. Together with the fact that the modulation wavevector is very short, this shows that the major part of the modulation is an acoustic-like displacement wave with a polarization mainly along $\vec{a}$.

Amplitudes of secondary importance (0.025 Å) are found for the z-displacements of the Ta atoms. Displacements of neighbouring atoms within one chain are approximately 90° out of phase (table 5), and these displacements can be interpreted as representing the CDW on the Ta chains. A more detailed picture of the structure of the CDW state can be obtained from the so-called t-plots of the interatomic distances [15].

As an example, consider the distance between atoms Ta1 and Se1a (table 6). Neighbouring atoms are at a distance of about 2.65 Å, but the precise values are different in each unit cell (variation of L_i in equation (5)). All these distances are summarized in an interval $[0, 1\rangle$ for t (trace 1 in figure 3). Distances on a single curve which are close in t-value refer to atom pairs far apart in the structure. However, the curves corresponding to different distances are correlated, and figure 3 displays the variation in the distances towards the eight Se atoms in the first coordination sphere of Ta1. It is found that these variations are small, with a total range of about 0.1 Å. The maximum value of the variation of a single contact is even smaller at 0.06 Å. These observations reflect the fact that the short Ta-to-Se contacts represent chemical bonds, and that these chemical bonds remain in the modulated structure. Similar features are observed for the coordination polyhedra of Ta2a and Ta2b (figures 4 and 5).

It has been proposed that the structure of $(TaSe_4)_2I$ contains Se_2^{2-} anions [2]. In the basic structure such a pair is formed by a Se1 and a Se2 atom at a distance of 2.39 Å. In the modulated

Table 6. Selected interatomic distances (Å). There are minor differences between distances involving atoms labelled a, b, c, or d.

Atom 1	Atom 2	Basic structure	Minimum	Maximum	Variation
Ta1	Ta2†	3.19	3.08	3.30	0.22
Ta1	Se1†	2.62	2.59	2.65	0.06
Ta1	Se2†	2.67	2.64	2.70	0.06
Ta2	Se1†	2.70	2.67	2.74	0.07
Ta2	Se2†	2.59	2.56	2.62	0.06
Se1	Se2†	2.39	2.38	2.40	0.02
Se1	Se2‡	3.30	3.29	3.31	0.02
Se1	Se2†	3.49	3.44	3.55	0.11
I	Se1	3.20	3.17	3.24	0.07
I	Se2	3.86	3.81	3.92	0.11

† Within a chain.
‡ Between chains.

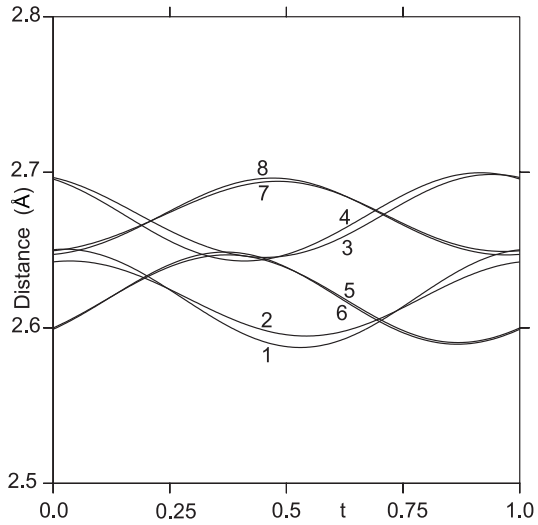

Figure 3. Interatomic distances between Ta1 and the eight surrounding Se atoms as a function of the fourth superspace coordinate t (equation (5)). The numbers 1 to 8 refer to the distances of Ta1 and the atoms at $z \approx -0.12$: Se1a (1), Se1b (2), Se2a (3), Se2b (4), and the atoms at $z \approx 0.12$: Se1c (5), Se1d (6), Se2c (6), Se2d (8).

structure there are four crystallographically independent Se_2^{2-} anions, but the t-plot shows that all of them are at virtually constant distances, with a maximum variation of 0.02 Å (figure 6 and table 6). This result gives additional support for the presence of Se_2^{2-} anions, and it shows that these anions are preserved in the modulated structure.

