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POLARIZATION-OPTICAL OBSERVATION OF FERROELASTIC DOMAINS IN THE INCOMMENSURATE PHASE OF BaMnF$_4$

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The first direct observation by means of polarized light microscopy of the ferroelastic domains of the incommensurate phase (average monoclinic symmetry) of BaMnF$_4$ is reported.

INTRODUCTION

BaMnF$_4$ has been the subject of many studies because it displays a variety of unusual physical properties (review papers Reference 1 and 2). It is pyroelectric at all temperatures below the melting point (915 K). At about 250K (T_i), it undergoes a weakly first order[3,4,5] structural transition from an orthorhombic high-temperature phase (A2$_1$am)[6] to an incommensurate (INC) phase.[7] Below the Néel temperature (25K) a three-dimensional antiferromagnetic spin ordering sets in.[7] The INC phase is characterized by the absence of a lock-in transition and a very weak temperature dependence of the modulation wave vector.[8] In addition, this evolution with temperature is strongly sample dependent.[9]

It is now well established that the structural transition is of improper ferroelastic type, with the average symmetry of the INC phase being monoclinic (P2$_1$). The lowering of the point group symmetry was predicted in a theoretical paper[10] to explain the magnetoelectric phenomena observed at low temperatures, but it is only in recent years that it has been experimentally verified. Evidence for lowering of symmetry has been given in an optical study in which a small rotation (angle β of Figure 1b) of the index ellipsoid relative to the orthorhombic orientation was found in the INC phase.[3] However, it was surprising that no temperature depence of that rotation was observed. Thereafter in two independent diffraction studies (γ-ray[11] and high resolution X-ray[12]) the splitting of the crystal into ferroelastic domain states (Figure 1b) has been confirmed and the monoclinic distortion established as a function of temperature. Upon cooling the distortion angle (α) increases from T_i to about 5 min at $\sim$ 20K in agreement with the evolution expected for an improper ferroelastic.[11] In a very recent paper, Asahi *et al.*[13] have determined the temperature dependence of both the rotation angle β and the gyration g and found an increase with decreasing temperature similar to that of the monoclinic distortion.

On the other hand, using the (3 + 1) dimensional formalism, an analysis of the symmetry of the diffraction pattern of the INC phase has further confirmed the domain splitting.[14] In this study the INC structure of the ferroelastic domains has also been determined. It can be derived from the structure of the high temperature phase by a rigid-body rotation of MnF_6 octahedra along the polar axis (*a*-axis) and a related rectilinear motion of Ba-ions in the (b, c) plane.

In this work, we shall present a first direct observation of these domains.

EXPERIMENTAL

The sample crystals were grown by the Bridgman technique and provided by P. St-Grégoire (University of Montpellier, France). All samples used originated from the same crystal ($3 \times 6 \times 10$ mm^3, in a, b, c directions, respectively). Only (100)-cut platelets were studied. Their typical dimensions after polishing were $[0.1$ to $0.3] \times 3 \times 2$ mm^3. The crystallographic orientation was checked by X-rays and by determining the value and orientation of the birefringence $\Delta n_{b,c}$ (compare Figure 1). At room temperature $\Delta n_{b,c}$ was found to be 0.025 for $\lambda = 588$ nm, in agreement with refractive index data given in the literature[5,15] ($n_a = 1.499(1)$, $n_b = 1.480(1)$, $n_c = 1.505(1)$).

Observations were made in the temperature range 300K to 6K, using a helium flow cryostat (Oxford Instruments CF204 special, adapted for studies under a Leitz Orthoplan polarizing microscope). Intensity measurements of the transmitted light close to the orthorhombic extinction positions were realized with a microphotometer (Leitz MPV1).

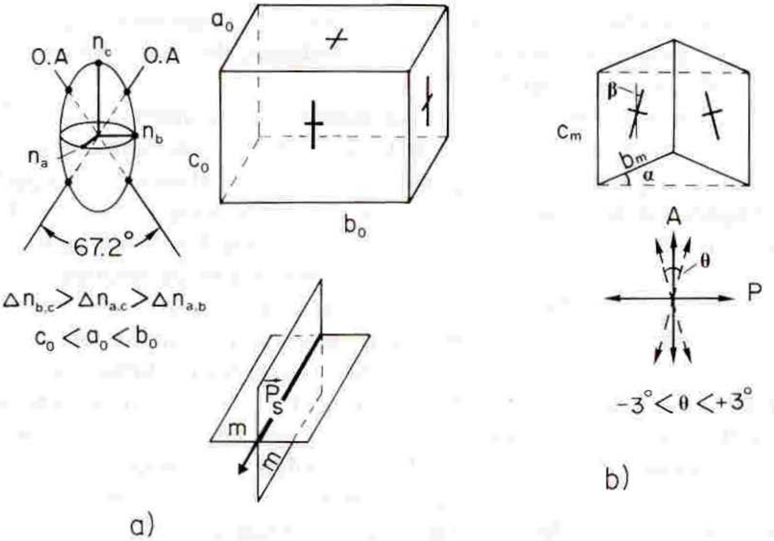

FIGURE 1 (a) Correlation of the orientation of mirror planes m, polar axis 2 (|| spontaneous polarization P_S), crystallographic axes (a_o, b_o, c_o) and optical indicatrix (O.A.: optical axis, n_i: refractive index, $\Delta n_{i,j}$: birefringence) in the orthorhombic phase. (b) Projection of a schematic representation of the monoclinic ferroelastic domains (α: monoclinic distortion, β: rotation of the indicatrix) along the polar axis 2 ($\| a_m = a_o$) and employed uncrossing (θ) of polars (A: analyzer, P: polarizer) for contrast formation.

