Diffraction evidence of the formation of defect-density waves in incommensurate modulated structures

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(Submitted 14 December 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 3, 171–174 (10 February 1994)

Diffraction evidence of the formation of defect-density waves in incommensurate modulated phases has been found for the first time by an x-ray method. The test samples were thiourea crystals. A new state of the modulated structure is established. It is characterized by a superposition of several modulation waves along a single crystallographic direction.

Many crystals with incommensurate phases exhibit a memory effect, which consists of the appearance of thermal anomalies in physical properties after a prolonged hold of the crystal at a constant temperature T_0 in the incommensurate phase.[1-3] The effect is linked with an interaction of structural modulations with mobile defects in the crystal. It is assumed that during the hold of the sample at the constant temperature this interaction leads to a periodic change in the concentration of defects, a "defect-density wave," with a period equal to the period of the structural modulations at T_0. During subsequent scans of the crystal temperature near T_0, the defect-density wave "captures" structural modulations, thereby causing anomalies in physical properties.[4]

Although a theoretical model of defect-density waves has been developed well, and although this model succeeds in explaining experimental results at a qualitative level, we do not yet have any direct structural data which confirm the existence of these waves.[3] In the present letter we report a study of structural aspects of the memory effect in incommensurate phases in the particular case of thiourea [$SC(NH_2)_2$] crystals.

Thiourea was selected because of the detailed studies of incommensurate phases which have been carried out on these crystals by a variety of methods. The modulated structure of $SC(NH_2)_2$ forms in the temperature interval 202–169 K between a paraelectric phase ($Pnma$) and a ferroelectric phase ($P2_1ma$). The structure of the incommensurate phase is characterized by rotations of the $SC(NH_2)_2$ molecules around the **b** axis with a wave vector $\mathbf{q}=\delta\mathbf{b}^*$ ($\delta=1/7$–$1/9$), as is manifested in x-ray measurements in the form of satellite reflections along the [010] direction.[5]

An x-ray study was carried out on a Siemens D500 diffractometer (CuKα radiation) with a helium cryostat in which the temperature could be regulated within 0.1 K in the range 4.2–300 K. The structural state of the crystal was determined from diffraction cross sections near the (400) reciprocal-lattice site in the direction of the $\mathbf{b}^*$ axis.

Figure 1a shows a typical distribution of the diffracted intensity near the (400) site at a given temperature T_0 in the interval of the incommensurate phase. We see

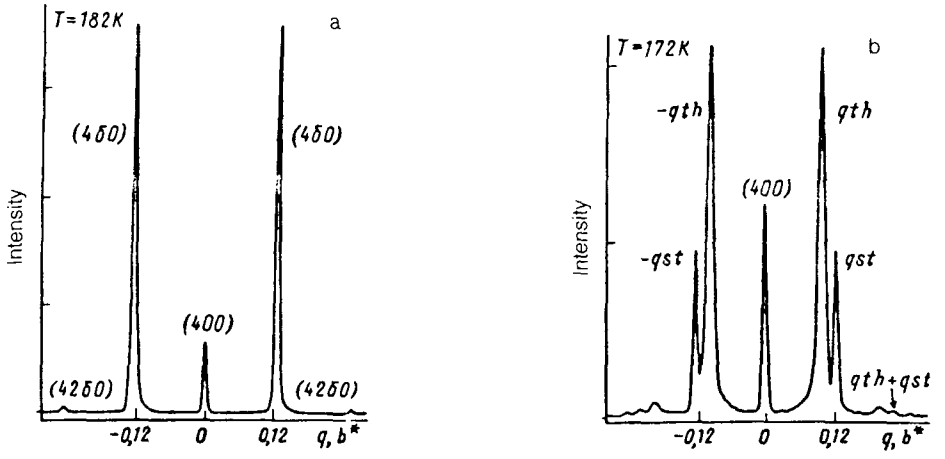

FIG. 1. Diffraction patterns of an incommensurately modulated state of thiourea. a—At $T_0 = 182$ K; b—at $T = 172$ K after thermal stabilization at T_0 (182 K).

structural and superstructural peaks, which characterize a modulation of the structure along the **b*** direction. The equilibrium temperature dependence of the wave vector and that of the intensity of the structural and superstructural reflections of the test crystal, determined from the measured spectra, agree with data in the literature.[5] During a subsequent hold of the sample at a constant temperature T_0 (182 K in the case at hand) for a day, no changes occurred in the position or shape of the reflections. This result indicates that there were no significant changes in the crystal structure. However, a shift of the sample temperature away from T_0, within the interval in which the incommensurate phase exists, led to a pronounced change in the diffraction image: a splitting of the first-order satellite reflections into two peaks (Fig. 1b). This splitting indicates the formation of two coexisting modulation waves along the [010] direction in the crystal.

Figure 2 shows the transformation of the diffraction spectra as the crystal temperature is varied after thermal stabilization at T_0. A decomposition of such spectra revealed that a modulation wave with an unaltered wave vector $\mathbf{q}_{st}$ (a stabilization wave), corresponding to the equilibrium value at the point of the thermal stabilization in the original crystal, and a modulation wave whose wave vector $\mathbf{q}_{th}$ varies with the temperature (an equilibrium wave) coexist in the sample at each temperature point in the incommensurate phase, except the temperature of the thermal stabilization. This circumstance is reflected in Fig. 2: The stabilization satellite reflections do not change position when the temperature is changed, while the equilibrium superstructure reflections shift toward a structural reflection as the temperature is lowered, as in a sample not subjected to a preliminary thermal stabilization.

