# On the Neutron Scattering Study of the CDW/PSD Transition in 2H - $TaSe_2$ and 2H - $NbSe_2$ by Moncton, Axe and DiSalvo

by

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Abstract

Re-investigation of published neutron scattering data on 2H-$TaSe_2$ shows that the published periodic structural distortion phase angles are incorrect and thus so are the accepted atomic displacements. Furthermore an ambiguity of $\pm\pi$ leaves the sense of the atomic displacements undetermined. This leads to a new multi-domain model for the incommensurate superlattice involving contributions from both the preferred phase $\Phi$ and $\Phi+\pi$. This $\pm\pi$ ambiguity is not finally resolved until the incommensurate/commensurate transition.

The atomic displacements involved in the commensurate CDW/PSD phase of 2H - $TaSe_2$ were first determined by a combination of the neutron scattering study of Moncton et al[1] and the Raman scattering study of Holy et al[2]. Moncton et als's structure factor expressions used the atomic displacements given by

$$\underset{\sim}{U}_{\ell\kappa} = \sum_{\underset{\sim}{q}} \tfrac{1}{2} [\underset{\sim}{e}_{\nu\kappa}(\underset{\sim}{q}) e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{\ell}} + \underset{\sim}{e}^{*}_{\nu\kappa}(\underset{\sim}{q}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_{\ell}}] \qquad (1)$$

for the $\kappa^{th}$ atom in the $\ell^{th}$ unit cell. The eigenvector $\underset{\sim}{e}_{\nu\kappa}(\underset{\sim}{q})$ has $\Sigma_1$ symmetry and gives characteristic atomic displacements as shown in Fig. (7) of Moncton et al. Note that $\underset{\sim}{e}_{\nu\kappa}(\underset{\sim}{q})$ points in the direction of $\underset{\sim}{q}$. By fitting the structure factor data, the independent parameters necessary to specify the eigenvector, $\underset{\sim}{e}_{\nu\kappa}(\underset{\sim}{q})$, were determined and listed in Table 1 of Moncton et al[1]. However this fit is insensitive to a change in the overall phase of the eigenvector $\underset{\sim}{e}_{\nu\kappa} \rightarrow e^{i\phi}\underset{\sim}{e}_{\nu\kappa}$. The Raman scattering study[2] showed the presence of an inversion centre within the commensurate phase and this is consistent only with the unknown phase $\phi$ being either $+90^{o}$ or $-90^{o}$. Moncton et al[1] chose $\phi = -90^{o}$. Given $\phi$, the resultant atomic displacement pattern was drawn in Fig. (9) of Moncton et al[1].

This would seem to have cleared up the question of the atomic displacements. There has, however, existed a degree of confusion in the existing literature as to the listed phase angles in Table 1 of Moncton et al. Firstly, whether they are consistent with the atomic displacement pattern drawn in Fig. (9) of the same paper and secondly whether they are consistent with the experimentally determined superlattice structure factors.

In particular Holy et al[2] gives the displacement of the $i^{th}$ Ta ion in the $\ell^{th}$ layer ($\ell = \pm 1$) as

$$\underset{\sim}{U}_{\ell}(\underset{\sim}{R}_i) = \mathrm{Im} \sum_{j=1}^{3} (\underset{\sim}{q}_j/q)\, \phi_{\ell}^{j} \exp(i\underset{\sim}{q}_j.\underset{\sim}{R}_i) \qquad (2)$$