Fig 2 and Fig 3a have been inter-changed by the printer

Fig 3a →
(caption on p. 296)

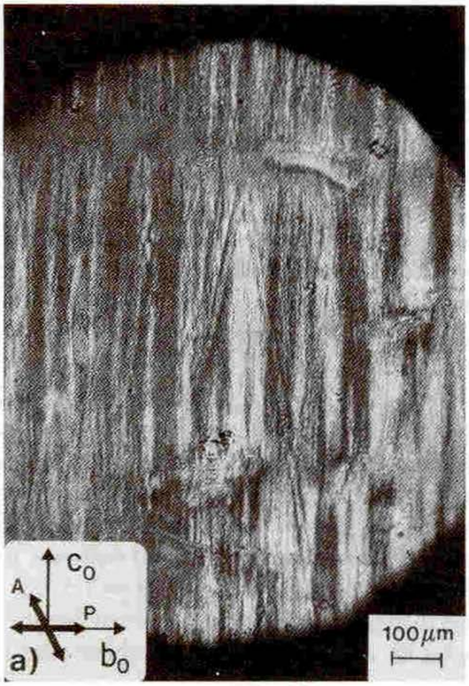

FIGURE 2 Example of the most frequent type of domain pattern observed (thickness of sample 166μm, T = 10K, white light).

RESULTS

After having brought a (100)-cut platelet at room temperature in the orthorhombic extinction position between crossed polarizers and subsequent cooling of the sample with the analyzer slightly uncrossed, the monoclinic domains begin to become visible at about 200K. A typical result is shown in Figure 2, in which very narrow lamellar domains with composition planes running approximately parallel to (010) are visible. On the microscopic level, the plane is parallel to the puckered sheets formed by MnF_6 octahedra which give rise to the predominantly 2-D magnetic spin ordering above the Néel temperature.

On the passage from the 2mm to the 2 symmetry the (001) mirror is also lost and in principle may give rise to a second kind of twin wall, perpendicular to the former. However, on several examined samples such (001) walls have not been observed, in agreement with the results from γ-ray and X-ray studies,[11,12] which showed a doubling of the diffraction spots along the b^*-axis, but not along the c^*-axis. Hence, one has to assume that the latter type of wall is energetically unfavorable, a result which is not astonishing, considering the highly anisotropic character of the structure.[6]

The domain pattern usually changed after every renewed descent below the transition temperature T_i, but with the ratio of the twin states staying always about 1 to 1, in agreement with the X-ray structural analysis.[14]

On a few platelets domains larger than those on Figure 2 have been observed which permitted measurement of the angle between the extinction positions of the two domain states. Figures 3a and 3b show such domains in opposite contrast, corresponding to the left hand and right hand uncrossing of the analyzer, respectively. One remarks a somewhat fibrous aspect of the domains which seems to be related to the rather strong curvature of the domain walls in the depth of the sample.

On Figure 4 is shown the transmitted light intensity of the two domain states when the crystal is mounted between two polars and when the analyzer is uncrossed in clockwise and anticlockwise manner, starting from the extinction position of the orthorhombic phase. By searching the minimum of these functions, one finds that they are separated by 11 (±2) min of arc at T = 6K, and λ = 643 nm and for a crystal thickness of 270 μm. No attempt has been made so far to optimize the thickness for contrast formation, nor to separate the effects of rotatory power and birefringence as was done in the optical studies.[3,13] One can see (Figure 4) that the difference in transmitted light intensity increases with the uncrossing angle θ. This effect can unfortunately not be fully exploited because of the accompanying increasing glare. Thus a compromise for optimal contrast for observation or photography was found at an uncrossing angle of $2\theta \simeq 2.5°$ for that particular sample which seems to behave differently than the sample of Figure 3 ($2\theta \simeq 1.6°$, thickness 128μm). Measurements at other temperatures show that the angle between the