Outside the temperature interval of the modulated structure ($T_c < T < T_i$), which was detected independently from the characteristic changes in the lattice constants, the equilibrium satellite reflections disappear, while the stabilization peaks persist even

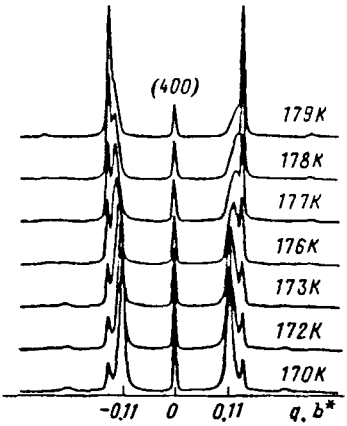

FIG. 2. Evolution of the dynamics of the diffraction structures with the temperature after thermal stabilization at $T_0 = 182$ K.

outside this region[1)] (Fig. 3). Their intensities decrease sharply, but their half-widths are the same as in the incommensurate region, indicating a large spatial extent (> 1000 Å) of the stabilization modulations in the crystal.

The satellite peaks outside the region of the incommensurate phase characterize a modulation-deformed state of the crystal with ordered defects. If we assume the formation of defect-density waves in the incommensurate phase, then we must assume that they persist for a certain time (determined by the diffusive mobility) even outside the incommensurate region. On the other hand, the scattering of x rays by defects does not in itself give rise to individual peaks unless new phases are formed as a result. Consequently, the preservation of the stabilization satellite peaks is due to diffraction by the basic lattice of the crystal, which is distorted in a periodic fashion. It is natural to suggest that these distortions are periodic deformations of the lattice caused by a periodic distribution of defects in a defect-density wave which are not at equilibrium at these temperatures. The low intensity of the stabilization peaks indicates that these deformations are of small amplitude. Consequently, the stabilization peaks reflect a wave distribution of defects and are evidence, from the standpoint of diffraction, of the existence of defect-density waves.

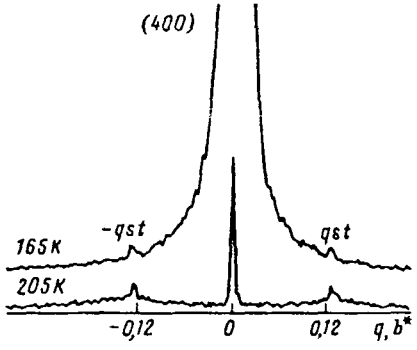

FIG. 3. Some typical diffraction patterns of thiourea outside the region of the incommensurate phase (162 K corresponds to the ferrophase, and 205 K to the paraphase) after thermal stabilization.

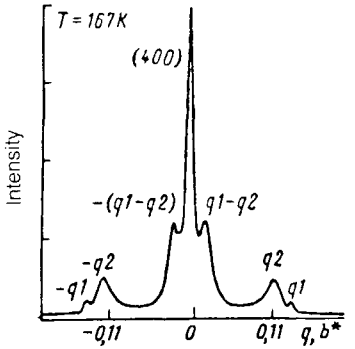

FIG. 4. Diffraction pattern of a superposition modulated state after the induction of two defect-density waves.

The stabilization peaks are metastable throughout the region in which they exist. In the region of the incommensurate modulated phase, their intensity is transferred to equilibrium satellite reflections during subsequent holds of the crystal away from T_0; outside the modulation region, intensity is transferred to the main peak.

Analysis of the diffraction patterns yields certain conclusions regarding the structural state of the crystal during the coexistence of several modulations in a single crystallographic direction. Two situations are possible here: Either the crystal has a domain-like structure, with different modulation waves in neighboring domains, or there is a superposition of coexisting modulation waves throughout the volume of the crystal. In the second case, the diffraction patterns should acquire some additional satellite reflections characterized by sum wave vectors ($\mathbf{q}_{st}+\mathbf{q}_{th}$) and difference wave vectors ($\mathbf{q}_{st}-\mathbf{q}_{th}$); this is what is found experimentally (Figs. 1b and 4). Along with the first-order satellite reflections in Fig. 1b we see some second-order reflections. Between them we see peaks corresponding to the sum wave vector $\mathbf{q}=\mathbf{q}_{st}+\mathbf{q}_{th}$. Consequently, these results are unambiguous evidence of the observation of a new state of incommensurate modulated structures, characterized by superposition of several modulation waves in a single crystallographic direction.

Annealing at various temperatures in the incommensurate phase can induce complex modulations in the crystal, consisting of several stabilization waves. The resultant modulation of the structure occurs through a superposition of these waves again in this case. As an example, Fig. 4 shows a diffraction pattern on which we can see a superposition of two stabilization waves. In addition to the stabilization reflections corresponding to the wave vectors $\mathbf{q}_1$ and $\mathbf{q}_2$, some additional peaks are formed near a structural reflection. These additional peaks are characterized by the difference wave vector $\mathbf{q}=\mathbf{q}_1-\mathbf{q}_2$.

In conclusion we would like to point out that the simultaneous coexistence of several modulation waves over the entire incommensurate range differs from the formation of a plateau on the temperature dependence of the wave vector. Such a plateau has been proposed previously and has been used to explain memory effects in such systems.[4] According to structural data reported here, the memory effect reflects an equality of the periods of the coexisting structural modulations near the temperature of the thermal stabilization.

We wish to thank V. K. Magataev for furnishing the crystals used in this study.

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Translated by D. Parsons