where $\phi_{\ell}^{j}$, the complex amplitude of the distortion, is given as $\phi_{\ell}^{j} = \varepsilon a_o e^{\ell(3.94i)}$. Within the notation of Moncton et al this corresponds to $\varepsilon_{1x}^{1} = \varepsilon a_o = 0.048$ Å and $\phi_{1x}^{1} = 3.94$ radians = $(\pi + 0.80)$ radians or equivalently $\varepsilon_{1x}^{1} = -0.048$ Å and $\phi_{1x}^{1} = +0.80$ radians. i.e. $\phi_{1x}^{1}$ is given the opposite sign to the value listed in Moncton et al's Table 1. Wilson[3], in his Table 1, states that this is because ...."the Ta phase angle, $\phi_{1x}^{1}$, in the pre-print version of Ref. 1(b)[4], erroneously carried a minus sign". Wilson[3] has calculated the atomic displacements assuming the correctness of Moncton et als phase angles. He has used a slightly different notation for the unit cell, however a comparison of Fig. (1) of Wilson[3] with Figures (7) and (9) of Moncton et al[1] shows which atoms are equivalent. If we compare the sign of the Se $\underset{\sim}{c}$-axis vertical displacements of atoms e, f and g in Wilson's Fig. (7) with the corresponding atoms in Moncton et al's Fig. 9(d) we find that the former are down, down and up whereas the latter are up, down and up. Thus we have a clear discrepancy between the phase angles, as listed in Table 1, and the atomic displacements, as drawn in Fig. (9) of Moncton et al. Similarly Wilson[3] calculates the magnitudes of the horizontal displacements (parallel to $\underset{\sim}{q}_1$) of atoms e, f and g as +0.012, +0.003 and -0.015 Å in his Table II yet Fig. 9(b) of Moncton et al clearly shows the displacement magnitude of atom e being much smaller than that of the other two.

As a result of this confusion it was felt necessary to re-fit the structure factor data. The presence of the inversion centre was assumed and thus only Layer I displacements need specifying. In general then the atomic displacements took the form:

$$\underset{\sim}{U}_{Ta}(\underset{\sim}{r}_{Ta}) = \sum_i \hat{\underset{\sim}{q}}_i \, \varepsilon^1_{1x} \cos(\underset{\sim}{q}_i \cdot \underset{\sim}{r}_{Ta} + \phi^1_{1x} + \Phi)$$

and

$$\underset{\sim}{U}_{Se}(\underset{\sim}{r}_{Se}) = \sum_i \hat{\underset{\sim}{q}}_i \, \varepsilon^1_{3x} \cos(\underset{\sim}{q}_i \cdot \underset{\sim}{r}_{Se} + \phi^1_{3x} + \Phi) + \sum_i \hat{\underset{\sim}{z}} \, \varepsilon^1_{3z} \cos(\underset{\sim}{q}_i \cdot \underset{\sim}{r}_{Se} + \phi^1_{3z} + \Phi)$$

where Table I of Moncton et al gives

$$\left.\begin{array}{ll} \varepsilon^1_{1x} = -0.048 \text{ Å}, & \phi^1_{1x} = -0.80 \text{ rads.}, \\ \varepsilon^1_{3x} = +.009 \text{ Å}, & \phi^1_{3x} = 0.36 \text{ rads.}, \\ \varepsilon^1_{3z} = -0.0172 \text{ Å} \text{ and} & \phi^1_{3z} = -0.28 \text{ rads.} \end{array}\right\} \quad (3)$$

Moncton et al[1] chose $\Phi$ to be $-90^\circ$ to ensure inversion symmetry.

We calculated the superlattice intensities for 2 choices of phase angles.

(1) For the phase angles as given above, corresponding to Table I of Moncton et al[1] and

(2) For $\phi^1_{1x} = -0.80$ rads., $\phi^1_{3x} = 1.036$ rads., and $\phi^1_{3x} = +0.28$ rads. We are unable to normalize these $|F|^2$ values as this would require comparison with the Bragg peaks. However this is unimportant as Moncton et als Fig. (8) has a $\log_{10}|F|^2$ vertical scale. Thus suppose the

normalization constant is K. Then $|F|^2_{\text{normalized}} = K|F|^2_{\text{calculated}}$

$$\therefore \log_{10}|F|^2_{\text{normalized}} = \log_{10}K + \log_{10}|F|^2_{\text{calculated}}$$

and the normalization constant merely moves the $\log_{10}|F|^2$ versus superlattice reflection curve up and down the vertical axis. Fig. (1) shows a comparison between the experimental superlattice structure factors and the calculated ones for the above 2 cases with K chosen such that experimental and calculated intensities are the same for the (206) reflection.

