

## Order-Disorder Phase Transition in Stage-2 $\text{Ag}_x\text{TiS}_2$

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### Abstract

Based on the phenomenological Landau-Lifshitz theory of phase transitions it is shown that the order-disorder transition observed around 200 K in the intercalated silver atoms between  $\text{TiS}_2$  sandwiches for a stage-2  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ) system belongs to the three-state Potts universality class. The corresponding critical exponents can be measured experimentally using synchrotron radiation.

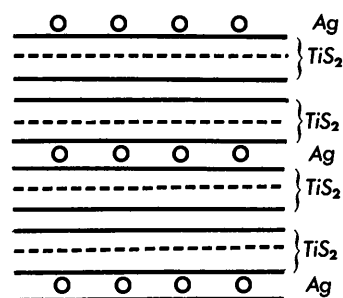
### Introduction

Intercalated transition-metal dichalcogenides ( $\text{Li}_x\text{TiS}_2$ ,  $\text{Ag}_x\text{TiS}_2$ , etc.) are interesting materials from both theoretical and applications points of view. In technology they find application as cathodes in high-energy-density batteries. On the other hand their quasi-two-dimensional (Q2D) properties are of keen theoretical interest. A recent X-ray diffraction experiment (Ohshima & Moss, 1983) at room temperature of disordered stage-2  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ) revealed that the Ag atoms in the intercalated (basal) plane occupy the octahedral sites (Fig. 1). As the temperature is lowered, Ag atoms order in the  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  two-dimensional structure in the intercalated plane at an ordering temperature ( $T_c < 200$  K). We are interested in the nature of this particular order-disorder phase transition.

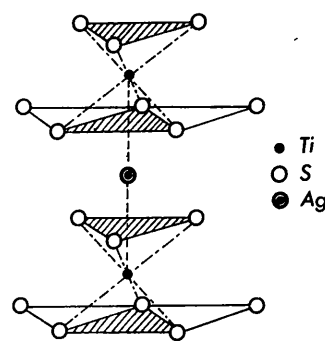
Scholz & Frindt (1980) proposed that the Ag atoms prefer octahedral sites in the basal plane between every two  $\text{TiS}_2$  sandwich (Fig. 1a) layers and that there is no change of the host-lattice stacking, i.e. the Ag atoms occupy positions in the sulfur van der Waals gap directly between Ti atoms (Fig. 1b) which are positioned vertically above and below. The vibrations of the atoms at their equilibrium lattice sites in the intercalated plane were found to be large, indicating both weak bonding and correspondingly rapid diffusion as well as large static displacements of the Ag atoms from the average lattice sites (Ohshima & Moss, 1983). The diffuse scattering originating from correlations among intercalated Ag atoms in the basal plane can be treated as purely 2D scattering, because the 'correlation length' normal to the layer between Ag-atom planes is very short compared with the nearest-neighbor Ag-plane separation (Ohshima &

Moss, 1983). This feature of the rodlike diffuse scattering suggests that a disordered 2D lattice gas is appropriate to describe this system.

At low temperatures there is qualitative evidence (Ohshima & Moss, 1983) that the elastic displacements favor the  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  2D ordering. The conduction electrons are contributed mainly to the Ti in the  $\text{TiS}_2$  layers in the Q2D  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ) metallic system. The displacements of those Ag atoms which occupy the nearest-neighbor  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  2D ordered lattice points is expansive (repulsive interaction) while the next-nearest-neighbor occupancy is contractive (attractive interaction). This indicates that the low-temperature 2D ordered phase is stable.



(a)



(b)

Fig. 1. (a) Schematic diagram showing intercalation of Ag atoms in the basal plane between alternate layers of a  $\text{TiS}_2$  sandwich in the disordered stage-2  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ). (b) The Ag atoms occupy positions in the sulfur van der Waals gap directly between Ti atoms, which are positioned vertically above and below.

