
**MAGNETISM
AND FERROELECTRICITY**

Unusual Spontaneous Twisting of an $(\text{NH}_4)_2\text{SO}_4$ Crystal in a Torsion Pendulum below the Curie Point

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Received September 19, 2000

Abstract—It is found that the ferroelectric phase transition in the ammonium sulphate crystal $(\text{NH}_4)_2\text{SO}_4$ at $T_C = 223$ K is accompanied by spontaneous twisting of samples around the a , b , and c crystallographic axes in the ferroelectric phase. This twisting, observed with a torsion pendulum, cannot be explained solely by the change in symmetry $mmm \rightarrow mm2$ at the Curie point. It is supposed that the twisting is connected with a complex rearrangement of the structural elements of the crystalline lattice below the Curie temperature. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The effect of spontaneous twisting of a sample in a torsion pendulum at temperatures lower than the Curie point (T_C) was first observed in pure proper ferroelastics $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ [1]. Later, this twisting was observed in other ferroelastics, for example, in K_2ZnCl_4 [2], in crystals of the KH_2PO_4 family [3], in KLiSO_4 [4], and in some other materials. In all these cases, crystals undergo displacive phase transitions (PTs) which are accompanied by the appearance of new components of the shear deformation in the ferroelectric phase. Such components are absent in the high-symmetry phase. If no new components of the shear deformation appear at T_C , as, for instance, in a $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ crystal at the ferroelectric phase transition ($T_C = 858$ K) from the tetragonal phase ($4mm$ point symmetry group) to another tetragonal phase ($4/mmm$), then the twisting effect is not observed [5].

In this connection, it is of interest to clarify if a ferroelectric ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ sample will be twisted as a result of a rhombic–rhombic PT when the temperature is changed. It is known [6] that this crystal has three components of shear deformation in the ferroelectric and paraelectric phases. In addition, none of these components is a new shear component, but all of them undergo an abrupt change at T_C [7, 8]. Moreover, an anomalous behavior of the elastic and nonelastic properties of the crystal subjected to twist deformations was detected in the vicinity of T_C . This behavior is likely to be due to jumplike changes in the shear components of the elastic rigidity at T_C [9].

Ammonium sulfate crystals undergo the ferroelectric PT from the high-temperature rhombic phase with

$D_{2h}^{16}(\text{Pnam})$ symmetry into the low-temperature rhombic phase with $C_{2v}^9(\text{Pna}2)$ symmetry at the Curie temperature $T_C = 223$ K [10, 11]. This transition is accompanied by the appearance of a spontaneous polarization P_s along the c axis. The P_s changes its sign at a temperature of about 85 K [12]. Some characteristic features (such as a small value of the Curie–Weiss constant ($C_{CW} = 33.8$ K), an anomalous behavior of the spontaneous polarization in the vicinity of the 85-K temperature, etc.) allow one to classify $(\text{NH}_4)_2\text{SO}_4$ as a weak ferroelectric [13]. The mechanism of the ferroelectric PT in this crystal is quite complex and is still not completely understood in detail. The $(\text{NH}_4)_2\text{SO}_4$ crystal unit cell contains 60 atoms or four formula units. It is fairly difficult to describe the structural rearrangement of this crystal at T_C . According to the idea formulated in [14], one can suppose that two ferroelectric sublattices are formed in $(\text{NH}_4)_2\text{SO}_4$, as well as in some other weak ferroelectrics, at the temperature of the ferroelectric PT. These sublattices have oppositely directed spontaneous polarizations P_{s1} and P_{s2} (subscripts 1 and 2 indicate the corresponding ferroelectric sublattices) with different temperature dependences. The spontaneous polarizations P_{s1} and P_{s2} are due to displacements of the tetrahedrons $(\text{NH}_4)_1$ and $(\text{NH}_4)_2$ along the c axis. Twisting of these tetrahedrons is caused by a rearrangement inside the $(\text{SO}_4)_1$ and $(\text{SO}_4)_2$ groups. It is assumed that the distortion of the $(\text{SO}_4)_1$ and $(\text{SO}_4)_2$ groups and their rotation at some angle take place at the Curie temperature. Their rotation angle depends on the temperature of the sample (below the Curie point).

