Multiwave modulated states in TMA-$ZnCl_4$ crystals

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It has been shown by an x-ray method that a uniaxial stress in TMA-$ZnCl_4$ crystals induces structural states in which several modulation waves coexist along the same crystallographic direction. Depending on the temperature and the loading conditions, there may be either a superposition of several modulation waves throughout the volume or a domain-like structure in the sample.

Crystals of tetrachlorozincate-tetramethylammonium, $\{N(CH_3)_4\}_2ZnCl_4$ (TMA-$ZnCl_4$), have the β-K_2SO_4 structure in the original high-temperature phase (space group $Pmcn$) ($\mathbf{b} > \mathbf{c} > \mathbf{a}$). At atmospheric pressure they undergo five structural phase transitions: $Pmcn$—(incommensurate phase)—$P2_1cn-P112_1/n-P12_1/c1-P2_12_12_1$, at 23, 7, 3.4, -92, and -112 °C. The only polar phase, $P2_1cn$, is bounded on the right along the temperature axis by the incommensurate phase and on the left by the ferroelastic $P112_1/n$ phase. Modulations in the incommensurate phase are characterized by a wave vector $\mathbf{q}_1 = (\frac{2}{5}+\delta)\mathbf{c}^*$, where δ is a parameter of the incommensurability, and $\mathbf{c}$ is the lattice constant of the original phase. In the polar phase, the spontaneous polarization is directed along the $\mathbf{a}$ axis, and the lattice constant along the $\mathbf{c}$ axis is five times that in the original phase ($\mathbf{q}_2 = \frac{2}{5}\mathbf{c}^*$). In the ferroelastic phase, there is a tripling of the lattice constant along the $\mathbf{c}$ axis ($\mathbf{q}_3 = \frac{1}{3}\mathbf{c}^*$).

The crystal lattice of these crystals is known to be sensitive to external perturbations. In particular, a hydrostatic pressure $p > 1$ kbar erases the polar phase.[1] Measurements[2] of the dielectric constant and spontaneous polarization have shown that the polar phase also disappears completely during uniaxial compression of the crystal along directions perpendicular to the spontaneous polarization. It was found that the critical load σ_{cr} is smaller than p_{cr} by a factor of about 40.

In this letter we are reporting a study of structural aspects of the effect of a uniaxial stress on the phase diagram of TMA-$ZnCl_4$ in the region in which the polar phase exists.

For the experiments, platelets with dimensions of $2 \times 3 \times 3.5$ mm were cut from a TMA-$ZnCl_4$ single crystal; the faces of the platelets were oriented along the crystallographic a, b, and c axes, respectively. The experiments were carried out on a Siemens D-500 x-ray diffractometer (Cu $K\alpha_1$ radiation). To reduce radiation damage to the test samples, we carried out the measurements at low doses (20 kV×8 mA). The stress was applied to the sample along the b axis (this was a σ_{yy} loading) in a special jig in a cryostat. The temperature and the degree of compression of the crystal were regulated within 0.1 °C and 0.5 bar, respectively. The structural state of the crystal was monitored on the basis of the position and profile of satellite reflections which accompany the (200) and (400) Bragg reflections in the modulated phases.

To see structural features of the suppression of the ferroelectricity, we applied a uniaxial stress at various points along the temperature scale in the polar phase. We also scanned the temperature interval including the polar phase with a constant load on the crystal.

It was found that the uniaxial stress causes a substantial change in the modulation state of the crystal in the temperature region of the polar phase. The diffraction patterns of the [*h*0*l*] site row (Fig. 1) contain various combinations of coexisting satellite reflections, depending on the temperature at which the stress is applied and depending on the degree of compression of the crystal. When the crystal is compressed in the low-temperature part of the polar phase, at $T=4$ °C (Fig. 1a), satellites appear on the diffraction pattern at the positions $\mathbf{q}_3=\frac{1}{3}\mathbf{c}^*$, along with the original satellites, in $\mathbf{q}_2=\frac{2}{5}\mathbf{c}^*$ positions. As the compression is raised, intensity is transferred from satellite reflections of the polar phase to satellites corresponding to the modulations with $\mathbf{q}_3=\frac{1}{3}\mathbf{c}^*$; i.e., the ferroelastic component of the modulations increases at the expense of the polar component. This process terminates in the complete disappearance of the satellites of the polar component at $\sigma_{yy}>23$ bar.

Figure 1b shows experimental results on compression of the crystal in the upper part of the polar phase, at $T=6.6$ °C. We see that in this case the compression leads to the appearance of an additional satellite on the diffraction pattern. This new satellite corresponds to modulations in the incommensurate phase of the unstressed crystal. As the compression is raised, the satellite of the incommensurate component of the modulations intensifies, and its center of gravity shifts, signifying an increase in the incommensurability parameter in the lattice. Again at this temperature, at critical stresses $\sigma_{yy}>33$ bar in the crystal, we are left with essentially only the ferroelastic component of the modulations, with $\mathbf{q}_3=\frac{1}{3}\mathbf{c}^*$.

