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COMPOSITE CRYSTALS: WHAT ARE THEY AND WHY ARE THEY SO COMMON IN THE ORGANIC SOLID STATE ?

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Abstract Composite crystals contain at least two components, which have different unit cells within the same crystal. Since the unit cells differ in volume by an in general non-integer factor, composite crystals are usually non-stoichiometric, and their occurence is related to the mixed valency of at least one of the components. Composite crystals therefore tend to have unusual solid state properties. Since there is a mutual interaction between the two components, each of the sub-lattices undergoes a distortion with the periodicity of the other component. Several examples of low-dimensional organic composite structures based on BEDT-TTF and its tetra-oxygen analog BEDO-TTF are discussed.

INTRODUCTION

As more complicated solids are being synthesized in the quest for new materials, structural phenomena once considered unusual are becoming increasingly common. Prime examples are modulations in crystals, and the discovery of composite structures.

The latter contain at least two components which have interpenetrating, but distinct lattices. The possibilities for the coexistence of two lattices in one crystal are restricted by space filling requirements. Two types of composite structures are known. In the first the two lattices form parallel columns, while the second type consists of interleaved sheets of the two components.

Since the ratio of the volumes of the unit cells of the two sub-lattices is in general non-integer, the two components will usually occur in non-stoichiometric ratios, *the stoichiometry being dictated by the ratio of the unit cell volumes.* For ionic or partially ionic compounds electroneutrality requirements imply that composite solids must contain ions of mixed valency. Since mixed-valency often gives rise to unusual properties, the search for solid state metals and superconductors is leading to the discovery of new

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composite solids. The list of inorganic and organic composite crystals given in Table I can undoubtedly be expanded with other cases in which a crystal structure analysis has been halted because of unexpected complications.

As the two sub-lattices coexist in the same crystal mutual interaction introduces a perturbing potential with the periodicity of the other sub-lattice. This leads to a periodic distortion, commonly described as a modulation. The diffraction pattern of a composite crystal is the superposition of the diffraction patterns of the two sublattices, *plus* satellite reflections which represent the distortion.

We will discuss the arrangements of the two sub-lattices in a composite crystal, the diffraction pattern, and the results of the diffraction analysis of three low-dimensional organic composite structures.

DESCRIPTION OF COMPOSITE STRUCTURES

The relation between two coexisting lattices in a crystal is given by the matrix equation:

$$\mathbf{A}^{(1)} = \sigma\, \mathbf{A}^{(2)} \qquad (1)$$

As fully described elsewhere,[1] the elements of the interlattice matrix σ are limited by the space limitations imposed on two interpenetrating but non-overlapping lattices. In *column composite structures* each of the component structures is column-like. The translational repeat in the column direction is different for each of the lattices (fig 1a). The translation vectors relating columns are not necessarily parallel for the two lattices, but are restrained by the space-filling requirements . *In layer composite structures,* also referred to as *misfit* layer structures,[2] the two components form parallel layers (fig 1b). The σ-matrix is again restricted by space limitations. Many of the known layer composite structures are inorganic sulfides (Table I), while the known organic composite structures are typically of the column type.

The symmetry of composite structures has been treated by Janner and Janssen[3] and by Van Smaalen,[4] and is based on the multi-dimensional spacegroup theory of DeWolff, Janner and Janssen.[5] In particular Van Smaalen[4] has discussed how the four-dimensional space group of the crystals is related to the four-dimensional space groups of the component sub-lattices. A description of the symmetry aspects of composite structures is outside the scope of this article.

