MAGNETISM
AND FERROELECTRICITY

Electrocaloric Effect and Anomalous Conductivity of the Ferroelectric NH_4HSO_4

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Abstract—An intensive electrocaloric effect in the uniaxial ferroelectric NH_4HSO_4 near the second-order phase transition ($T_1 \approx 271$ K) is studied. A high electrical conductivity of the NH_4HSO_4 crystal is revealed, and its temperature dependence is investigated. The results obtained are analyzed together with the data available for the ferroelectrics, which hold promise for the use as solid-state cooling agents.

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1. INTRODUCTION

In the 1980s–1990s, the application potential of the electrocaloric effect was considered to be very low because of its small magnitude at any rate in the low-temperature range [1]. The researchers, who were more optimistically inclined, continued the search, first, for ways to improve the corresponding properties of the already known ferroelectric compounds, second, for new promising materials, and third, for novel schemes of operation of electrocaloric refrigerators [2]. To date, the range of ferroelectrics exhibiting reasonably high intensive (ΔT_{ad}) and extensive (ΔS) caloric effects in the temperature interval 250–290 K is narrow and includes primarily compounds with a perovskite-related structure [3].

The magnitude of the electrocaloric effect, which is associated with the phase transitions, is determined primarily by a physical factor, more specifically by the degree of structural disordering in the original paraelectric phase in zero external electric field, which, in turn, determines, in a certain measure, the entropy of the transition to the ferroelectric or antiferroelectric phase. And it is only in the second place that the electrocaloric effect depends on the electric field strength, which is determined, to a considerable extent, not only by the voltage across the electrodes of the ferroelectric element but also by its linear dimensions in the direction of the applied field.

It is for these reasons that the search for promising materials is limited by the scope of lead-containing perovskites and their solid solutions, such as $PbSc_{1/2}Ta_{1/2}O_3$ (PST), $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), and $PbZr_{0.95}Ti_{0.05}O_3$ (PZT), in which phase transitions give rise to ordering of lead atoms that are disordered in the cubic phase [3]; at the same time, one is looking for optimum ways to reduce the linear dimensions of samples down to the thickness of thin films [4, 5]. Viewed from the ecological standpoint, however, the use of lead in the elements is certainly anything but an unfavorable factor. Another unfavorable factor is that the starting reagents (for instance, scandium oxide and zirconium oxide) used in synthesis of the perovskite-like ferroelectrics PST and PZT are rather expensive.

While crystals of other structural types are ranking below the perovskites in magnitude of the electrocaloric effect, many of them do not contain toxic elements, do not require expensive reagents for their synthesis, and are much less studied. An attractive representative of such crystals is NH_4HSO_4 [6]. When cooled below $T_1 = 270.9$ K, it features the onset of spontaneous polarization along the c axis of the pseudorhombic cell (space group $P2_1/c$), which smoothly increases practically to saturation (~0.8 $\mu C/cm^2$) to drop thereafter to zero at $T_2 = 159.3$ K, the temperature of the first-order transition to the antiferroelectric state ($P\bar{1}$). Considered in terms of theoretical model conceptions, both phase transitions involve ordering of the SO_4 tetrahedra, and this hypothesis is substantiated by the satisfactory agreement between the calculated and experimentally determined entropy ΔS_1 and Curie constant. Of particular significance appears to be the ratio of the transition entropies. On the one hand, the experimental value $\Delta S_1 = 0.2 R$ turned out to be much smaller than $\Delta S_2 = 0.8R > R\ln2$, while on the other, model considerations suggest that the transition between the ferroelectric and antiferroelectric phases should involve a substantially larger entropy, i.e., $\Delta S_2 = 1.4R = R\ln4$.

It thus appears conceivable that, in NH_4HSO_4 under certain conditions (for instance, in an electric field), one

could realize a change in entropy that occurs in perovskite-like oxides ($\Delta S = R\ln 4$) [7], i.e., that ammonium hydrosulfate near the phase transition at T_2 can turn out to become a material not inferior in electrocaloric parameters to solid-state cooling agents, which are presently used in the development of refrigerators [2–4]. That is what would justify interest in the studies of the electrocaloric effect in this crystal. We note, however, that the first-order phase transition in NH_4HSO_4 at T_2 is so clearly pronounced that the single crystal breaks down as a result of a large and abrupt increase in volume ($\delta V/V \approx 1.2\%$) [6].