Figure 1c shows diffraction patterns for compression of the crystal in the central part of the temperature region of the polar phase. Here we see a coexistence of satellites in $(\frac{2}{5}+\delta)\mathbf{c}^*$, $\frac{2}{5}\mathbf{c}^*$, and $\frac{1}{3}\mathbf{c}^*$ positions; i.e., the uniaxial stress induces multiwave modulations of the structure which are characterized by the coexistence, with the original satellite of the polar phase, of some satellite reflections corresponding to the incommensurate phase and the ferroelastic phase. As the compression is raised, intensity is initially pumped from the polar-component satellite into the satellites of the two other components of the modulations, and at $\sigma_{yy}>33$ bar we are essentially left with only the low-temperature ferroelastic component of the modulations.

Multiwave modulated states characterized by the coexistence of several satellite reflections on the diffraction patterns are also observed in the crystal under the condition $\sigma_{yy}=\text{const}$ as the temperature interval of the polar phase is scanned (Fig. 1d).

It is important to note that in all these cases the changes in the satellite reflections observed upon compression of the crystal are reversible, as can be seen from the restoration of the original state as the loading of the sample is reduced or terminated.

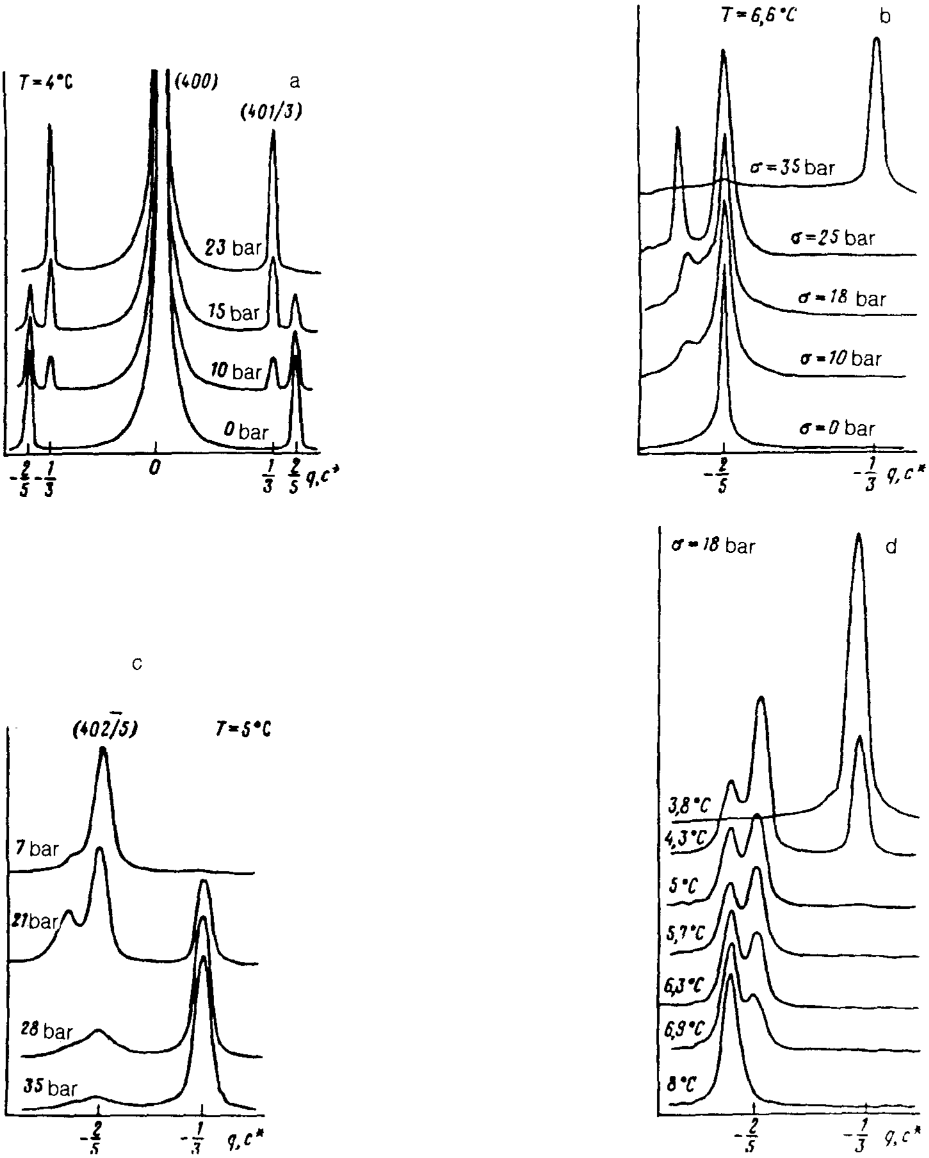

FIG. 1. Transformation of diffraction spectra of the polar phase of TMA-ZnCl$_4$ during mechanical loading. a—At a low temperature; b—at a high temperature; c—at an intermediate temperature; d—as the temperature is varied at a constant load.