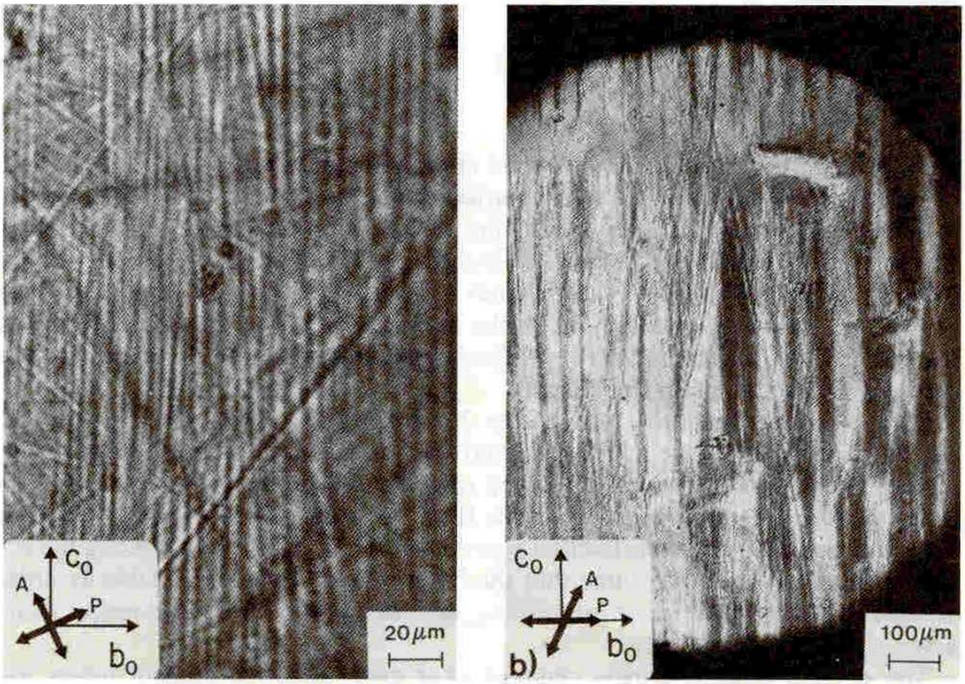

Fig2→

FIGURE 3 Example of unfrequent "larger" domains in opposite contrast configurations (thickness 128μm, T = 10K, white light). θ = +0.8° (a), θ = −0.8° (b).

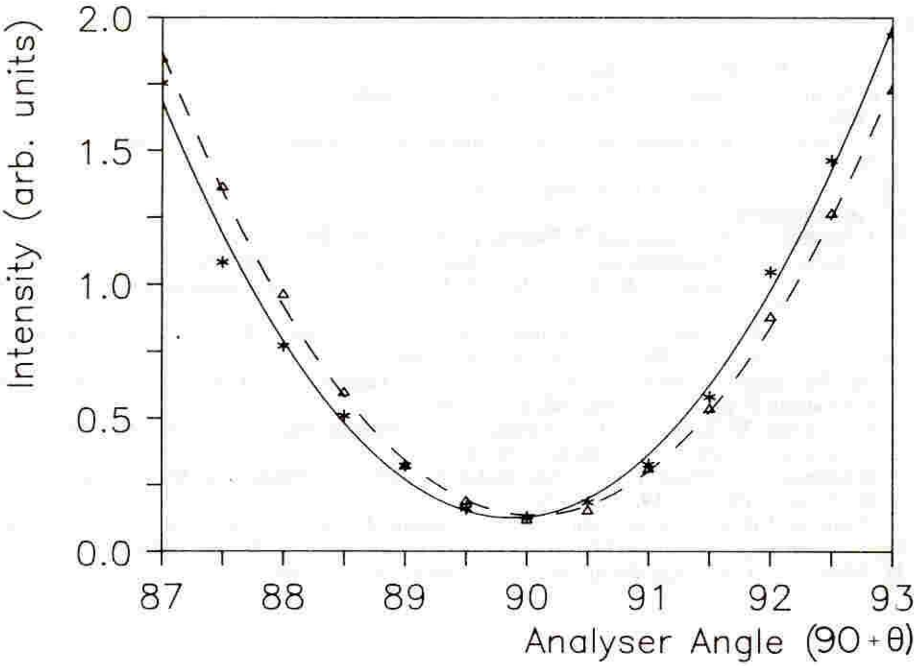

FIGURE 4 Transmitted light intensity versus analyzer angle (90° + θ) around the orthorhombic extinction position ($\theta = 0°$) for two adjacent monoclinic domains (thickness 270μm, $T = 6K$, $\lambda = 643$ nm); the measurements have been fitted by a $ax^2 + bx + c$ function.

two minimum intensities decreases when the temperature increases (about 5 min at 160K). It is of the same order of magnitude as the rotation of the index ellipsoid given by Asahi *et al.*[13]

CONCLUSION

The first direct observation in this study of the ferroelastic domains of the INC phase of $BaMnF_4$ is consistent with former γ-ray,[11] X-ray[12] and optical[3,13] measurements. This investigation has also shown the absence of (001) twin walls and the presence of (010) walls only, a result indirectly deduced earlier by diffraction studies. Moreover, the approximate 1 to 1 ratio of the two ferroelastic domain states found in the structural analysis[14] of the INC phase has also been confirmed.

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