### Order-disorder transition

The experimental observations mentioned above indicate that the sulfur bilayer which sandwiches Ag atoms can be considered as a separate two-dimensional system. At room temperature intercalated Ag atoms can occupy any site on a triangular lattice at random (Figs. 1a and 2a). This disordered state corresponds to a '1 × 1' structure with respect to the underlying lattice. At low temperatures ( $T_c < 200$  K) there is a fair amount of evidence (Ohshima & Moss, 1983) that Ag atoms order in a  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  two-dimensional ordered structure. In what follows we show that this order-disorder transition is a second-order (continuous) phase transition belonging to the three-state Potts universality class.

Within the context of Landau-Lifshitz theory (see, for example, Schick, 1981) the knowledge of the space group of the high-symmetry (disordered) phase and the superstructure of the low-symmetry (ordered) phase is sufficient to predict the corresponding universality class for a second-order phase transition. We systematically perform this analysis for the case of stage-2  $\text{Ag}_x\text{TiS}_2$ . The two-dimensional space-group symmetry of the bilayer (with disordered intercalated Ag atoms) corresponds to  $p3m1$  ( $C_{3v}^1$  in the Schoenflies notation). The corresponding point group is  $3m$ . The Brillouin zone with the wave vector  $\mathbf{k}$  is shown in Fig. 2(b).

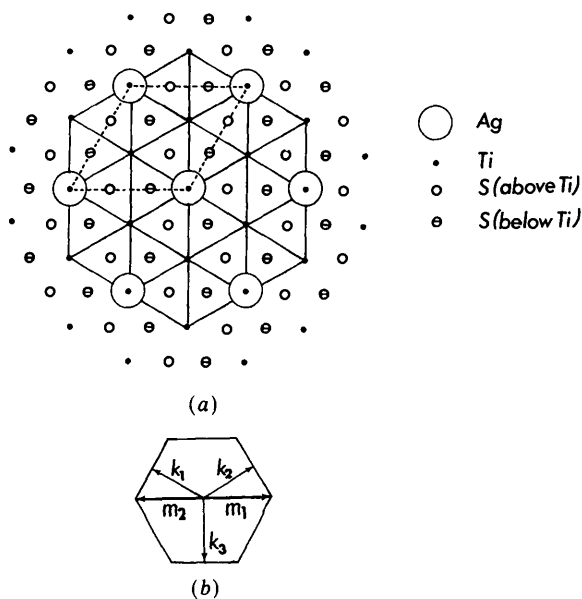


Fig. 2. (a) The  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  2D ordering of Ag atoms in the intercalation (basal) plane at low temperature ( $T_c < 200$  K) on a triangular lattice. The dashed boundary is the unit cell of the superstructure. The space-group symmetry of this pattern corresponds to  $p3m1$  ( $C_{3v}^1$ ) when the Ag atoms are in the disordered state. (b) Brillouin zone of the triangular lattice. The star  $\{\mathbf{m}\} = \{\mathbf{m}_1, \mathbf{m}_2\}$  corresponds to the  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  superstructure. The other stars, viz  $\{0\}$  and  $\{\mathbf{k}\} = \{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3\}$  lead to other superstructures summarized in Table 1.

The first step in the analysis is to apply the point-group operations on a wave vector  $\mathbf{k}$  to obtain both the group of  $\mathbf{k}$ ,  $g_{\mathbf{k}}$ , and the star of  $\mathbf{k}$ ,  $\{\mathbf{k}\}$ . The group of  $\mathbf{k}$  consists of all those point-symmetry elements which leave the vector  $\mathbf{k}$  invariant modulo a reciprocal-lattice vector. The wave vector  $\mathbf{k}_s$  corresponding to an ordered phase generally lies at a point of high symmetry in the Brillouin zone. The set of vectors  $\{\mathbf{k}_s\}$ , which can be obtained from  $\mathbf{k}_s$  by applying the point-group operations, and which are not related to each other by a reciprocal-lattice vector, form the star of  $\mathbf{k}_s$ . There are three stars associated with the  $p3m1$  space group, namely  $\{0\} = \{(0, 0)\}$ ,  $\{\mathbf{k}\} = \{(1/2, 0), (0, -1/2), (-1/2, 1/2)\}$  and  $\{\mathbf{m}\} = \{(-1/3, 2/3), (1/3, 1/3)\}$ .

