Dislocation instability of an incommensurate phase in connection with the floating phase in an NH_4HSeO_4 crystal

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A temporal instability of an incommensurate phase in NH_4HSeO_4 has been detected for the first time on the basis of the NMR spectra of ^{77}Se. This instability is probably caused by a dislocation-induced floating of this phase. The critical temperature for the process, $T_{cr} = -2$ °C, is interpreted as a phase transition to a floating phase.

An incommensurate phase with a population modulation by the protons of two-valley hydrogen-bond potentials was recently discovered in the NH_4HSeO_4 crystal.[1] In the present letter we report the first observation of a new phase between the incommensurate and paraelectric phases. This new phase probably corresponds to the so-called floating phase. In addition, we offer an interpretation of the instability of the incommensurate phase observed in the NH_4HSeO_4 crystal.[2] In the present experiments we used the method of high-resolution NMR of the rare ^{77}Se nuclei.

As a free NH_4HSeO_4 crystal (with unpinned ends) is cooled from room temperature at 0.2 deg/min, the known sequence of phase transitions is observed: paraelectric ($T_i = -13$ °C) $\rightleftarrows$ incommensurate ($T_{c_1} = -24$ °C) $\rightleftarrows$ ferroelectric ($T_{c_2} = -175$ °C) $\rightleftarrows$ low-temperature phase.[1,3] If the crystal is held at room temperature for about 30 h in the incommensurate phase, however, the NMR spectrum begins to change (Fig. 1). The continuum of frequencies characteristic of modulated structures (the hatched spectrum) breaks up into distinct lines, whose intensities gradually decrease. At the same time, new lines appear in the spectrum and intensify. After about 2 h, these temporal changes in the spectrum cease. Analysis of the orientational dependences

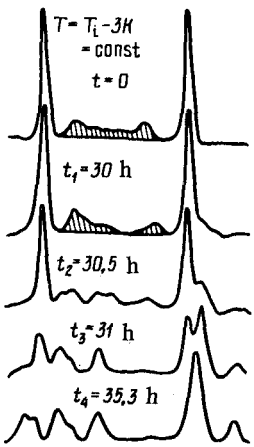

FIG. 1. Time evolution of the spectrum of ^{77}Se in the incommensurate phase of the NH_4HSeO_4 crystal. The spectrum for $t = 0$ is that found immediately after the temperature $T = T_i - 3$ K is reached.

shows that the steady-state spectrum consists of lines of a previously unknown crystallographic modification (denoted here as phase VI) and the weak residual spectrum of the incommensurate phase. If, after this delay, the crystal is cooled to temperatures corresponding to the deep ferroelectric phase, or if the crystal is heated to room temperature, then the spectrum of the two-phase system persists over this entire region, exhibiting no changes of any sort. At room temperature the spectrum of the paraelectric phase is gradually restored. When the cooling-heating cycle is repeated, we observe a memory effect: The changes in the spectrum of the incommensurate phase arise after the crystal is held for only 3 h at a constant temperature. During subsequent cooling-heating cycles, the transition to the incommensurate phase is not detected, since the "decay" of the spectrum begins above T_i. The intensity of the spectrum of modification VI increases from cycle to cycle, and the restoration of the spectrum of the paraelectric phase at room temperature occurs progressively more slowly (Fig. 2). It is important to note that when phase VI appears, the sample becomes cloudy. The application of a uniaxial pressure ~ 10 kt/cm^2 metric kilotons per square centimeter) along the a axis sharply stimulates the spectral decay described above, shortening the lifetime of the incommensurate phase to 3 h in the first cooling-heating cycle. The same result is found at lower pressures.

In some other experiments, a crystal which had not been studied previously was held at a constant temperature above the transition to the incommensurate phase. Unexpectedly, the temporal changes in the spectrum corresponding to the formation of phase VI and the development of a cloudiness in the crystal occurred even in this case. The effect was observed only below a certain threshold temperature $T_f \approx -2$ °C, which varied within a few degrees from sample to sample. The measurements were taken under uniaxial pressure in order to reduce the time we had to wait for the decay of the spectrum and in order to determine T_f more accurately.

The appearance of cloudiness in a free sample is a regional effect, and in a sample under stress the cloudiness propagates away from the plane where the load is applied.

The thermodynamic state of the NH_4HSeO_4 crystal is therefore unstable at temperatures between the ferroelectric phase and T_f. One of the simplest explanations for

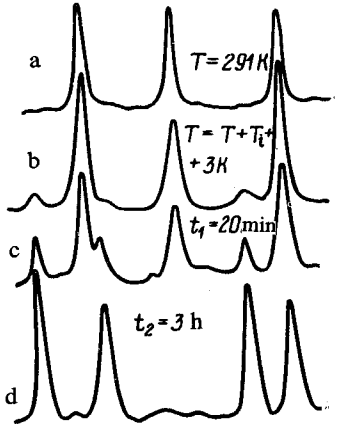

FIG. 2. NMR spectra of ^{77}Se in a crystal which has undergone repeated cooling-heating cycles: cooling below $T_i \leftrightarrow$heating to room temperature. A load $p = 10$ kt/cm^2 was applied to the crystal to accelerate events. a—Spectrum of the paraelectric phase restored after a hold at room temperature; b, c, d—case in which the changes in the spectrum begin above T_i. The growth of lines of phase VI along the time scale is clearly evident.

the nonequilibrium processes in the incommensurate phase might be a diffusion of impurities under the influence of local stresses caused by a modulation wave.[4] This interpretation, however, cannot explain the existence of kinetic processes above T_i and the development of a cloudiness in the crystal. This cloudiness suggests that the diffusion processes are correlated over scale lengths on the order of the wavelength of visible light. We wish to suggest that the mechanism triggering the instability is a nonconservative dislocation climb through a network of point defects under the influence of the uniaxial pressure or growth stresses. Confirmation of this mechanism comes from the fact that crystals grown independently differ slightly in the lifetime of the incommensurate phase and in the time required for restoration of the paraelectric phase.

In contrast with the homogeneously ordered crystals, in which the contribution of dislocations to the thermodynamics is insignificant,[5] the role of dislocations or walls may become important in crystals with a spatially inhomogeneous order parameter.[6] This possibility has been demonstrated for the particular case of the ANNNI model[6,7]:

$$\mathcal{H} = -\sum_{\mathbf{x}\vec{\delta}_1} I_1(\vec{\delta}_1)\sigma_{\mathbf{x}}\sigma_{\mathbf{x}+\vec{\delta}_1} + \sum_{\mathbf{x}\vec{\delta}_2} I_2(\vec{\delta}_2)\sigma_{\mathbf{x}}\sigma_{\mathbf{x}+\vec{\delta}_2}, \quad (1)$$

where $\sigma_{\mathbf{x}} = \pm 1$, the first term describes the coupling of nearest neighbors, and the second term describes the coupling with next-nearest neighbors.

This model with competing interactions was originally used to describe incommensurate structures. Villain and Bak[6] later showed that in the two-dimensional case and under the condition $I_1 \approx 2I_2$, i.e., when the couplings in the various coordination spheres are approximately the same, there exists a floating phase above the incommensurate phase. In this floating phase, the long-range order is disrupted by the macroscopic density of dislocations and walls. We believe that it is this phase which exists below T_f. We interpret phase VI as a modification which grows from a dislocation melt. We are offering this mechanism as a working hypotheses which describes and relates several experimental facts.

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