In the present study, which we consider as a first stage in our related research, we focused attention on the effect of an electric field on NH_4HSO_4 only in the vicinity of the second-order phase transition at T_1 with the purpose of exploring the possibility of using an adiabatic calorimeter in the determination of small levels of an actually intensive electrocaloric effect and comparing the results obtained with the electrocaloric effects observed in other ferroelectrics.

2. EXPERIMENTAL TECHNIQUES AND THE SAMPLE

Direct measurements are possible only as applied to intensive caloric effects of any origin. A thermocouple, with one of its junctions fixed in the sample, records directly the temperature of the sample and its change under application and withdrawal of the field. In another version, a differential thermocouple is employed, which permits one to measure the temperature difference between the sample and a massive block with a heat capacity substantially higher than that of the sample. A sensor measuring the "absolute" temperature, a thermocouple or thermometer, is fixed at the block. An analysis performed for the magnetocaloric effect [8] revealed that the error of the determination of $\Delta T_{ad} \approx 1$–10 K by these methods can be as high as 8–15% for different reasons, primarily because of the difficulties encountered in maintaining adiabatic conditions under application and removal of the field, as well as of the inherent inertia in the operation of temperature sensors.

Because we intended to study the vicinity of the second-order phase transition in NH_4HSO_4, which was found [6] to involve a small change in entropy, it was expected that the intensive electrocaloric effect would be weak. Therefore, we chose an adiabatic calorimeter as a measuring tool which, while not capable of directly determining ΔT_{ad}, would, first, provide close-to-adiabatic experimental conditions, and, second, exhibits a high sensitivity to small changes in the temperature. Moreover, in order to analyze the temperature change ΔT_{exp} accompanying the turning on and turning off of the electric field, we would need the data obtained earlier in comprehensive studies of the heat capacity of ammo-

nium hydrosulfate by the same adiabatic calorimeter technique [6].

The NH_4HSO_4 crystal sample chosen for the study was a rectangular parallelepiped measuring $16.9 \times 25.0 \times 4.5$ mm, with silver electrodes deposited by vacuum sublimation on its major faces perpendicular to the c ferroelectric axis; a voltage U generating an electric field inside the sample was applied to the electrodes. Thin mica platelets wound around by constantan wire ($d = 0.1$ mm) and polished aluminum foil, which served as heaters, were coupled through a heat-conducting adhesive to the silver-coated faces symmetrically with respect to the sample. The sample + heater system was suspended on thin filaments ($d \sim 0.1$ mm) inside an adiabatic screen. The temperature of the sample was monitored with a high-precision platinum resistance thermometer attached to the adiabatic screen. The temperature difference between the adiabatic screen and the sample was monitored by a copper–constantan thermopile whose output was supplied to the automatic control circuit including a high-sensitivity photocompensation amplifier, a temperature control, a power amplifier, and an adiabatic screen heater.

The experiment on the determination of the intensive electrocaloric effect, in essence, was as follows. In the first stage, the sample was heated (cooled) to the temperature at which the experiments were to be conducted and the temperature course (i.e., the rate and linearity of the drift of the sample temperature) was recorded. The optimum rates were $dT/dt \approx \pm(5$–$10) \times 10^{-4}$ K/min. Next, an electric field was applied to the sample electrodes, which abruptly raised the temperature of the ferroelectric by ΔT_{exp} through the electrocaloric effect. The temperature course was continued to be measured during a certain time, including a period after the electric field withdrawal. A possibility was also provided to measure, if required, the effect of electric field at a constant temperature. Conversely, by properly varying the temperature of the sample and repeating the above operations, one could gain information on the temperature dependence of the electrocaloric effect. The determination of ΔT_{exp} under application and removal of the electric field permits one to check the electrocaloric effect reproducibility and to verify the absence of losses.

3. EXPERIMENTAL RESULTS

The studies of the electrocaloric effect of the NH_4HSO_4 sample were performed under switching on and switching off the electric voltages of 690 and 88 V, which correspond to electric field strengths of 1.5 and 0.2 kV/cm, respectively.