The chains of Ta atoms parallel to the $\vec{c}$-axis support the notion of quasi-1D electron bands, with shortest distances between Ta1 and Ta2 in the basic structure. The sequence of Ta atoms along a chain in the monoclinic superstructure is $(\text{–Ta1–Ta2b–Ta1–Ta2a–})_\infty$. In figure 7 the t-plot is given of the seven short Ta–Ta distances within two periods along a chain. This plot shows that when two consecutive distances are shorter than average (e.g. the distances numbered 2 and 3 for point A), the neighbouring distances (numbered 1 and 4) are longer than average. This means that at point A a cluster of three Ta atoms is formed, that consists of Ta2b–Ta1–Ta2a. Again at point A, the distances 5 and 7 are longer than average, while the

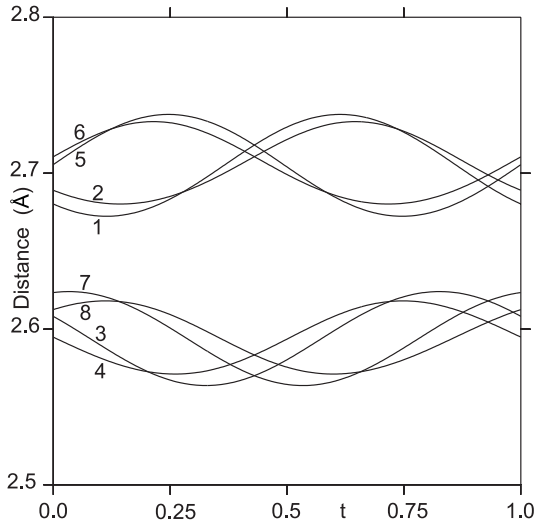

Figure 4. Interatomic distances between Ta2a and the eight surrounding Se atoms as a function of the fourth superspace coordinate t (equation (5)). The numbers 1 to 8 refer to the distances of Ta2a and the atoms at $z \approx 0.12$: Se1c (1), Se1d (2), Se2c (3), Se2d (4), and the atoms at $z \approx 0.37$: Se1c (5), Se1d (6), Se2d (7), Se2d (8).

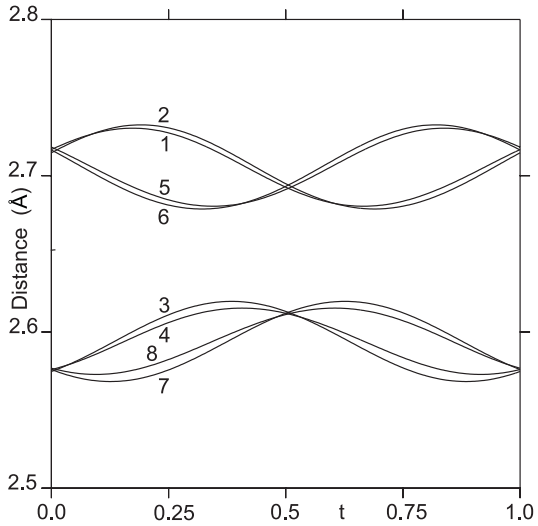

Figure 5. Interatomic distances between Ta2b and the eight surrounding Se atoms as a function of the fourth superspace coordinate t (equation (5)). The numbers 1 to 8 refer to the distances of Ta2b and the atoms at $z \approx -0.38$: Se1a (1), Se1b (2), Se2a (3), Se2b (4), and the atoms at $z \approx -0.12$: Se1a (5), Se1b (6), Se2a (6), Se2b (8).

distance numbered 6 has attained the shortest possible value. Thus it is found that for t-values around point A, the chain separates into clusters of three Ta atoms, isolated Ta atoms, and pairs of Ta atoms. For t-values around the point A′ and other A-type points, the situation is similar, but the clusters involve different Ta atoms. The points of type B represent transition points between clusters formed from one set of atoms and clusters formed from other atoms.

