

Formation of Titanium Sulphide Hexagonal Polytypes

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A mechanism which explains the formation of hexagonal polytypes of titanium sulphide is suggested. According to this mechanism, polytypes are generated by the interaction of stacking faults with a screw dislocation during solid-state transformations. A $2H \rightarrow 8H$ phase transformation seems to be the driving force for the expansion of stacking faults. All the structural information which has been so far collected on these polytypes is in perfect agreement with such a mechanism. A generalization to the interaction of stacking faults with several parallel screw dislocations is presented. The formation of polytypes with very long periods may be explained by this kind of interaction.

I. Introduction

The discovery of polytypism in titanium sulphide (Tronc & Huber, 1971, 1973) has been followed by investigations on mechanisms explaining such a phenomenon. Structural and morphological data concerning these polytypes have been collected; they have allowed us to suggest a formation mechanism for titanium sulphide rhombohedral polytypes (Legendre, Moret, Tronc & Huber, 1975). A similar mechanism had been earlier propounded to explain the formation of zinc sulphide polytypes (Daniels, 1966; Alexander, Kalman, Mardix & Steinberger, 1970). Data supporting this mechanism for the formation of titanium sulphide hexagonal polytypes are reported in this paper.

II. Growth conditions, structure and morphology of titanium sulphide polytypes

Non-stoichiometric titanium sulphide prismatic crystals ($l < 1$ mm) are prepared by direct synthesis from the elements subsequently followed by vapour transport. These operations are carried out in an evacuated quartz tube. Polytypic structures are obtained with the following preparation conditions: temperature close to 900°C and initial-mixture composition $\text{TiS}_{1.7}$.

In these structures, S atoms are close-packed, Ti atoms being located in octahedral voids of the S packing. Alternate metallic layers are only partly occupied. A polytype is characterized by the stacking sequence of S atoms.

The structure and morphology of crystals prepared under different conditions in two identical tubes have been investigated by optical microscopy and X-ray diffraction. In each batch most of the crystals have the same structure ($2H$ for tube 1 and $4H$ for tube 2): a 'basic' structure seems to be connected with growth conditions in each tube (Table 1). Moreover, the proportion of crystal regions with periods longer than that of the basic structure in most cases is small.

Table 1. Growth conditions in the two tubes

	Tube I	Tube II
Initial-mixture composition	$\text{TiS}_{1.7}$	$\text{TiS}_{1.7}$
Growth-region temperature	920°C	850°C
Temperature gradient	30°C	100°C
Heating duration	2 months	12 days
Basic structure	$2H$	$4H$

In polystructural crystals these zones are easily located: they always correspond to discontinuities. As can be seen in Fig. 1, these discontinuities are different for hexagonal or rhombohedral polytypes: whereas hexagonal polytypes can be distinguished from the basic structure by a variation of the optical reflecting power, rhombohedral polytypes may be located by the kinks of prismatic faces. It is the simplicity of the latter type of morphological discontinuity which allowed us to suggest a formation mechanism for rhombohedral polytypes: a shear of the $4H$ basic structure into blocks of equal thickness is able to explain such shapes in rhombohedral polytypic crystals (Mardix, Kalman & Steinberger, 1968). The periodicity of the slips which can produce such a structure in a crystal may be explained by the existence of a screw dislocation: in that case, atomic layers may be considered as helicoidal surfaces in which stacking faults may expand, producing a new periodicity given by the Burgers vector of the dislocation (Daniels, 1966). This mechanism has been confirmed by the coincidence between morphological and structural effects it is expected to produce and the experimental observations carried out on titanium sulphide rhombohedral polytypes (Legendre, Moret, Tronc & Huber, 1975). Hexagonal polytypic crystals never exhibit such simple-shaped morphological discontinuities, so the known structures and their coexistence are the only experimental data that may suggest a formation mechanism.

III. Hexagonal titanium sulphide polytypes

Excluding the $8H$ structure which has been found close to the $4H$ basic structure and which may be pro-

duced by the formation mechanism of rhombohedral polytypes, all hexagonal structures have been found in crystals mainly constituted by the $2H$ basic structure.

Hexagonal polytypes which have been discovered so far are mentioned in Table 2. In all these cases the origin of the crystal lattice is conventionally located on a completely occupied Ti layer. Consequently, the first sign in the Hägg (1943) notation corresponding to the Zhdanov (1945) symbol of each of these polytypic structures describes the relation between two successive S layers located on either side of a partly occupied Ti layer.