Figures 1a–1d present the data obtained from experiments on the determination of ΔT_{exp} at an electric field of 1.5 kV/cm for a series of temperatures close to that of the phase transition at T_1. The temperature course was recorded for both current directions through the
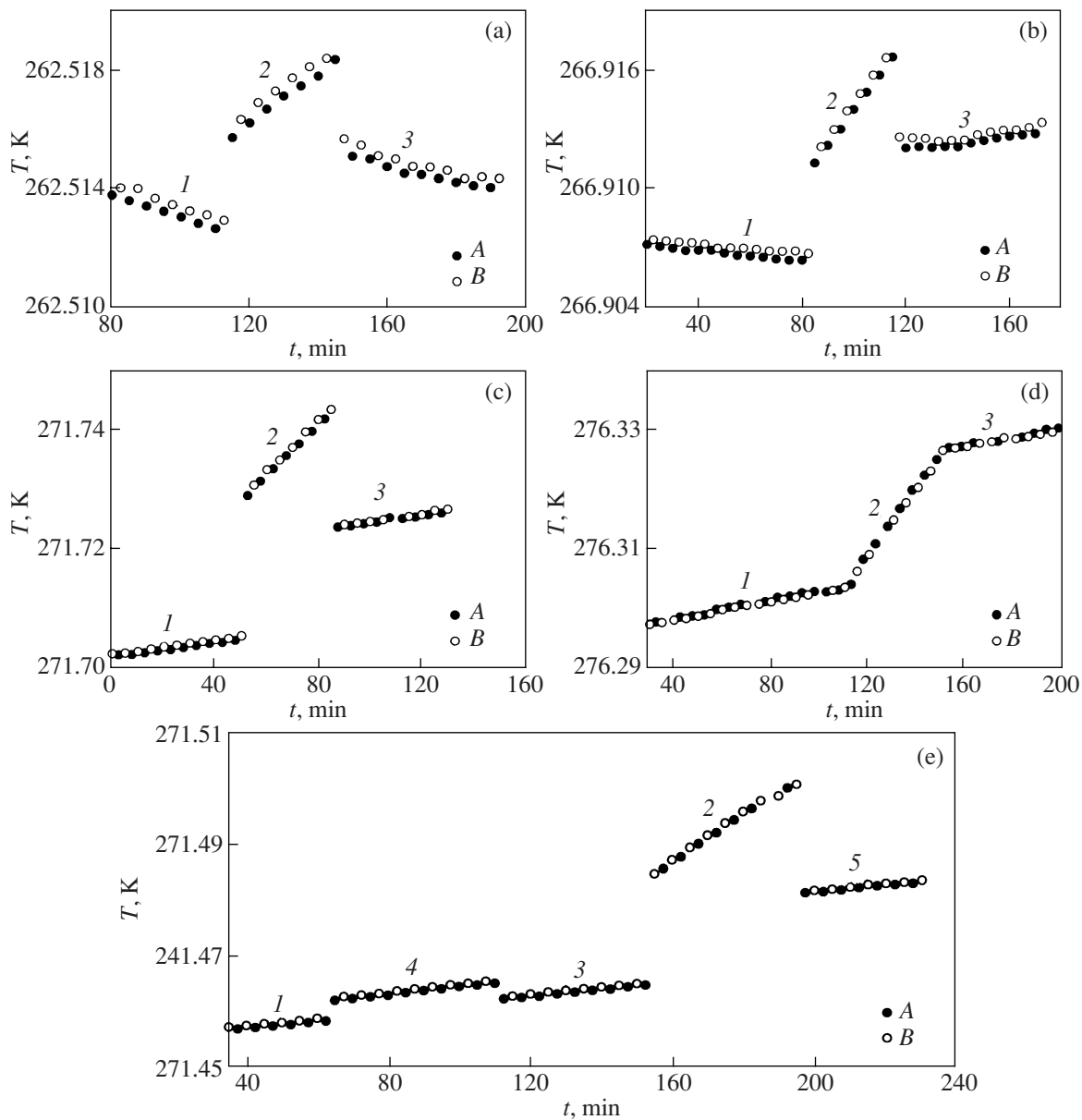
Fig. 1. Results of the ΔT_{exp} measurements near the phase transition point: (a) $T_1 - 8.5$ K, (b) $T_1 - 4.0$ K, (c) $T_1 + 0.8$ K, (d) $T_1 + 5.4$ K, and (e) $T_1 + 0.55$ K for the processes occurring at $E = (1, 3, 5)$ 0, (2) 1.5, and (4) 0.2 kV/cm. Designations: A and B are the temperature courses for different directions of the current flow in the circuit of the platinum resistance thermometer.

thermometer circuit, thus permitting one to estimate the error due to spurious (contact) thermopowers.