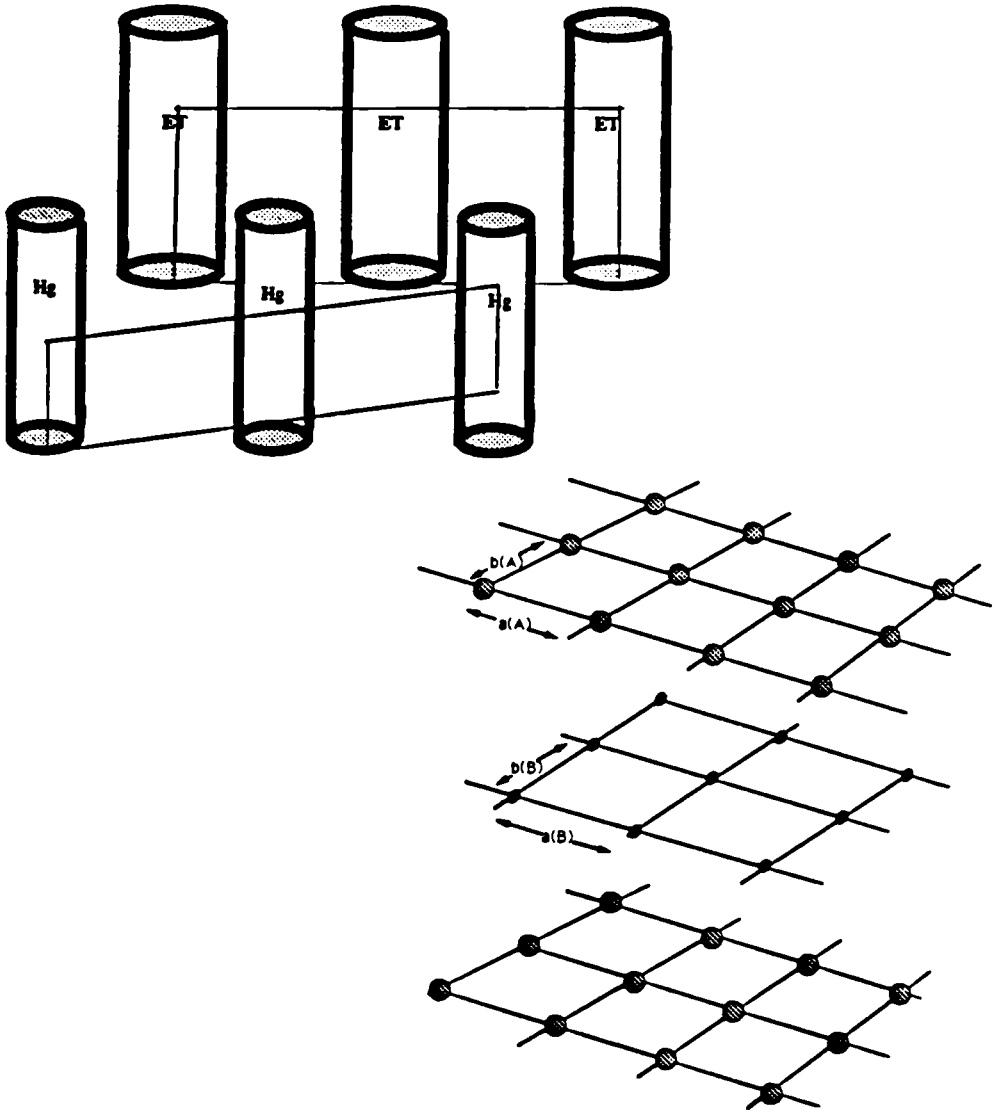

FIGURE 1a (left) Schematic drawing of a column composite structure. A face of the unit cell of each of the sublattices is indicated.

FIGURE 1b (right) Schematic drawing of a layer composite structure. The translational repeats within the two layers may differ in both length and direction in the layer. The two translation vectors, c(A) and c(B), relating identical layers must have the same projection onto the normal to the layers.

X-RAY SCATTERING

The X-ray pattern of a composite structure is in part a superposition of the scattering of the individual component lattices. However, the modulations introduced by the inter-lattice interaction gives rise to the occurence of satellite reflections in the diffraction pattern. The complete pattern of most two-component composite structures can be described with a set of four indices, h k *l* and m, of which three describe the scattering of one sub-lattice, and two of these three and a fourth index that of the second sub-lattice. For example the hk*l*0 reflections and the hk0m reflections represent the main reflections of each of the two reciprocal lattices, but in addition are *l* -th order and m-th order satellites of sublattices 1 and 2 respectively. A general hk*l*m reflection is both an m-th order satellite of sub-lattice 1 and an *l*-th order satellite of sub-lattice 2. Thus, the X-ray scattering expression for all lattice point contains contributions from at least two scattering processes.[1]

EXAMPLES OF LOW-DIMENSIONAL ORGANIC SOLIDS WITH COMPOSITE STRUCTURES

We will give three examples of composite structures from our recent work. Two of these are low dimensional metals, while the third is a narrow gap semiconductor.

1) $BO_{2.4}I_3$

BO, or BEDO-TTF, the oxygen analog of BEDT-TTF was first synthesized by Wudl and coworkers.[6] Its iodine salt[7] has a composite structure with different periodicities of the two components along the **b**-axis. The component cell volumes have a ratio V(I)/V(BO)=2.4 , which directly leads to the stoichiometry given, and a net charge of the BO cations of 0.42 Å, thus illlustrating the mixed valency of incommensurate composite crystals. The **b**-axis projection of the *average structure* of the two lattices is shown in figure 2. However, the interaction between the iodine atoms and the ethylene hydrogens of the BO molecule causes both lattices to be modulated, with a period equal to the periodicity of the other lattice. The amplitude of the displacement wave of the BO molecules is 0.033Å, and the displacement is approximately along the molecule's long molecular axis. The direction of the static displacements is dictated by the short S--S contacts of only 3.402Å, in the direction perpendicular to both the stacking axis and the long molecular

Table I Examples of known composite structures.