Table 2. Hexagonal polytypes discovered to date

Ramsdell notation	Zhdanov symbol	Reference
$2H$	11	Bartram (1958)
$4H$	22	
$8H$	3212	Tronc & Huber (1973)
$10H$	321112	
$12H$	321321	
$18H$		Legendre (1976)
$24H$		Tronc & Huber (1973)
$26H$	$(3212)_2 321112$	Legendre & Huber (1976)
$40H$		Tronc & Huber (1973)
$120H$		Legendre (1976)

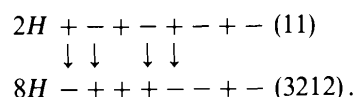
Excluding the $2H$ structure, which is a basic structure, the most frequent hexagonal structures are $8H$, $10H$ and $12H$. The frequent coalescence of these polytypes often complicates their identification.

III A. Formation of hexagonal polytypes with medium-sized stacking sequence

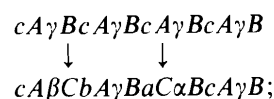
As it had been pointed out, in most of the crystals possessing a hexagonal polytypic structure in some part of their volume, the main part of the crystal is constituted by the $2H$ structure which seems to be the basic structure for transformations producing polytypes. So, if the mechanism we are suggesting explains their formation, hexagonal polytypic structures may result from the expansion of stacking faults in a $2H$ crystal in which one or several screw dislocations are located; the Burgers vectors of these dislocations are multiples of the c lattice parameter of the $2H$ structure (c_{2H}). This hypothesis is supported by the fact that the polytypes whose periods are not multiples of c_{4H} ($10H$, $18H$, $26H$) have only been found in $2H$ basic structure crystals.

III A.1. $8H$ structure. If a screw dislocation with a Burgers vector equal to eight times d_S (d_S : distance between two successive S layers) is located in a $2H$ crystal, the transformation of the $2H$ basic structure

into a $8H$ (3212) structure may be described with the Hägg notation in the following way:



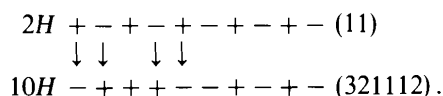
This transformation involves two double faults. Each of these faults is limited in the crystal by an elementary dipole of Shockley partial dislocations. The Burgers vectors of these partial dislocations have the same length but opposite signs. The modification of atomic positions during this transformation may be described as follows:



capital letters: positions of S layers, lower-case letters: positions of completely filled Ti layers, Greek letters: positions of partly filled Ti layers.

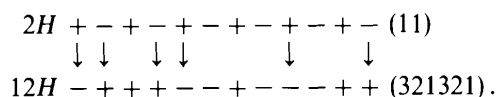
It should be noted that this type of double fault does not cause any slipping of blocks, *i.e.* it only involves S layers with a hexagonal environment. As the fault only concerns the S layer and its neighbouring metallic layers, the hexagonal character of the structure is maintained.

III A.2. $10H$ structure. The same mechanism is able to account for the transformation of the $2H$ basic structure into the $10H$ (321112) hexagonal structure. The existence of a screw dislocation with a $10 d_S$ Burgers vector has to be considered.



The frequent coexistence of $8H$ and $10H$ polytypes in crystals based on the $2H$ structure is in agreement with such a mechanism.

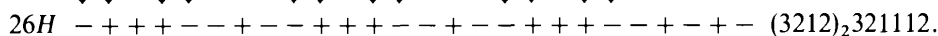
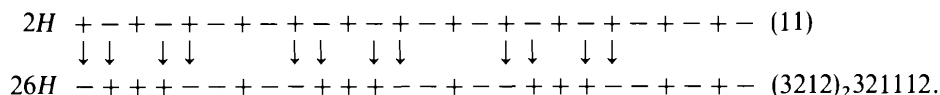
III A.3. $12H$ structure. The $12H$ (321321) structure which has been found in coalescence with $8H$ may result from $2H$ in the following way:



A screw dislocation with a $12 d_S$ Burgers vector has to be located in the crystal.

III A.4. $26H$ structure. The structure of a $26H$ polytype has been recently determined (Legendre & Huber, 1976). Its Zhdanov symbol $(3212)_2 321112$ clearly shows that it consists of three $8H$ blocks followed by a $2H$ block.

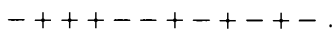
In the case of $10H$, one $8H$ block only is followed by a $2H$ block.