Quite clearly the second case is the correct one and corresponds to the fit obtained in Fig. (8) of Moncton et al. We do not challenge this fit then but rather claim that the phase angles as listed are inconsistent with the fit and need adjustment to case (2) above

$$\text{i.e. } \phi^1_{1x} = -0.80 \text{ rads.}, \quad \phi^1_{3x} = 1.036 \text{ rads.}, \text{ and } \phi^1_{3z} = +0.28 \text{ rads.} \quad (4)$$

It should also be pointed out that the above fit is just as good if we reverse the atomic displacements corresponding to a choice of $\phi = +90^\circ$ and not $\phi = -90^\circ$. Thus there remains an ambiguity in the determination of the sense of these atomic displacements.

In a recent paper[5] we attempt to resolve this ambiguity by electrostatic and short-range energy calculations of the phase dependence of the energy of the periodic structural distortion wave. There is a fine balance between Se-Se short-range repulsion and the

CDW-Ta ion interaction energy terms. The analysis reveals the phase dependence of the various terms and allows the different contributions to the stability of the distortion waves to be discussed more completely than previously. It is shown that the phasing of the PSD and CDW waves is determined, except for an ambiguity of $\pi$ rad, by minimizing (harmonic) energy terms which vary as the square of the PSD wave amplitude. This phasing is established above the normal/incommensurate onset temperature To. The remaining $\pi$ ambiguity is not resolved finally until the incommensurate/commensurate transition temperature $T_c$, by minimizing the (anharmonic) energy terms which vary as the third power of the PSD wave amplitude.

Our analysis leads naturally to a new structural model for the incommensurate superlattice for $T_c \leq T \leq T_o$, involving a multi-domain structure with contributions from both the preferred phase $\phi$ and $\phi+\pi$. These differ essentially only in the sense of the PSD displacements in alternate domains (Fig. 2a). The model is the logical consequence of a softening mode phase transition and provides a very simple structural explanation for the observed incommensurate superlattice periodicity, $3.08a_{\hat{x}}$ at onset, and its temperature dependence [5,6]. In order to explain the quasi-continuous variation of $q$ and $\delta$ with T, and to provide a general explanation of the observed diffraction patterns, it is necessary to invoke disorder of the domain structure. It is easy to build both spatial and temporal disorder into the model so that the domain centres do not fall on a regular superlattice (Fig. 2b).

Acknowledgements

This work was supported by the Australian Research Grants Committee and The University of Melbourne. RLW is grateful for a Commonwealth Post-Graduate Award.

## References

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Figure Captions

Figure 1: Comparison of observed (indicated by dot with error bar) and computed structure factors for the commensurate superlattice structure of 2H-$TaSe_2$. The dotted line corresponds to the amplitudes and phases listed in Table 1 of reference [1], whereas the full line corresponds to our revised values of the phases ($\phi_{1x}^{1}$ = -0.80 rad; $\phi_{3x}^{1}$ = 1.036 rad and $\phi_{3z}^{1}$ = +0.28 rad). Clearly the latter provides the better fit.

Figure 2a: Schematic representation of electron density distribution in the CDW in the incommensurate superlattice structure regime $T_c \lesssim T \lesssim T_o$. The PSD displacements ($\phi = 210^{o}$) corresponding to the black domains are favoured by the anharmonic interaction energy terms. Thus as T is lowered the black domains will extend at the expense of the white domains ($\phi = \underline{210^{o}} + \pi$). Drawings of other intermediate stages are given in ref. (5).