The results are unrelated to a nonuniform distribution of the load or of the temperature along the crystal, as can be seen from the fact that the ratio of the intensities of the coexisting satellite reflections is the same for the various regions (~ 100 μm in size) of the sample which are involved in the x-ray diffraction. A uniaxial stress in the

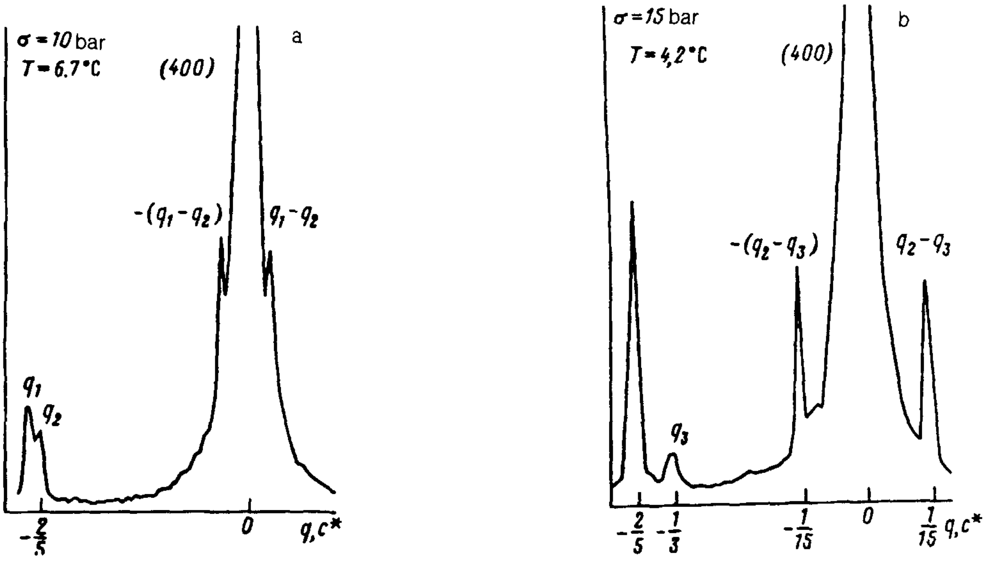

FIG. 2. Diffraction spectra representing a superposition of modulation waves of (a) the incommensurate phase and the polar phase and (b) the polar phase and the ferroelastic phase.

region of the polar phase of the TMA-ZnCl$_4$ crystal thus transforms initial modulations with $\mathbf{q}_2 = \frac{2}{5}\mathbf{c}^*$ into a modulated state with several components, namely, $\mathbf{q}_1 = (\frac{2}{5} + \delta)\mathbf{c}^*$, $\mathbf{q}_2 = \frac{2}{5}\mathbf{c}^*$, and $\mathbf{q}_3 = \frac{1}{3}\mathbf{c}^*$, which correspond to the incommensurate phase, the polar phase, and the ferroelastic phase in the unstressed crystal.

When the satellite reflections coexist on the diffraction patterns, two different situations are observed. The difference indicates a difference in the nature of the realization of the multiwave modulations in the crystal. On the diffraction patterns in Fig. 2, in the case of a coexistence of the satellite reflections $\mathbf{q}_1 = (\frac{2}{5} + \delta)\mathbf{c}^*$, $\mathbf{q}_2 = \frac{2}{5}\mathbf{c}^*$ and $\mathbf{q}_2 = \frac{2}{5}\mathbf{c}^*$, $\mathbf{q}_3 = \frac{1}{3}\mathbf{c}^*$, we also observe some additional satellite reflections, corresponding to modulation wave vectors $\mathbf{q}_1 - \mathbf{q}_2 = \delta\mathbf{c}^*$ (Fig. 2a) and $\mathbf{q}_2 - \mathbf{q}_3 = \frac{1}{15}\mathbf{c}^*$ (Fig. 2b), respectively. This situation arises when the crystal is deformed in the high- and mid-temperature parts of the polar phase. The observation of difference wave vectors in reciprocal space is unambiguous evidence that the modulation of the structure in this case is characterized by a superposition of waves of coexisting **q** components. The suppression of ferroelectricity during compression of the crystal in this case consists of a decrease in the amplitude of the modulation of the polar component, to the point that it disappears, since the intensities of the satellites of the different components are governed by the amplitudes of the waves involved in the superposition.

In the case of compression in the low-temperature part of the polar phase (Fig. 1a), we did not detect difference wave vectors. It may be that in this case the crystal consists of alternating regions (domains) with different modulation vectors. The suppression of the polar phase during compression of the crystal is explained in this case as resulting from a decrease in the volume fraction of the domains of this phase and their complete disappearance at the critical stresses. Further research will be required in order to resolve the question of whether energy conditions favor the realization of a superposition structure or a domain structure of the multiwave modulated states during the application of a uniaxial stress.

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