III B. Existence of a $2H \rightarrow 8H$ transformation

The existence of such structural transformations always causing local $2H \rightarrow 8H$ modifications means that the $8H$ structure into which the $2H$ structure is transformed is a stable phase.

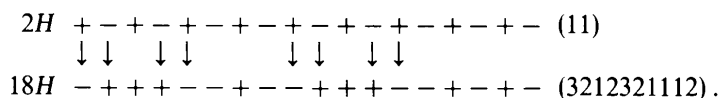
The transformation producing the $12H$ polytype is slightly different. The $2H$ structure block which is being transformed may be divided into two parts: the first, $8 d_s$ thick, is transformed in the same way as other hexagonal polytypes into an $8H$ block. The transformation of the second part, $4 d_s$ thick, involves two simple stacking faults. The latter modification is easy to understand: if it does not occur, the resulting structure is:



In that case, a large $2H$ block would still be in existence. Such a situation is unlikely to occur because $2H$ is not a stable structure in these conditions: it is transformed into $8H$. A modification concerning the four signs on the right of the Hägg notation has therefore to be considered.

On the other hand, the $2 d_s$ -thick block which makes $10H$ and $26H$ polytypes different from the $8H$ structure is not transformed.

Consequently, these polytypes ($10H$ and $26H$) surely are the most stable structures that can be obtained under such conditions of transformation; the most stable structure ($8H$) is impossible to obtain because of the real periodicity of the crystal (the B_c length). The existence of the $18H$ polytype also agrees with this formation mechanism. Its probable structure is 3212321112.



The fact that the most frequent polytypes that appear in a $2H$ basic structure are $8H$, $10H$ and $12H$ is further evidence for the existence of a $2H \rightarrow 8H$ transformation. If the $2H \rightarrow 8H$ transformation is actually the driving force for the formation of hexagonal polytypes, the most frequent polytypes should result from the most frequent screw dislocations: short Burgers-vector dislocations.

On the other hand, the Burgers vectors of screw dislocations producing polytypes have to be longer than the period of the structure into which the crystal is transformed ($8H$). So, the comparatively frequent existence of $8H$, $10H$, $12H$ and the absence of $6H$ may be understood.

Finally, the expansion of double faults generating hexagonal polytypes may be induced by a simple phase transformation: $2H \rightarrow 8H$. The formation of structures with periods different from $8d_s$ is simply produced by the existence of screw dislocations with Burgers vectors whose length are not multiples of $8d_s$.

III C. Formation of hexagonal polytypes with long stacking sequence

In spite of the coherence of most of the results obtained, some details disagree with the mechanism we suggest. For example, the existence of $24H$, $40H$ and $120H$ structures is not indeed possible to explain: in that case, only the $8H$ structure should appear because the periods of these polytypes are multiples of $8d_s$.

Moreover, a major objection may be raised to the mechanism we suggest: according to it, the period of the polytype resulting from the interaction between a stacking fault and a screw dislocation is equal to the Burgers-vector length of the dislocation. So, the formation of long-period polytypes such as $40H$ or $120H$ is highly improbable because the energy involved in screw-dislocation formation is proportional to the square of the B_c length.

An estimation of this energy has been published for ZnS by Rai (1971): it has been stated that the energy requirement for the creation of a screw dislocation with a Burgers vector approximately 100 layers long is very close to the sublimation energy of ZnS. In spite of the fact that long Burgers vectors (100 \AA) have been observed in ZnS (Mardix, Lang & Blech, 1971) another explanation has to be suggested for the formation of long-period hexagonal polytypes.

The observation of crystal defects supplies new information for a better knowledge of the formation of titanium sulphide polytypes: X-ray topography often shows that several screw dislocations are located in the same crystal (Legendre, Huber & Sauvage, 1977). This frequent situation leads us to consider the influence of several screw dislocations on stacking-fault

expansion.

III C.1. Formation mechanism. Let us consider two screw dislocations in a crystal with different Burgers vectors parallel to c . The lengths of these vectors are supposed to be multiples of the c lattice parameter of the $2H$ basic structure: $V_{B_1} = k_1c$, $V_{B_2} = k_2c$ with k_1 and k_2 integers.

