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Transmission-electron-microscopy observation of the memory effect through the pattern of discommensurations in barium sodium niobate

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We report the first observation in direct space of a manifestation of the memory effect specific to incommensurate (INC) materials. It is found, using transmission electron microscopy, that barium sodium niobate samples cooled rapidly after annealing in the INC phase exhibit at room temperature two distinct regions with different configurations and spacings of discommensurations. These results are correlated to x-ray diffraction data.

The existence of a memory effect specific to incommensurate (INC) systems has been pointed out on theoretical[1] and on experimental grounds.[2] It consists of the fact that if a sample is maintained a sufficient amount of time at a temperature T_A within the INC phase, the properties of the system observed in a subsequent temperature scan differ from those observed in the absence of annealing at T_A, and the modifications of the properties are specific to the annealing temperature T_A.

During fast temperature scans, a prominent modification is the freezing-in of the modulation wave vector, in a certain temperature interval away from T_A, at the wave-vector value realized at T_A or at a value close to it.

Among INC materials displaying the memory effect, barium sodium niobate[3] (BSN) exhibits two remarkable features. In the first place, the freezing-in of the wave vector extends to several tens of degrees away from T_A,[4] while in other available examples it is confined to an interval of a few degrees. On the other hand, by fastly cooling the samples from T_A (which lies within the range of the INC phase $\sim$250–300 °C) one observes,[4] below the range of freezing-in of the wave vector, a splitting of the INC satellite reflections into two components whose positions, widths, and relative intensities at room temperature (RT) depend on the location of T_A within the INC phase.

In this Rapid Communication, we investigate the latter aspect of the memory effect by a transmission-electron-microscopy (TEM) investigation in direct space. We have examined at RT the pattern of discommensurations (DC) in BSN subsequent to an annealing at various temperatures T_A situated within the INC phase, or in the high-temperature phase.

This study constitutes the first probing of the nature of the memory effect in direct space at the microscopic level. Up to now, in BSN as in other substances, the memory effect had been revealed either through the measurement of macroscopic quantities or by diffraction experiments.

BSN (001) plates were prepared by mechanical polishing followed by ionic beam thinning. TEM observations were achieved with a Siemens 100-kV microscope provided with a top-entry goniometer. Several observations were made on every sample. Between two observations, the sample was removed from the TEM sample holder, annealed in a furnace for durations of 15–60 h (in order to "saturate" the memory effect[5]), then rapidly cooled to RT. Dark field images were obtained at RT in the TEM by selecting INC-satellite reflections.[6]

In the absence of annealing (e.g., after thermally cycling the sample), we observe the same type of pattern as described in several recent TEM observations of BSN.[6] The pictures reveal the presence of discommensurations which have the form of wavy lines, generally directed along either the [110] or the [1$\bar{1}$0] direction (referred to the axes of the high-temperature tetragonal phase). A number of nodes formed by the merging of four DC's are observed on the pictures, in agreement with the $\pi/2$ phase shift associated to each DC in BSN.[6] Two other types of walls are also detected. (i) Walls separating ferroelectric domains which appear as irregularly shaped closed loops. These walls, as well as the associated ferroelectric displacements were shown to have no interplay with the INC modulation.[2,6,7] They will not be discussed further here. (ii) Walls separating ferroelastic domains, whose intersections with the (001) plane, appear as lines parallel to [100] or to [010].

In the dark field images one of the two ferroelastic domains surrounding a ferroelastic wall appears clear and the other is dark. An appropriate tilt of the sample allows one to reverse the contrast of the two domains. This contrast is related to the fact that, at RT, two adjacent domains correspond to distinct satellite reflections.[7]

The regularity of the DC's observed in each domain is very poor. However, it is possible to estimate, from the average distance between DC's, the value of the incommensurability parameter $\delta \approx 1\%$, in agreement with previous TEM data[6] and diffraction results.[7]

Qualitative and quantitative differences with the preceding situation are observed in annealed samples.