It is obvious that the rearrangement of different structural elements of a crystal at $T = T_C$ can lead to a

complex deformation of ammonium sulfate samples in the ferroelectric phase. The main purpose of this work was to measure the spontaneous twist of ammonium sulfate crystal samples under a change in temperature in the vicinity of T_C and in the range corresponding to the ferroelectric phase. We also investigated the mechanism of this phenomenon by analyzing the macroscopic deformation of a sample in a torsion pendulum.

1. EXPERIMENTAL

The $(\text{NH}_4)_2\text{SO}_4$ crystals were grown by the isothermal evaporation method at $T = 303$ K from a saturated water solution with $\text{pH} = 4$. To prepare the ammonium sulfate solution, a twice-recrystallized substance was used. Samples for measurements were cut out in the form of bars with the rectangular cross section having a size of $2 \times 2 \times 18$ mm. The length of these bars was oriented along the a , b , or c crystallographic axes. We will refer to these samples as x -, y -, and z -oriented samples, respectively.

The amount of the twist deformation was measured by means of a setup, based on an inverse torsion pendulum [15], with the relative error not exceeding $\pm 5 \times 10^{-5}$. The twist deformation created in the sample led to the rotation of the disk of the pendulum torsion system at some angle. The rotation angle φ was measured by capacitive sensors in the case of considerable twist deformations and by photoelectric sensors in the case of small deformations. The experimental curves $\varphi(T)$ were automatically recorded by an XY -coordinate recorder. The sample temperature was measured with an error of ± 0.5 K.

2. RESULTS AND DISCUSSION

The results of measurements of twist deformations X obtained in the cooling regime with a cooling rate of about 0.2 K/min for samples with x , y , and z orientations are shown in Fig. 1. It is clear that the twist deformations are absent in the paraelectric phase at $T > T_C = 223$ K. However, the samples of all three orientations are spontaneously twisted in the ferroelectric phase. The X_x , X_y , and X_z deformations are initially changed in a jump at T_C , and then a gradually increasing twist deformation is observed in the $X_x(T)$, $X_y(T)$, and $X_z(T)$ dependences in the course of cooling in the ferroelectric phase. The maximal value of the X deformation is observed for samples of the z orientation, while the minimal one is observed for samples of the x orientation. For samples of the z and y orientations, the jumps in deformation ΔX at T_C were found to be $\Delta X_z = 3 \times 10^{-3}$ and $\Delta X_y = 1.2 \times 10^{-3}$, respectively. The temperature dependence of the spontaneous twist of the $(\text{NH}_4)_2\text{SO}_4$ samples, recorded in the heating and cooling regimes, demonstrates a qualitatively similar behavior (Fig. 2). Since the dependences of $\ln(X - \Delta X)$ upon $\ln(T_C - T)$ shown in Fig. 3 are linear over the interval $\Delta T = T_C -$

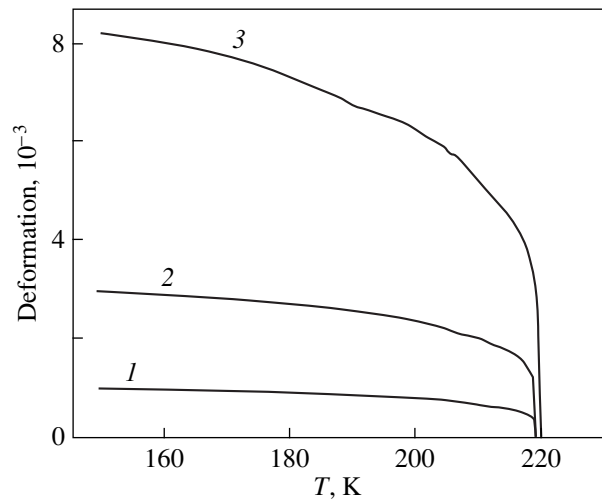


Fig. 1. Temperature dependences of the X twist deformations for samples of (1) x , (2) y , and (3) z orientations.