We define the general form of the scalar density function,  $\rho(\mathbf{r})$ , which describes the intercalated Ag-atom superlattice as

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}). \quad (1)$$

Here  $\rho(\mathbf{r})$  and  $\rho_0(\mathbf{r})$  are the atomic density functions for Ag which characterize the disordered and the ordered phases, respectively. We can expand  $\delta\rho(\mathbf{r})$  in a series of basis functions of the corresponding irreducible representation of the high-symmetry (disordered) phase. In particular,

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{k}} n_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{r}), \quad (2)$$

where  $n_{\mathbf{k}}$  are the coefficients in the expansion. Landau-Lifshitz rules [without invoking the second Landau rule (Rottman, 1981; Schick, 1981)] then enable one to obtain all possible representations for a given allowed  $\mathbf{k}$ . The second Landau rule indicates a first-order transition whenever a third-order invariant can be constructed. In two dimensions, however, fluctuations are known to affect the nature of the phase transition and the second Landau rule is violated, particularly in the case of the three-state and the four-state Potts models (Baxter, 1973). If the symmetry of the low-symmetry (ordered) phase corresponds to an allowed representation then the transition to this phase is continuous.

Since the space-group symmetry of  $\delta\rho(\mathbf{r})$  and  $\rho(\mathbf{r})$  in (1) is the same, the translational invariance of the basis functions determines the intercalated Ag atomic density function  $\rho(\mathbf{r})$ . Thus the superlattice structure is known. We have summarized the results in Table 1 for the space group  $p3m1$ , which corresponds to the symmetry of the Ag intercalated plane. From the table it is clear that the order-disorder transition leading to a  $\sqrt{3} \times \sqrt{3}$   $R30^\circ$  superstructure at low temperature corresponds to the star  $\{\mathbf{m}\}$  in Fig. 2 and belongs to the three-state Potts universality class.

The ordering density associated with this superstructure is given by

$$\rho_i = \rho + 2C \cos [2\pi/3(2n - m)] - 2S \sin [2\pi/3(2n - m)], \quad (3)$$

Table 1. Allowed representations classified by the star of  $\mathbf{k}$  and the small representations for space group  $p3m1$ 

Small representations are defined by Rottman (1981). The symbols appearing in the brackets for the point group of  $\mathbf{k}$  are in the Schoenflies notation. The different stars are:  $\{0\} = \{(0, 0)\}$ ,  $\{\mathbf{k}\} = \{(1/2, 0), (0, -1/2), (-1/2, 1/2)\}$  and  $\{\mathbf{m}\} = \{(-1/3, 2/3), (1/3, 1/3)\}$ . The symbols used for LGW Hamiltonians correspond to the ones given by Rottman (1981). There is an additional representation associated with the star  $\{\mathbf{m}\}$  which also leads to the three-state Potts model (see Hatch & Stokes, 1984).

Space-group symmetry	Star of $\mathbf{k}$	Point group of $\mathbf{k}$	Allowed small representation	Possible allowed orderings ( $n \times m$ )	Universality class and LGW Hamiltonian
$p3m1 (C_{3v}^1)$	$\{0\}$	$3m (C_{3v})$	$A_2$ $E$	—	Ising (1) Three-state Potts (2d)
	$\{\mathbf{k}\}$	$m(C_2)$	$A'$ $A''$	$c(2 \times 2)$ $p(2 \times 2)$	Four-state Potts (3b) Domany-Riedel type (3a)
	$\{\mathbf{m}\}$	$3 (C_3)$	$A$ $E$	$p(\sqrt{3} \times \sqrt{3}) R30^\circ$ $p(\sqrt{3} \times \sqrt{3}) R30^\circ$	Three-state Potts (2d) Three-state Potts (2d)

where  $\rho_i$  is the ensemble average of the occupation number  $n_i = 0, 1$  (where  $n_i = 0, 1$  corresponds to the absence or presence of an Ag atom at site  $i$ ), and  $n, m$  are integers.  $C$  and  $S$  are ensemble averages of the two components of the order parameter, respectively. These components are given by

$$\psi_1 = (1/N) \sum_{\mathbf{r}} n_i \cos(\mathbf{q} \cdot \mathbf{r}), \quad (4)$$

$$\psi_2 = (1/N) \sum_{\mathbf{r}} n_i \sin(\mathbf{q} \cdot \mathbf{r}), \quad (5)$$

where  $\mathbf{q}$  belongs to the star  $\{\mathbf{m}\}$  and  $N$  denotes the total number of sites on the lattice.