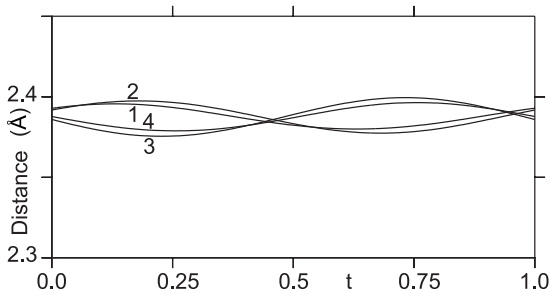

Figure 6. Interatomic distances between Se atoms forming Se_2^{2-} pairs as a function of the fourth superspace coordinate t (equation (5)). The distance plots are numbered as follows: 1: Se1a–Se2a; 2: Se1b–Se2b; 3: Se1c–Se2c; 4: Se1d–Se2d.

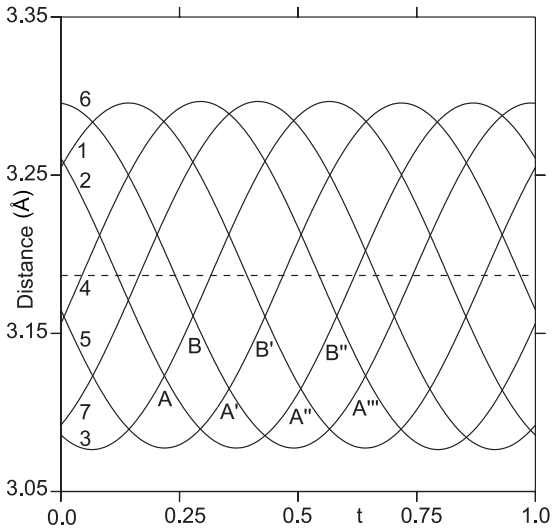

Figure 7. Interatomic distances between consecutive Ta atoms along a chain as a function of the fourth coordinate t (equation (5)). Shown are the seven distances along the chain of eight atoms Ta1 ($z = -0.25$)–Ta2b–Ta1–Ta2a–Ta1–Ta2b–Ta1–Ta2a ($z = 1.5$). They are numbered 1 to 7 in this order. Special t-values are denoted by letters A, A′, ... The dashed line denotes the average distance of 3.18 Å, which is the same for all atom pairs.

Consideration of all variations in the shortest Ta–Ta contacts thus shows that the superstructure involves the formation of clusters of three Ta atoms, the formation of Ta-atom pairs, and the presence of isolated Ta atoms. This is considered evidence that the phase transition represents the formation of a CDW on the chains of Ta atoms. The CDW modulation should not be interpreted as the formation of tetramers, as was suggested previously [16, 17].

The effect of the major part of the displacement on the distances between neighbouring atoms is very small. This has been checked by comparing t-plots computed for the true modulated structure with t-plots in which only the z-displacements were taken into account (not shown). For the domain that is described here, the modulation wavevector is (0, 0.128, 0.151) and the major displacement amplitudes are parallel to $\vec{a}$. This shows that the acoustic part of the modulation is almost exclusively a transverse wave. The longitudinal part of the modulation wave mainly relates to the CDW.

5.2. Landau theory for the phase transition

A theoretical description of the phase transition, based on a Landau type of free energy, has been given by Lorenzo *et al* [10, 11]. They used a free-energy expansion based on two order parameters corresponding to different normal modes of the space group $I422$ at the zone centre.

Here it is noted that the CDW is an incommensurate modulation, and the normal modes to be considered are those corresponding to the irreducible representations (irreps) labelled by the wavevector $\vec{q}^1 = (\alpha, \alpha, \gamma)$. Following [18] and the analysis for α-U by Walker [19], it is easy to derive that the distortions are described by a four-dimensional complex order parameter, defined as

$$\psi_j = \psi_j^0 \exp(\vec{q}^j \cdot \vec{r}) \tag{7}$$

where $\vec{q}^j$ $(j = 1, \ldots, 4)$ are given in equation (2).