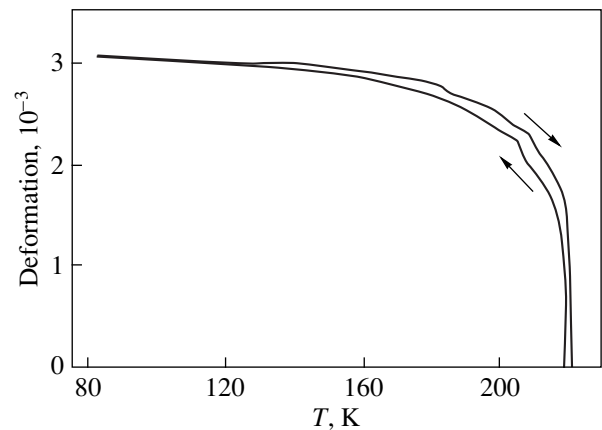


Fig. 2. Temperature dependences of the twist deformation X for the z -oriented sample in the heating and cooling runs. Arrows indicate the directions of the temperature change.

$T \approx 20$ K, the experimental $X(T)$ curves were approximated over this interval by a power-law function:

$$(X - \Delta X) = A(T_C - T)^n, \quad (1)$$

where A is a temperature-independent factor and n is the exponent.

The slope of the linear parts of the $\ln(X - \Delta X) = f\{\ln(T_C - T)\}$ plots is the same for samples of the y and z orientations. From this slope, the exponent n in Eq. (1) was found to be ≈ 0.5 .

To understand the reason for the sample twisting in the torsion pendulum, let us first find the relation between the twisting angle and the characteristics of the crystal in the case where a torque M is applied to the sample. Since one of the sample ends is fixed in the pendulum and the torque M is applied to the other end, a nonuniform deformation will be produced in the sample in torsion oscillations. It is obvious that this defor-

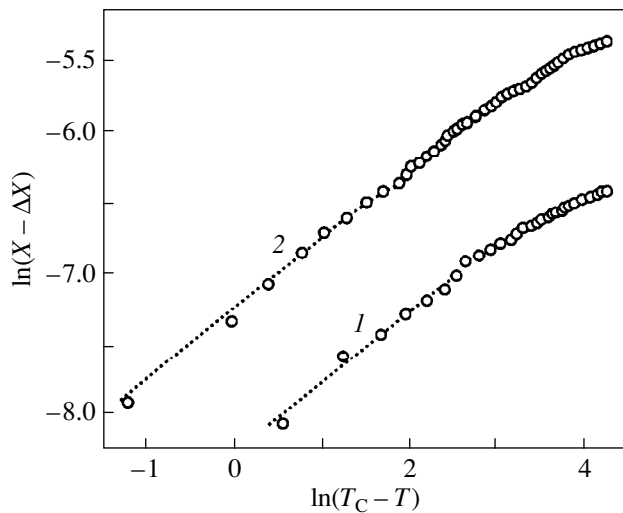


Fig. 3. Dependences of $\ln(X - \Delta X)$ upon $\ln(T_C - T)$ for samples of (1) y and (2) z orientations.

mation is varied both along the sample length and over any of its cross sections as one moves away from the torsion axis. In any cross section of the sample, the shear deformation is maximal at the periphery, i.e., in the exterior layers, while the deformation of the central part of the sample along the torsion axis is absent.

Note that, in the torsion pendulum, the elastic torsional rigidities C_x , C_y , and C_z are functions of different components of the shear rigidity for samples of the x , y , and z orientations, namely, $C_x = f(C_{55}; C_{66})$, $C_y = f(C_{44}; C_{66})$, and $C_z = f(C_{44}; C_{55})$.