One can construct the Landau-Ginzburg-Wilson (LGW) Hamiltonian for an irreducible representation from the invariance of basis functions under the symmetry operations of the high-symmetry phase. In the present case of an order-disorder transition in the  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ) dichalcogenide system the LGW Hamiltonian turns out to be

$$\mathcal{H} = \frac{1}{2} r \left( \sum_{i=1}^2 \psi_i^2 \right) + \frac{1}{2} \sum_{i=1}^2 (\nabla \psi_i)^2 + u \left( \sum_{i=1}^2 \psi_i^2 \right)^2 + w_1 (\psi_1^3 - 3\psi_1\psi_2^2) + t_1 (\psi_1^3 - 3\psi_1\psi_2^2)^2 + \dots \quad (6)$$

The form of the LGW Hamiltonian indicates the universality class. Equation (6) corresponds to the three-state Potts universality class. The corresponding critical exponents associated with various singularities in thermodynamic quantities are

$$\alpha = 1/3, \quad \beta = 1/9, \quad \gamma = 13/9, \quad \nu = 5/6, \quad (7)$$

using standard notation (Stanley, 1971).

### Concluding remarks

We note first that mean-field theories do not incorporate fluctuations. Fluctuations are prominent in low dimensions and can affect the nature of the phase transition. Therefore the above results should be considered valid subject to the standard *caveat* about the role of fluctuations in low dimensions. However, it seems likely that our prediction of a second-order transition will be unaffected by the fluctuations, since it is known that the three-state Potts model in 2D is

second order (Baxter, 1973). Second, the actual ordered structure may be more complicated than the idealized  $\sqrt{3} \times \sqrt{3} R30^\circ$  2D ordering of Ag atoms because three-dimensional effects may intervene or domain pinning may persist in such systems. Third, we note that there may be other transitions leading to different superstructures (Table 1) corresponding to some other values of  $x$  ( $0 \leq x \leq 1$ ) in  $\text{Ag}_x\text{TiS}_2$ . In particular,  $x = 1/8$  and  $x = 1/4$  correspond to  $p(2 \times 2)$  and  $c(2 \times 2)$  superstructures, respectively. Within the mean-field theory (without invoking the second Landau rule) transitions leading to these intercalated superstructures are second order. The  $p(2 \times 2)$  and  $c(2 \times 2)$  orderings are associated with the star  $\{\mathbf{k}\}$  (Table 1 and Fig. 2b) and the corresponding transitions belong to the Domany & Riedel (1978) type and the four-state Potts universality classes, respectively. It would be very interesting to perform experiments in the vicinity of the above values of  $x$  to try to observe these superstructures.

It was pointed out recently (Hatch & Stokes, 1985) that for a layer weakly coupled to the bulk the symmetry of the layer can include more symmetry elements than the 17 two-dimensional space groups. This indicates that the 80 diperiodic space groups in three dimensions (Wood, 1964; Ipatova & Kitaev, 1985) may be more appropriate to characterize the symmetry of layers in dichalcogenide systems. This may be the case for the system under consideration. Diperic symmetry closely approximates a symmetry that is higher than the true symmetry. Therefore diperic symmetry is approximate for a bonded layer but becomes exact as the layer becomes isolated. Nevertheless, the use of diperic space groups to characterize the high-symmetry phase does not affect the universality class.

The symmetry of the disordered state in the intercalation plane in  $\text{Ag}_x\text{TiS}_2$  ( $x \sim 1/6$ ) is the same as that of the (111) plane of elemental semiconductors, e.g. silicon. The  $\sqrt{3} \times \sqrt{3} R30^\circ$  ordered state is analogous to the case of noble-gas (He, Kr, etc.) physisorption on the honeycomb lattice of graphite (Schick, 1981). The Potts model has been extensively studied theoretically in various contexts including phase transitions on surfaces. The use of synchrotron

radiation as an intense source of X-rays enables the precise measurement of some of the critical exponents ( $\beta$  and  $\gamma$ ). Careful experiments should be performed to understand the nature of the transition discussed here and to gain a better insight into the ordering of intercalated atoms in other dichalcogenide systems. We hope to accomplish a detailed study of this transition in the future.