Figures 1 and 2(a) show pictures obtained in a sample annealed $\sim$100 °C above the range of the INC phase

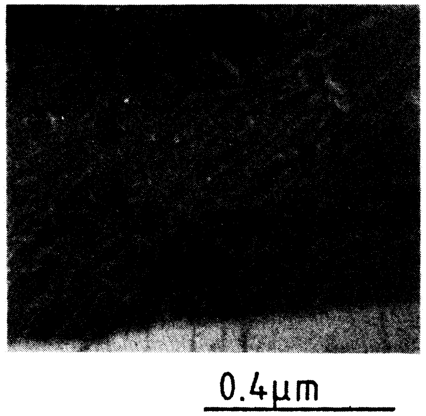

FIG. 1. RT dark-field image from satellite reflections. This micrograph shows a region where the DC's appear as lines regularly spaced and well aligned along the [110] direction. Such regions with ordered pattern of DC's can only be obtained after an annealing in the normal phase (here $T_A \approx 400\,^\circ\mathrm{C}$).

($T_A \simeq 400\,^\circ\mathrm{C}$) and then rapidly cooled to RT. DC's are visible inside ferroelastic domains. In comparison to the unannealed situation, one can find regions where the DC's are more regularly spaced, less wavy shaped, and better oriented along the expected [110] or [1$\bar{1}$0] direction (see Fig. 1). In two adjacent domains they have perpendicular directions [see Fig. 2(a)]. The value of δ deduced from the DC spacing is $\simeq 1\%$ as in the unannealed procedure.

Figures 2(b) and 2(c) show micrographs corresponding to a sample annealed at two distinct temperatures *within* the INC phase and subsequently quenched down to RT. Several remarkable features can be distinguished.

(i) In the large ferroelastic domain, the pattern of DC's is not uniform. Two regions are clearly visible. In the first one, the DC's possess their expected [110] orientation, but they are very irregularly shaped and spaced. In this region the density of DC's is significantly higher than in the cases discussed above. For instance, for an annealing at $T_A = 275\,^\circ\mathrm{C}$ one finds $\delta_F \approx 4\%$ [Fig. 2(b)]. At 265 °C one measures $\delta_F \approx 1.5\%$.

(ii) In the other region, which is adjacent to the ferroelastic domain wall, there are few DC's. Their density corresponds to a value of δ an order of magnitude smaller than δ_F: $\delta_f \approx 0.5\%$. Besides, these DC's do not possess the expected [110] orientation. Instead they mostly lie perpendicularly to the ferroelastic wall (i.e., parallel to [100]). However, a careful examination shows that they are constituted by a succession of little steps having the usual [110] orientation.

(iii) The boundary between the high DC-density region (HDR) and the low DC-density region (LDR) appears constituted by a set of nodes aligned on a line parallel to the ferroelastic wall.

(iv) The LDR extends the entire range of the perpendicular narrow ferroelastic domain (appearing dark on the picture) as checked by inverting the contrast between the two domains.

(v) The extension of the LDR depends in a very sensitive way on the annealing temperature [Figs. 2(b) and 2(c)]. This extension is larger at 275 °C than at 265 °C.