For an anisotropic sample (for instance, of the z orientation) of a rectangular cross section, in the case of a linear relation between the stress σ and the deformation X , the twisting angle is

$$\varphi_z = Ml/C_z, \quad (2)$$

where l is the sample length and C_z is the torsional rigidity.

Suppose, for simplicity, that we deal with a pure ferroelastic crystal having a novel shear deformation component X_5 , which appears spontaneously at T_C . In this case, the shear component σ_5 of the external stress is related to the deformation X_5 as

$$\sigma_5 = C_{55}X_5. \quad (3)$$

Then, one can write down the torque causing the sample to twist around the z axis in the form

$$M = 2 \int \sigma z dS = 2a \int_0^{a/2} C_{55}X_5 z dz = C_{55}X_5 \frac{a^3}{4}, \quad (4)$$

where a is the transverse dimension of the sample.

The torsional rigidity C_z for samples of the z orientation can be written, according to [16], as

$$C_z = \frac{64a^2}{\pi^4} \sum_k \sum_n \frac{1}{kn} \frac{\int_0^a \sin \frac{kx\pi}{a} dx \int_0^a \sin \frac{ny\pi}{a} dy}{\frac{k^2}{C_{44}} + \frac{n^2}{C_{55}}} \quad (5)$$

$$= \frac{256a^2}{\pi^6 l} \sum_k \sum_n \frac{1}{kn} \frac{1}{\frac{k^2}{C_{44}} + \frac{n^2}{C_{55}}},$$

where the coefficients n and k take the values $n = 1, 3, 5, \dots$; and $k = 1, 3, 5, \dots$ in the temperature interval near T_C . If, for example, the C_{55} component becomes "soft" ($C_{55} \ll C_{44}$) when the temperature approaches T_C , then Eq. (5) will have the form

$$C_z = \frac{256a^2}{\pi^6} C_{55} \sum_1 \sum_2, \quad (6)$$

where

$$\sum_1 = \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{8}, \quad \sum_2 = \sum_{k=1}^{\infty} \frac{1}{k^4} = \frac{\pi^4}{96}. \quad (7)$$

Thus, we have

$$C_z = C_{55}a^4/3. \quad (8)$$

Substituting Eqs. (4) and (8) into Eq. (2), we get

$$\varphi_z = \frac{3l}{4a} X_5. \quad (9)$$

It is seen that, in the vicinity of the Curie point, the twisting angle φ of the sample in the torsion pendulum is proportional to the shear deformation X of the proper ferroelectric crystal. The coefficient of proportionality in Eq. (9) depends only on the sample geometry and does not depend on the elastic properties of the crystal. One can assume that this relation is also valid for the case of spontaneous deformation of the samples in the absence of external forces. Then, according to Eq. (9), the sample will twist if some component of the shear deformation X appears as a result of the PT, as is the case with the ferroelectric PT. However, $(\text{NH}_4)_2\text{SO}_4$ is not a proper ferroelastic, and a spontaneous twisting of $(\text{NH}_4)_2\text{SO}_4$ crystals in a torsion pendulum at $T \leq T_C$ is quite an unexpected phenomenon. It cannot be solely due to the change in symmetry $mmm \rightarrow mm2$ at the PT.

However, we should take into account that, in spite of the fact that no softening of the elastic rigidity components of the crystal takes place at the Curie point, an abrupt change in both the longitudinal and the shear components of the elastic compliance matrix was detected [8]. The latter can serve as the reason for the

sample twisting in the torsion pendulum with changing temperature.