Two possibilities have to be considered for the expansion of the stacking faults in such a crystal: if the stacking faults which expand around dislocations do not possess any common volume of expansion, the crystal has to be divided into three structurally different regions. The first is constituted by the crystal part in which no fault expands; so its structure is the basic structure. Each of the two other regions contains a screw dislocation and is swept by the expansion of a stacking fault. The structure periods of these regions along c are given by the Burgers vector of the screw dislocation they contain, i.e. k_1c and k_2c . Accurate measurements of the intensities of diffracted spots have

shown that these structures may be simultaneously present in the same mosaic block (Tronc & Huber, 1973).

On the other hand, if the expansion areas of the stacking faults have a common region, a new structure is created in this region. Its period along c is given by the least common multiple (l.c.m.) of the Burgers vectors of the dislocations. Consequently, k_1c , k_2c and l.c.m. (k_1, k_2) c periods are obtained.

The X-ray beams diffracted by k_1c and k_2c periods coincide with the beams diffracted by a l.c.m. (k_1, k_2) c period. So, no definite information on the simultaneous coexistence of such structures may be given by the position of the spots on a diffraction pattern. On the other hand, a precise study of the distribution of the intensity in some diffracted beams is able to differentiate between these structures.

III C.2. Experimental results supporting the formation mechanism of long-period polytypes. This formation mechanism of long-period hexagonal polytypes is more satisfactory with respect to energy considerations than that involving only one screw dislocation: long-period polytypes may be produced by two dislocations with medium-sized B_v , no highly improbable dislocation with a long B_v being involved.

If such a mechanism is applied to $2H$ crystals in which screw dislocations with B_v length equal to 8, 10 and 12 d_s are located (producing the frequent $8H$, $10H$ and $12H$ polytypes), the $2H$ structure is transformed into $24H$ [l.c.m. (8, 12)], $40H$ [l.c.m. (8, 10)], $60H$ [l.c.m. (10, 12)]. So, the existence of $24H$ and $40H$ polytypes reported by Tronc & Huber (1973) may be explained.

In spite of some positive radiocrystallographic data, the existence of the $60H$ [l.c.m. (10, 12)] structure has not been definitely proved. Furthermore, if in a $2H$ crystal three screw dislocations with B_v length equal to 8, 10 and 12 d_s are located, a l.c.m. (8, 10, 12) period may appear ($120H$). Accordingly the existence of the $120H$ polytypic structure in the crystal shown in Fig. 2 may be understood.

The fact that all the polytypes we have found are consistent with the formation mechanism we have described seems to verify it.

This mechanism, moreover, suggests that the formation of polytypes does not occur during crystal growth. Thus, it is similar to that described by Alexander, Kalman, Mardix & Steinberger (1970) for the formation of ZnS polytypes.

The observation of the crystal shown in Fig. 3 clearly proves that the hexagonal polytypes of titanium sulphide appear after the crystal growth. On this photograph, it can be seen that the (b) ($8H + 10H$) region is not a prolongation of the two $2H$ blocks which are on both sides of it. So, block (a) cannot have grown after block (b). The formation of $8H + 10H$ polytypes in the $2H$ crystal have certainly induced some disintegration of the basic structure, as can be seen on the photograph at level (b).

Considering all these reasons, one may think that the mechanism which has been suggested in this paper is able to explain the formation of titanium sulphide polytypes.

Nevertheless some unanswered questions are left open: especially that concerning the influence of non-stoichiometry on the formation of TiS polytypes. The occupation rate of partially occupied Ti layers may indeed have a double influence. The first is thermodynamical: stability of phases is related to composition. The second concerns the kinetics of stacking-fault expansion, because Ti atoms are involved in this mechanism.

IV. Conclusion

In this paper only the structural aspect of polytypism in titanium sulphide has been studied. Nevertheless, the basic cause of such a phenomenon has to be kept in mind. As it has been pointed out, it is a simple phase change which makes the stacking faults expand. The formation of polytypes almost identical to $8H$ during the transformation of the $2H$ basic structure agrees with this point of view. The conditions of these phase transformations are not clearly defined, hence some investigations on the stability of the various basic structures we have met ($2H$, $4H$) have to be considered. Such a task seems to be rather difficult because of the energetic equivalence of the various structures: the stability domains of these structures are indeed so close that they may appear in the same preparation tube. So, very accurate knowledge of preparation conditions is essential.