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**A full-symmetry translation function: the influence of model misorientation.** By J. RIUS and C. MIRAVITLLES, *Instituto 'Jaime Almera' CSIC, c/. Martí i Franqués, s/n Box 30, 102 Barcelona, Spain*

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### Abstract

A translation function is described which takes into account the full space-group symmetry. It can be easily computed by means of a standard Fourier program with modified coefficients and seems to be applicable if search-model orientation errors are less than 5°. This function has been tested on three structures.

At present most medium-sized molecular crystal structures are solved almost automatically using direct methods. However, if the systematic application of direct methods fails, and if the geometry of the molecule under study is totally or partially known, there exists another possibility for solving the structure. It consists of first obtaining the proper orientation of the molecule using a rotation function. Occasionally, direct methods furnish an *E* map which already reveals a structural fragment properly oriented but misplaced with respect to a permissible origin for the unit cell. The oriented molecule is then positioned with respect to the crystal symmetry elements by means of the so-called translation functions, which work either in intensity space (Tollin & Cochran, 1964; Tollin, 1966; Crowther & Blow, 1967; Karle, 1972; Langs, 1975; Beurskens, 1981; Harada, Lifchitz, Berthou & Jolles, 1981) or in vector space (Huber, 1965; Braun, Hornstra & Leenhouts, 1969; Nordman & Schilling, 1970).

The translation function  $\tau(\mathbf{r})$  discussed in this paper is defined as the sum of the products of the observed and calculated cross-Patterson functions over the unit cell, for a given position  $\mathbf{r}$  of the input molecule in the unit cell, i.e.

$$\begin{aligned}\tau(\mathbf{r}) &= V \int_{\text{unit cell}} \text{cross-}P_o(\mathbf{x}) \times \text{cross-}P_c(\mathbf{x}) d^3\mathbf{x} \\ &= V^{-1} \sum_{\mathbf{h}} |\mathbf{F}'_o(\mathbf{h})|^2 |\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2.\end{aligned}\quad (1)$$

Crowther & Blow (1967) showed that

$$|\mathbf{F}'_o(\mathbf{h})|^2 = |\mathbf{F}_o(\mathbf{h})|^2 - \sum_j |\mathbf{S}_j(\mathbf{h})|^2, \quad (2)$$

where  $\mathbf{F}_o(\mathbf{h})$  is the observed structure factor and  $\mathbf{S}_j(\mathbf{h})$  [hereafter:  $\mathbf{S}_j(\mathbf{h}) = \mathbf{S}_j$  and  $\mathbf{F}_o(\mathbf{h}) = \mathbf{F}_o$ ] is the molecular structure factor computed with the atomic coordinates obtained after applying the rotation matrix  $R_j$  to the input oriented molecule, referred to a fixed local origin in the molecule.

The Fourier coefficients of the calculated cross-Patterson expressed as a continuous function of the molecular position  $\mathbf{r}$  can be evaluated after Crowther & Blow (1967) and Harada *et al.* (1981) by means of the following expression:

$$\begin{aligned}|\mathbf{F}'_c(\mathbf{h}, \mathbf{r})|^2 &= \text{Re} 2 \sum_j \sum_{k>j} \mathbf{S}_j \mathbf{S}_k^* \exp[-i2\pi \mathbf{h} \mathbf{t}_{kj}] \\ &\quad \times \exp[-i2\pi \mathbf{h}_{kj} \mathbf{r}]\end{aligned}\quad (3)$$

with  $\mathbf{t}_{kj} = \mathbf{t}_k - \mathbf{t}_j$ ,  $\mathbf{h}_{kj} = \mathbf{h}(R_k - R_j)$  and  $\mathbf{t}_j$  = translation of the *j*th space-group symmetry operation. Introducing (2) and