The complex stressed state of a sample realized under the experimental conditions is characterized by the torsional shear modulus G . This modulus is determined by both the corresponding shear components of the elastic compliance tensor and the longitudinal compliance component along the twisting axis [17], which are mutually related. This can be verified by comparing the temperature dependences of the twist deformation of a z -oriented sample in the vicinity of T_C in two cases, namely, in the presence and in the absence of an external tensile stress σ_t applied to the sample along the c axis (Fig. 4). It is clearly visible that, in the presence of the tensile stress $\sigma_t = 3 \times 10^5$ Pa, the deformation X_z is changed more sharply in the vicinity of T_C ; that is, the twist and stretching deformations of the $(\text{NH}_4)_2\text{SO}_4$ monocrystal are tightly connected with each other.

Since the rotation of the SO_4 tetrahedrons takes place in the $(\text{NH}_4)_2\text{SO}_4$ structure when it is cooled from the paraelectric phase through T_C and their rotation angle has a pronounced temperature dependence in the ferroelectric phase, one can assume that the SO_4 tetrahedron rotation is connected with the twist deformation and the spontaneous twisting of the sample. At the same time, the displacement of the SO_4 groups in the course of the PT contributes to the tensile and compressive deformation (longitudinal deformations). In other words, the twist deformations of $(\text{NH}_4)_2\text{SO}_4$ are connected with the microscopic mechanism of the ferroelectric PT, while the spontaneous twisting of samples is due to the spontaneous polarization of the crystal.

It is obvious that, in the case of torsional oscillations, a nonuniform deformation appears in the sample along its radius. This deformation is characterized by the gradient terms $\partial X_{12}/\partial y$ and $\partial X_{13}/\partial z$ for x -oriented samples, $\partial X_{21}/\partial x$ and $\partial X_{23}/\partial z$ for y -oriented samples, and $\partial X_{31}/\partial x$ and $\partial X_{32}/\partial y$ for z -oriented samples.

It is known that the n th-rank tensor is transformed according to the same irreducible representation as the product of its n coordinates does. In particular, the P_3 polarization, which is the first-rank tensor, is transformed as its z coordinate. The X_{31} deformation (the second-rank tensor) is transformed according to the same irreducible representation as the product of its coordinates zx . Therefore, in the case of samples of the z orientation, the nonuniform deformations $\partial X_5/\partial x$ and $\partial X_4/\partial y$ are transformed as the polarization P_3 . For this reason, if in samples of the z orientation the spontaneous polarization P_3 appears in a jump at T_C , then the nonuniform deformations $\partial X_5/\partial x$ and $\partial X_4/\partial y$, which initiate the rotation, also appear in a jump simultaneously with this polarization. Due to the inverse piezoeffect, the jump of the polarization P_3 at T_C should lead to an abrupt change in the X_1 , X_2 , and X_3 deformations, which are related to P_3 by the piezoelectric moduli d_{31} ,

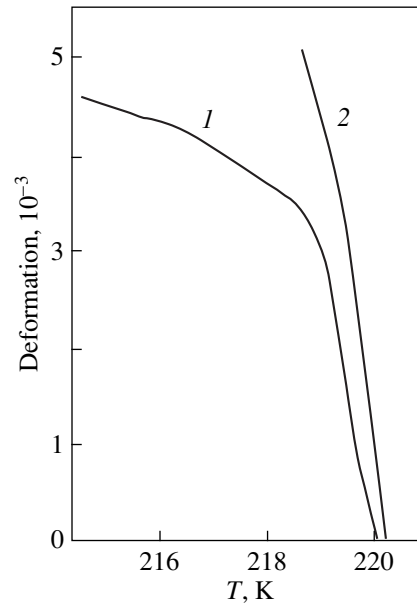


Fig. 4. Temperature dependences of the twist deformation X for a sample of z orientation in the vicinity of T_C : (1) for zero external stress and (2) for external tensile stress $\sigma = 3 \times 10^5$ Pa applied along the twisting axis.

d_{32} , and d_{33} [6]. Note that the abrupt change in the longitudinal and shear components of the elastic compliance was experimentally observed in $(\text{NH}_4)_2\text{SO}_4$ at the first-order ferroelectric PT [8].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-02-16055.

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Translated by A. Sonin