Polytypism is a rather unusual phenomenon despite the fact that stacking faults and screw dislocations are very common defects. This remark points out that some limiting conditions for the formation of polytypes have to be considered. One of these conditions is related to the energy of the phase transformation: if the energy is too weak, stacking faults do not expand; if it is too great, the crystal lattice is altered without any influence on the defects, *i.e.* without the formation of any polytypic structure. Another condition concerns the number of crystal defects: if no defects (no dislocations) are present in a crystal, no polytypic structures will appear; on the other hand, if the crystal is too much disordered, the expansion of a stacking fault may be restricted by other stacking faults or point defects and the polytypic regions may be too small for X-ray detection. In fact, according to this mechanism and to experimental data, polytypes are very perfect crystals with very few defects, which combine and produce a new order. Moreover, the length of Burgers vectors of dislocations producing polytypes has to be longer than the period of the structure into which the crystal is transformed. So, in spite of the existence of other formation mechanisms, the comparative scarcity of polytypic structures may be understood.

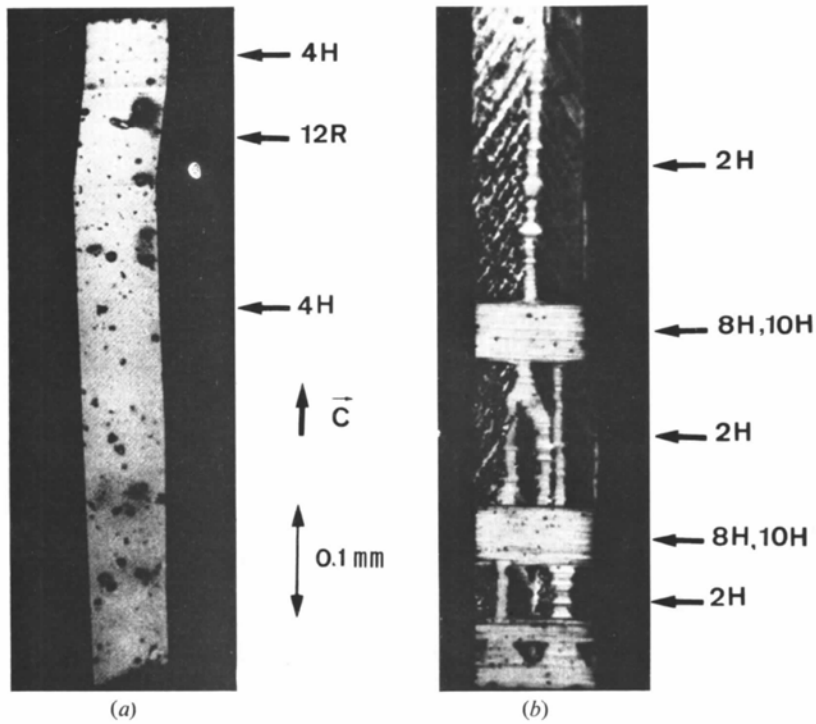


Fig. 1. $\text{TiS}_{1.7}$ prismatic crystals. (a) A 12R structure is located in a 4H crystal. (b) A 8H+10H mixture is located in a 2H crystal.

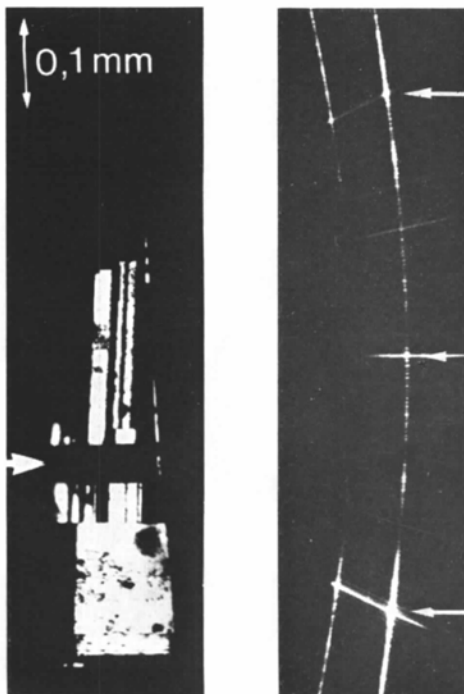


Fig. 2. Crystal in which 2H and 120H structures are in coalescence. The 120H structure is located at the level indicated by the arrow (same scale as in Fig. 1). Its characteristic spectrum has been obtained by a microcollimated X-ray convergent beam. The arrows indicate the spots of the 2H basic structure.