Figure 2b: Domain model showing disorder with respect to the domain centres. Domain walls may easily propagate sideways, allowing both spatial and temporal disorder.

-0.07
-0.03
-0.02
0.09
$F_o^2 - F_c^2$
102
104
105
106
107
108
200
201
202
203
205
206
400
401
402
403
500
501
200
400
500
$\bar{1}30$
130
$\bar{1}60$
230
$\bar{2}60$
hkl

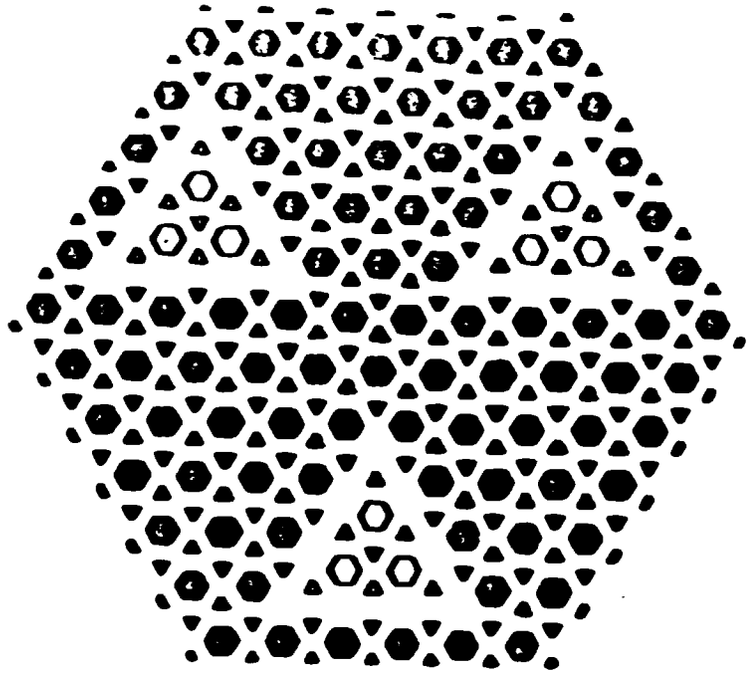

Fig 2a.

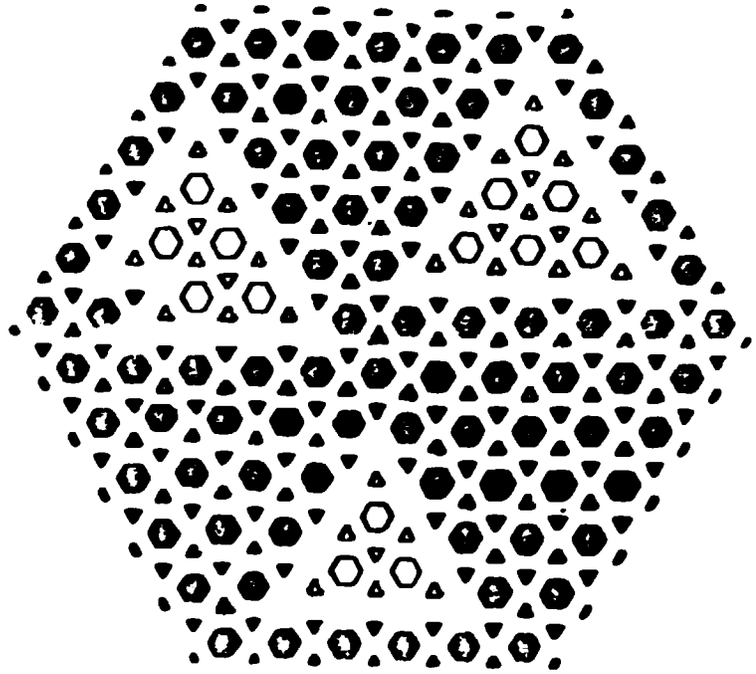

Fig. 2 b