Inorganic	**layer/column**	**Reference**
$Hg_{3-\delta}AsF_6$	c	11
$La_{1.2}CrS_{3.2}$	*l*	12
$(SnS)_{1.18}NbS_2$	*l*	13
$Sr_{14-x}Ca_xCu_{24}O_{41}$	*l*	14
Organic		
$(TTF)_7I_{5-x}$	c	15
$BO_{2.4}I_3$	c	7
$(ET)Hg_{0.776}(SCN)_2$	c	8
$(ET)_2HgBr_4.TCE$	c	10
$(ET)_4Hg_{2.89}Br_8$	c	16
$Bz_9M_2I_9.CHCl_3$	c	17
$TMA^+TCNQ^{2/3-}(I_3^-)^{1/3}$	c	18

TTF= tetrathiofulvalene, TCE= trichloroethane

Bz= benzophenone; M= Na^+, K^+

TMA= tetramethyl ammonium, TCNQ= tetracyanoquinodimethanide

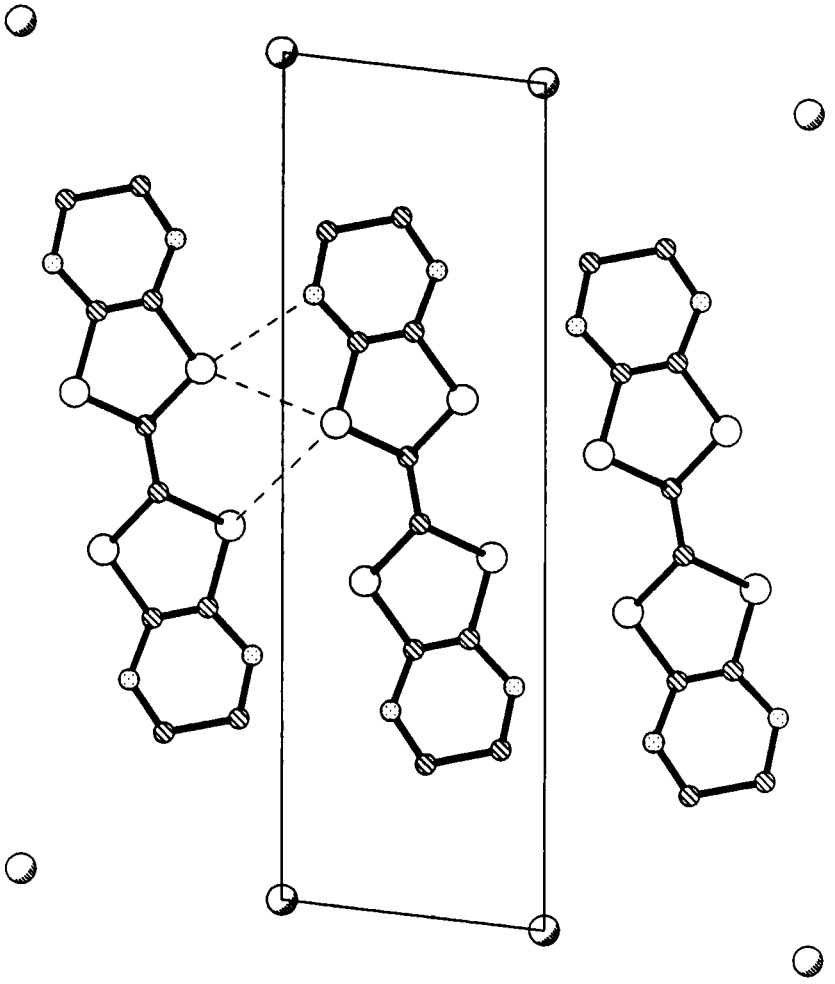

FIGURE 2 The projection of the unit cell of $BO_{2.4}I_3$ along the common **b**-axis direction. The triiodode counterions are at the corners of the unit cell. Two additional molecules in adjacent stacks are also shown to indicate the short interchalcogen contacts.

axis. The modulation introduced in the I_3^- iodine chains is much larger, and a main contributor to the intensity of the satellite reflections.

2) ET $Hg_{0.776}(SCN)_2$

The HgSCN salt of ET (3,4;3'4'-bis (ethylenedithio)-2.2',5,5'-tetrathiofulvalene or BEDT-TTF) was synthesized by Wang et al[8] using electrocrystallization methods. The lack of a stoichiometric composition is indicative of a composite structure, which was confirmed by X-ray diffraction photographs taken in our laboratory. Our structure analysis shows that the Hg atoms form one sub-lattice, while the ET and SCN molecular ions form the second sub-lattice, with a **b**-axis translation vector parallel to, but incommensurate with the **b**-axis of the first lattice. The ratio of the two unit cell volumes and the unit cell sharing of ET and SCN is in full agreement with the analytical stoichiometry. However, the incommensurability of the SCN and Hg components leads to a novel coordination of the Hg atoms, which varies continuously in different unit cells separated by a **b**-axis translation.