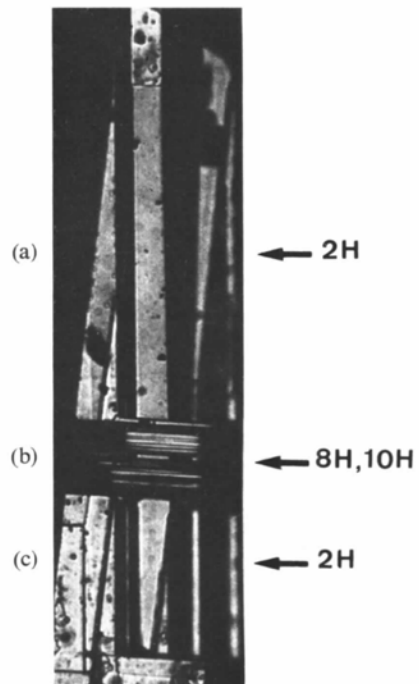


Fig. 3. Crystal in which the 8H+10H structural mixture corresponds to a disintegration of the 2H basic structure (same scale as in Fig. 1).

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Etude par Diffraction Neutronique à 0,04 K de la Perovskite d'Aluminium et d'Holmium

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At very low temperatures HoAlO_3 displays magnetic properties characteristic of singlet ground-state systems with the existence of a coupled electronic nuclear ordering induced by the hyperfine interactions. Neutron diffraction measurements at 0.04 K show the presence of an antiferromagnetic arrangement $G_x A_y$. The thermal dependence of the 001 reflexion leads to a value of the critical temperature of 0.16 K.

Introduction

La perovskite d'aluminium et d'holmium est un exemple de système magnétique à moments induits, particulièrement simple. A basse température son comportement peut être décrit dans un modèle à deux singulets. En effet des mesures de chaleur spécifique (de Combarieu, Michel, Peyrard & Sivardière, 1968) ont montré l'existence de deux niveaux de champ cristallin distants de 8 K et nettement séparés des autres niveaux excités. Dans ces conditions un moment magnétique ne peut apparaître en un site donné que dans une direction cristallographique bien déterminée. Cette direction peut être prévue en partie par des considérations de symétrie: le groupe d'espace cristallin de HoAlO_3 est le groupe orthorhombique $Pbnm$, les ions d'holmium étant placés sur le miroir défini par les axes d'ordre deux Ox et Oy . La direction d'anisotropie associée à un ion holmium est alors nécessairement soit parallèle soit perpendiculaire au plan xOy . En fait des expériences de diffraction neutronique sous champ à 4,2 K (Sivardière & Quezel-Ambrunaz, 1971) ont montré que l'aimantation reste toujours dans le plan xOy quelle que soit la direction du champ appliqué.

Les mesures de chaleur spécifique de la référence (de Combarieu, Michel, Peyrard & Sivardière, 1968) ne font apparaître aucune transition magnétique jusqu'à 0,3 K. Ce résultat indique que les interactions magnétiques sont trop faibles devant la séparation

énergétique des singulets de champ cristallin pour entraîner l'existence d'un ordre magnétique purement électronique. La prise en compte des interactions hyperfines (importantes dans l'holmium) permet de prévoir à plus basse température l'apparition d'un ordre couplé électronique et nucléaire. On peut penser *a priori* que la température de transition se situe entre 0,1 et 0,2 K si on compare les propriétés de l'ion Ho^{3+} dans HoAlO_3 par rapport à celles qu'il présente dans le grenat de gallium et d'holmium (Hammann & Ocio, 1977) et si on se réfère aux expressions théoriques des températures critiques trouvées pour ce type de système dans les références (Murao, 1971; Andres, 1971; Triplett & White, 1973; Hammann & Manneville, 1973).

Ces prévisions ont pu d'abord être vérifiées par des mesures de susceptibilité effectuées jusqu'à 0,05 K dans un cryostat à désaimantation adiabatique. Un comportement antiferromagnétique a été observé avec un maximum vers 0,2 K. La localisation de ce maximum a été peu précise. De grandes difficultés de thermalisation sont en effet apparues, qui sont dues à la très forte chaleur spécifique d'origine magnétique nucléaire et au très long temps de relaxation spin-réseau. Un retard de température a été mis en évidence au cours du réchauffement de l'étage de désaimantation entre ce dernier et le système magnétique de l'échantillon.

Pour effectuer les expériences de diffraction neutronique qui font l'objet de cette publication, un cryostat à dilution a été utilisé (Hammann & Ocio, 1977);