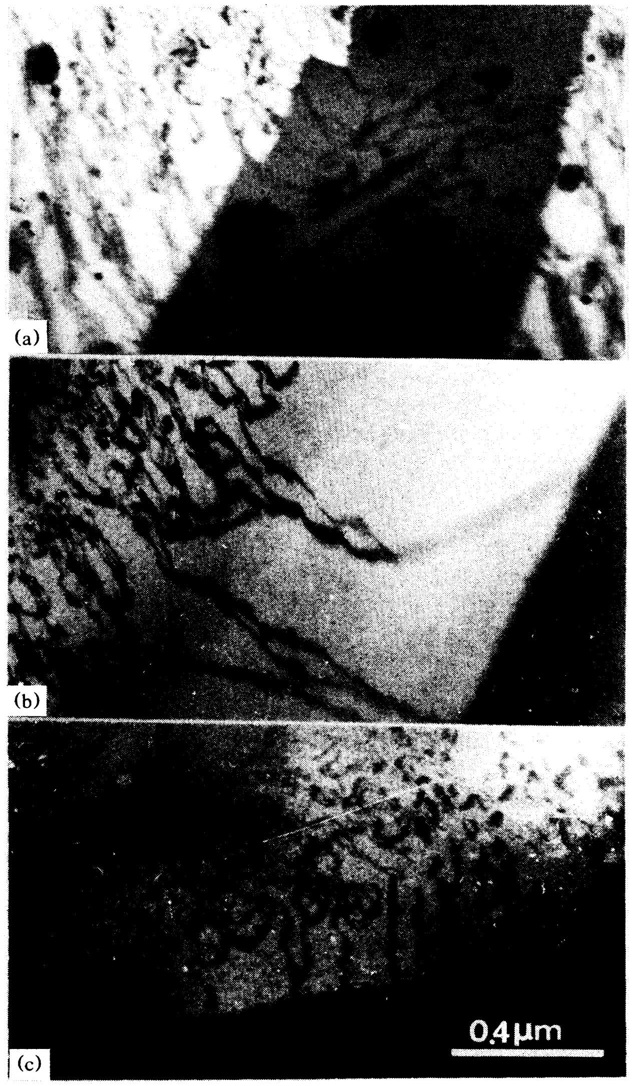

FIG. 2. Comparison of the pattern of DC's at RT for different annealing temperatures T_A. (a) $T_A \approx 400\,^\circ\mathrm{C}$, in each ferroelastic domain, appearing as extended white and black regions. The DC's pattern is homogeneous, corresponding to $\delta \approx 1\%$. The DC's are oriented along the [110] direction corresponding to an inclination at an angle of 45° with the ferroelastic domain walls. (b) $T_A \approx 275\,^\circ\mathrm{C}$ (within the INC phase); the pattern of DC's is not homogeneous. There are two regions, one with a high density of DC's (HDR) which are oriented along the [110] direction, the other with a low density of DC's (LDR) which are mostly oriented along the [100]. The boundary between the two regions is constituted by a set of nodes which are lines up parallel to the ferroelastic wall. (c) $T_A \approx 265\,^\circ\mathrm{C}$ (within the INC phase); the LDR is less extended than for $T_A \approx 275\,^\circ\mathrm{C}$.

At the latter temperature the LDR is confined to the vicinity of the ferroelastic wall.

The preceding results clarify the nature of the RT splitting of the satellite reflections into two components detected[4] by x-ray diffraction measurements in annealed samples. Indeed, the two satellite reflections can, consistently, be associated to the two distinct types of regions observed in the TEM images, respectively, the HDR (related to the δ_F INC parameter) and the LDR (related to δ_f).

Quantitatively, the values for δ_f and δ_F deduced from the present TEM images in direct space agree with the ones found in the x-ray diffraction spectra,[4] for samples quenched down to RT from the same annealing temperature T_A. On the other hand, the ratio (I_f/I_F) of the two x-ray intensities at RT increases with the annealing temperature T_A, consistently with the observed extension of the LDR which is larger at 275 °C than at 265 °C. Finally, the widths of the x-ray satellites obtained are larger when T_A belongs to the INC phase than when T_A is in the high-temperature phase in agreement with the less regular configuration of the DC's in the former conditions of annealing than in the latter ones.

Hence, the splitting of satellites observed at RT corresponds to an inhomogeneous state of the samples involving two types of regions (of typical size 1 μm) and characterized by different DC patterns.

This inhomogeneous state, at RT, is a manifestation of the memory effect since, as stressed above, it is obtained only if a prior annealing has been performed within the range of the INC phase. Moreover, it can be erased by an annealing in the normal phase.

In order to elucidate the origin of the phase separation at RT, we can rely on the results of high-resolution (double-diffraction) x-ray measurements of the basic-lattice Bragg reflections, performed at the temperatures T_A of the annealings (Fig. 3). These measurements show that within the range of the INC phase, two phases, with slightly different lattice parameters, actually coexist in the samples. Their respective volume, deduced from the relative intensity of the corresponding Bragg reflections, varies with T_A. Moreover, this variation can be precisely