The Hg atoms have four S nearest neighbors. But because of the incommensurability the vertical separation (i.e. along the **b**-axis) between Hg and S is continuously variable and equal to zero in some of the unit cells. At those points the Hg-S distance would be only 1.90Å, far shorter than the typical coordination distance of 2.40Å between these two atoms. This is the strong interaction between the two lattices which leads to the modulation of both, such as to relieve the Hg-S repulsions. An analysis of the modulational displacements,[9] shows large displacements of both SCN and Hg, with significant higher harmonic contributions to the Hg displacements. The modulation leads to a lengthening of the shortest distance in the average structure from 1.90 to 2.16Å. This is still shorter than common, but may be lengthened further by anharmonic components not included in the treatment. The ET modulational displacements are larger than in BO-iodide, the translational and rotational amplitudes are 0.086Å and 0.42° respectively. The amplitudes are larger than those of BO in $BO_{2.4}I_3$, where S..S intermolecular contacts are as short as 3.40Å, compared with 3.53Å in the HgSCN complex.

3) $(ET)_2 HgBr_4$.TCE (TCE = trichloroethane)

Unlike the compounds discussed above, which are organic metals, $(ET)_2HgBr_4$.TCE is a semiconductor with a band gap of 90meV.[10] It is a *commensurate* composite structure, in which the $HgBr_4$ lattice has twice the repeat of the lattice of the ET component, while the TCE molecules are disordered along the **b** axis, but discrete in the **b**-axis projection (fig 3.). At least at room temperature, at which the structure determination was performed, there is a disorder in the $HgBr_4$ columns, which can be displaced by **b**(ET)= 0.5 **b**($HgBr_4$), as evidenced by discrete streaks in k odd $HgBr_4$ lattice layers in the Weissenberg photograph. Thus this composite structure has one ordered and one disordered component. The interaction between the sublattices is too weak for satellite reflections to be observable.

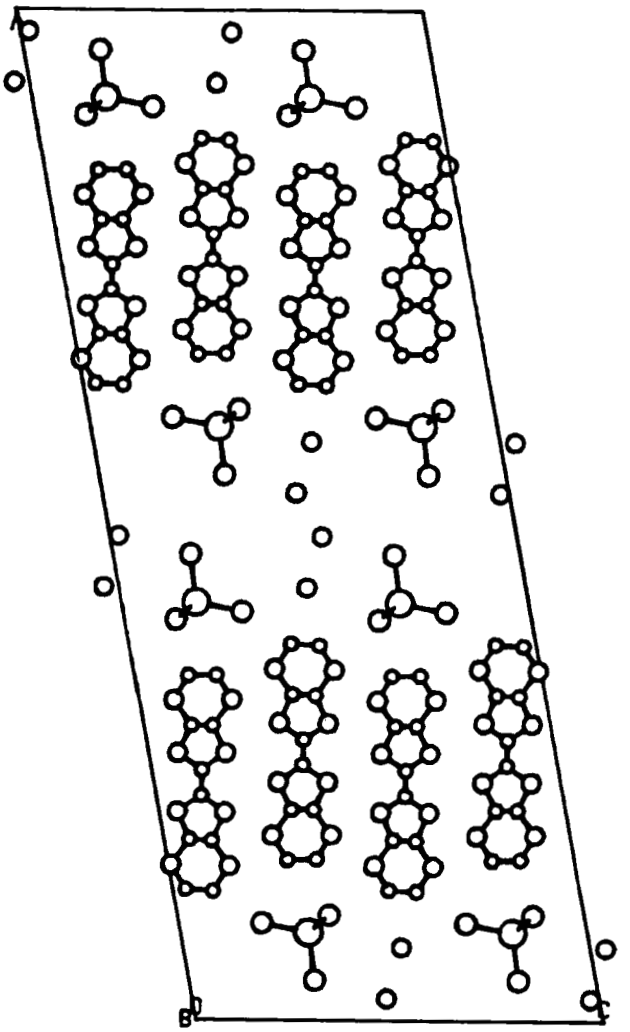

FIGURE 3 The projection of the unit cell of ET $HgBr_4$ along the common **b**-axis direction. Two Br atoms of the tetrahedral anion are superimposed in projection. The unconnected circles represent the positions of the chlorine atoms in the solvent molecules.

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