The free energy (F) up to fourth order, that is invariant under the operations of the space group $I422$, is

$$\begin{aligned} F = A \left\{ \sum_{j=1}^{4} |\psi_j^0|^2 \right\} + B_1 \left\{ \sum_{j=1}^{4} |\psi_j^0|^2 \right\}^2 + B_2 \left\{ |\psi_1^0|^2 |\psi_2^0|^2 + |\psi_3^0|^2 |\psi_4^0|^2 \right\} \\ + B_3 \left\{ |\psi_1^0|^2 |\psi_3^0|^2 + |\psi_1^0|^2 |\psi_4^0|^2 + |\psi_2^0|^2 |\psi_3^0|^2 + |\psi_2^0|^2 |\psi_4^0|^2 \right\} \\ + B_4 \left\{ \psi_1^0 \psi_2^0 \psi_3^{0*} \psi_4^{0*} + \psi_1^{0*} \psi_2^{0*} \psi_3^0 \psi_4^0 \right\}. \end{aligned} \tag{8}$$

A and B_k are real parameters, and A is assumed to change sign at the phase transition. B_1 is assumed to be sufficiently large and positive that for $T < T_{CDW}$ a minimum of the free energy is obtained at finite $|\psi_j|$. Dependent on the values of B_2, B_3, and B_4, four types of solution exist for $T < T_{CDW}$, that are classified as follows:

(a) $B_2 > 0$, $B_3 > 0$, and $B_4 > 0$. A minimum of the free energy is obtained when only one of the four parameters ψ_j^0 is non-zero. This is a single-q state, and there are four domains corresponding to the four order parameters. This solution corresponds to the actual structure with monoclinic symmetry, as determined in the present paper.

(b) $B_2 < 0$, $B_3 > \frac{1}{2}B_2$, and $B_4 > 0$. A minimum of the free energy is obtained for $|\psi_1^0| = |\psi_2^0| \neq 0$ (the first domain) or for $|\psi_3^0| = |\psi_4^0| \neq 0$ (the second domain). The modulation is a two-q state and there are two domains. With different sets of phases of the order parameters, these solutions correspond to the two orthorhombic superspace groups.

(c) $B_2 > 0$, $B_3 < 0$, and $B_4 > 0$. The minimum of the free energy is obtained for a two-q state with monoclinic symmetry. There are four domains.

(d) $B_4 < 0$. Depending on the values of the parameters B_2 and B_3, the minimum of the free energy may correspond to (b) or (c), or the solution is the four-q state with $|\psi_1^0| = |\psi_2^0| = |\psi_3^0| = |\psi_4^0|$. This solution corresponds to the structure model for the CDW state given by the $(3 + 3)$-dimensional tetragonal superspace group.

From this analysis it follows that the one-q state with monoclinic symmetry corresponds to a modulation according to a single irrep of $I422$. From the point of view of symmetry, the phase transition thus is allowed to be second order. Furthermore, it is found that the hypothetical orthorhombic and tetragonal symmetries for the CDW state could be obtained through a second-order phase transition. They might give the symmetries of the CDW state at elevated pressures.

6. Conclusions

We have determined the incommensurately modulated structure of $(TaSe_4)_2I$ as it exists below the transition temperature $T_{CDW} = 263$ K. It is shown that the modulation splits into two parts. The major part of the modulation involves equal displacements on all atoms of about 0.13 Å in a transverse direction. A modulation of secondary importance is found as displacements of about 0.025 Å on the Ta atoms only, parallel to the direction of the chains. This latter modulation is taken as evidence that a true CDW exists below T_{CDW}.

A peculiar feature of the phase transition is the appearance of the large acoustic-like modulation with no apparent relation to the CDW. A second peculiar feature of the CDW is the transverse component of the CDW wavevector. These features represent the relative phases of the CDW on neighbouring chains, and might be the result of the interactions between the CDW and the acoustic wave.

The analysis of the variations of the interatomic distances within the incommensurately modulated state shows that the CDW corresponds to the formation of clusters of three Ta atoms, alternating with clusters of two Ta atoms and isolated atoms. A Landau free-energy description is developed, that shows that symmetry arguments allow a second-order phase transition towards the CDW state.

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