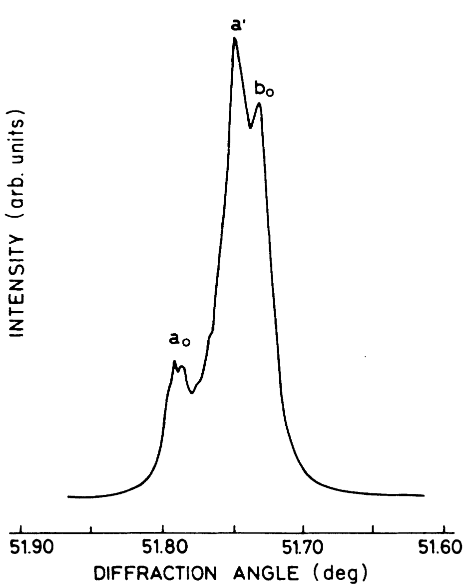

FIG. 3. Typical x-ray spectrum for Bragg reflections at temperatures situated within the INC phase. One observed two sets of lattice parameters (a_0, b_0) and (a') which correspond to the coexistence of two phases in the sample (see Ref. 8).

correlated to the relative intensity at RT, of the two satellite reflections discussed above, and observed after a rapid cooling down of the samples.

The latter property allows us to assert that the LDR and HDR regions which constitute the inhomogeneous state at RT occupy, respectively, the volumes of the two distinct phases existing at the T_A temperature of the annealing. The occurrence of different characteristics of the modulation in the two regions, at RT, can be qualitatively understood in the framework of the current interpretation of the memory effect.[1] This framework assumes that an ordering of defects takes place at the annealing temperature. This ordering is frozen-in during the subsequent fast temperature variation, and it influences the temperature dependence of the INC modulation. In the present system, a different ordering of defects is likely to take place in the two phases existing at T_A, and a different temperature dependence will therefore be induced in the INC wave vectors of the two phases during the rapid cooling down at RT. The presence of frozen-in defects waves at RT is likely to produce numerous pinning centers because the wavelengths of the modulation and of the defects ordering are not any more adapted. This is in agreement with the pronounced wavyness of the DC's in the HDR.

The nature of the two phases coexisting at T_A is not fully understood at present. It is conjectured[8,9] that the phase associated with the LDR is an INC phase with two perpendicular modulation wave vectors ($2q$ state), while the phase associated with the HDR is modulated in a single direction ($1q$ state).

The TEM observations presented here can provide indications for elucidating the nature of the two phases. Thus, the apparent correlation between the LDR and the ferroelastic walls could denote the fact that the onset of the corresponding INC phase occurs first by nucleating in these walls, then by extending through a sideward displacement of the walls [as observed in Fig. 2(b)] the fast cooling leaves the frozen-in boundary of the phase, parallel to the ferroelastic wall. Moreover, the nucleation of this INC phase inside a domain wall would be consistent with its supposed $2q$ nature since the structure of a wall is expected to be intermediate between those of the adjacent domains, and can be in the present case the superimposition of the two mutually perpendicular $1q$ states existing in the two domains.

The meaning of the unexpected orientation (turned by 45°) of the DC's in the LDR phase is not clear, but is probably related to the pattern of DC's in the $2q$ INC phase.[9]

In summary, the memory effect investigated in the present experiments has a dual aspect: (i) a memory of the spatial distribution of the regions occupied by two INC phases at T_A, which is revealed by the location of the boundaries between the LDR and the HDR at RT; (ii) in each type of region, a memory of the characteristics of the modulation prevailing at T_A, which is revealed by the different pattern of the DC's at RT, in the LDR and in the HDR, the memory being presumably written in the defects distribution.

A further understanding of the details of the TEM images requires investigating the DC pattern of the two INC phases at T_A. Up to now, TEM observations within the INC phase have been unsuccessful or not enough accurate.[6]

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[1]P. Lederer, G. Montambaux, J. P. Jamet, and M. Chauvin, J. Phys. (Paris) Lett. **45**, L627 (1984).

[2]J. P. Jamet and P. Lederer, J. Phys. (Paris) Lett. **44**, L257 (1983); H. G. Unruh, J. Phys. C **16**, 3245 (1983); G. Dolino, Jpn. J. Appl. Phys. Suppl. **24**, 153 (1985).

[3]J. C. Tolédano, J. Schneck, and G. Errandonéa, *Incommensurate Phases in Dielectrics, Modern Problem in Condensed Matter Sciences* (North-Holland, Amsterdam, 1985), Vol. 14-2, p. 233.

[4]J. M. Kiat, G. Calvarin, and J. Schneck, Jpn. J. Appl. Phys. Suppl. **24**, 832 (1985).

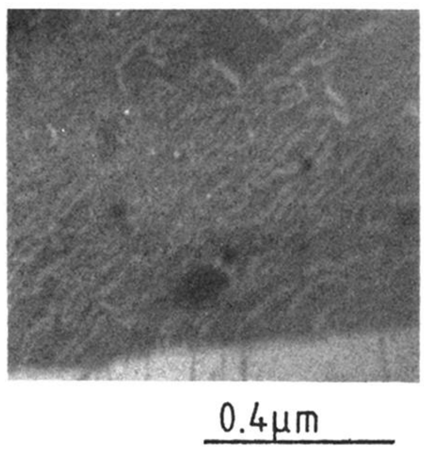
[5]G. Errandonea, J. C. Tolédano, A. Litzler, H. Savary, J. Schneck, and J. Aubrée, J. Phys. (Paris) Lett. **45**, L329 (1984).

[6]P. Xia-Qing, H. Mei-Shen, Y. Ming-Hui, and F. Duan, Phys. Status Solidi (a) **91**, 57 (1985); G. Van Tendeloo, S. Amelinkx, C. Manolikas, and W. Shulin, *ibid.* **91**, 483 (1985); S. Barre, H. Mutka, C. Roucau, and G. Errandonéa, Phase Transitions (to be published).

[7]J. Schneck and F. Denoyer, Phys. Rev. B **23**, 383 (1981); J. Schneck J. C. Tolédano, C. Joffrin, J. Aubrée, B. Joukoff, and A. Gabelotaud, *ibid.* **25**, 1766 (1982).

[8]J. M. Kiat, G. Calvarin, and J. Schneck (unpublished).

[9]J. C. Tolédano (unpublished).



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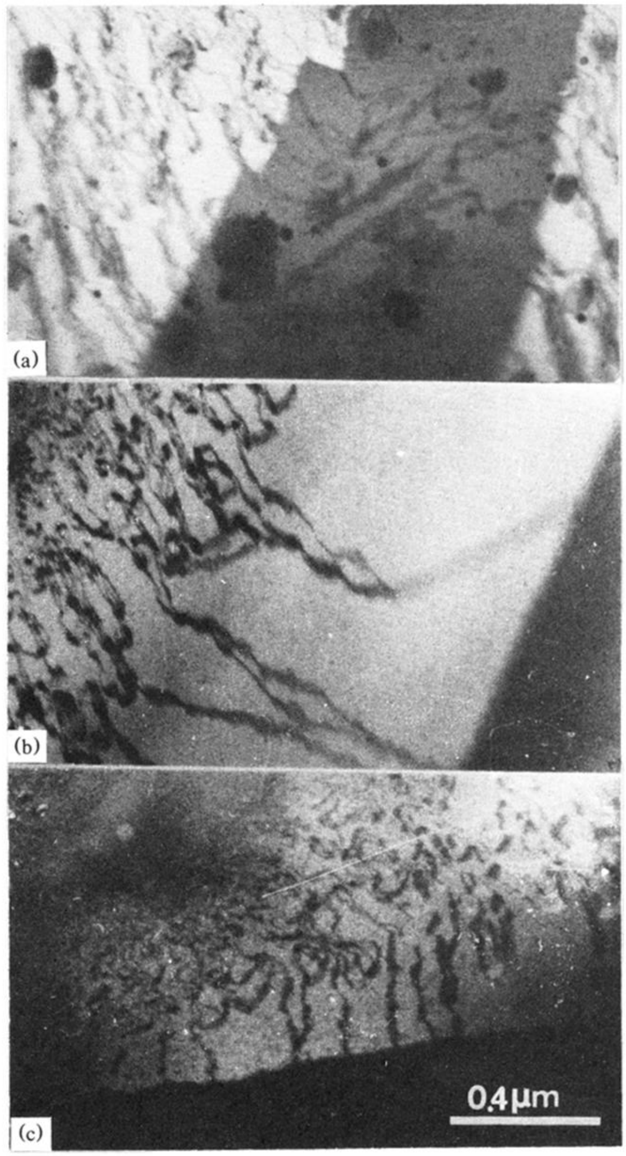

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