With zero external electric field applied, the rate of variation in the temperature of the sample was low; for instance, in the experiment illustrated graphically in Fig. 1a, it was $dT/d\tau \approx -5 \times 10^{-5}$ K/min, which, combined with its constancy, attested to quasi-adiabatic measurement conditions ($dS \approx 0$). The temperature measurement error associated with contact thermopowers did not exceed ±0.0002 K. Application of the external field brought about an electrocaloric effect-induced abrupt increase in the temperature: $\Delta T_{exp} \approx 0.0034$ K. The rate of temperature variation should not have

changed under applied electric field, but, in actual fact, it turned out considerably larger than it was for $E = 0$, namely, $dT/d\tau \approx 40 \times 10^{-5}$ K/min.

As a result, after the field was removed, the temperature of the sample did not regain the level corresponding to the extrapolation of the previous course to this interval of time (Fig. 1a). Although the rate of variation in the temperature of the sample did change to $dT/d\tau \approx -6 \times 10^{-5}$ K/min after the turn-off of the field, this value is still too small as compared to $dT/d\tau$ measured before the field application. The change in the temperature after the turn-off of the field was $\Delta T_{exp} \approx 0.0034$ K,

which coincides within experimental error with the value in the case of the field turn-on. These results suggest that the intensive electrocaloric effect in NH_4HSO_4 is a highly reversible process.

The measurements of ΔT_{exp} were conducted in this way in the range 253–289 K, which covered the region of the second-order phase transition between the paraelectric and ferroelectric states. As seen from Fig. 1, the magnitude of the intensive electrocaloric effect continues to grow above T_1 as well.

At T_1 + 5.4 K, the experimental results looked as shown in Fig. 1d. After the field turn-on, a jump in the temperature associated with the electrocaloric effect was seen, but the rate of temperature variation increased strongly. After the field withdrawal, the temperature followed the course parallel to that before the field application. As for the rate of temperature variation in the field-on regime, it grew with temperature throughout the range covered.

As a rule, the difference between the values of $dT/d\tau$ before the field turn-on and after the field withdrawal was small, with the situation similar to that presented in Fig. 1b observed on rare occasions only. But even in this case, the intensive electrocaloric effect was found to be a reversible process; indeed, ΔT_{exp} was measured to be 0.00466 and 0.00480 K after the field application and turn-off, respectively.

A pictorial example of the effect of field strength on ΔT_{exp} is provided by Fig. 1e, which presents the results of alternating switching on and switching off different electric fields. For instance, at 270.46 K, ΔT_{exp} is 0.0035 K for E = 0.2 kV/cm and 0.019 K for E = 1.5 kV/cm. We note that the electric field strength affects the magnitude of the change in the corresponding temperature course of the sample as well (Fig. 1e).

Figure 2a plots the temperature dependence of the experimentally determined ΔT_{exp} under application and withdrawal of a 1.5-kV/cm field. It was found that the intensive electrocaloric effect reaches a maximum (~0.023 K) at a temperature of 271.7 K. Thus, an electric field of 1.5 kV/cm led to an increase in the temperature of the phase transition between the paraelectric and ferroelectric phases by 0.8 K, which yields $dT/dE \approx$ 0.5 K/(kV/cm) for the derivative of the temperature with respect to the field.

The difference between the dependences $\Delta T_{exp}(T)$ obtained with the electric field turned on and turned off is relatively small throughout the temperature range studied, to reach ~10% at the temperature of the maximum. For such small values of ΔT_{exp}, which are characteristic of the NH_4HSO_4 ferroelectric, these differences can be considered insignificant.

Direct calorimetric measurements of ΔT_{ad} are impossible because for the experiment to be performed by the above technique, the sample has to have at the very least electrodes and a heater that possess a finite heat capacity, which is called the heat capacity of the
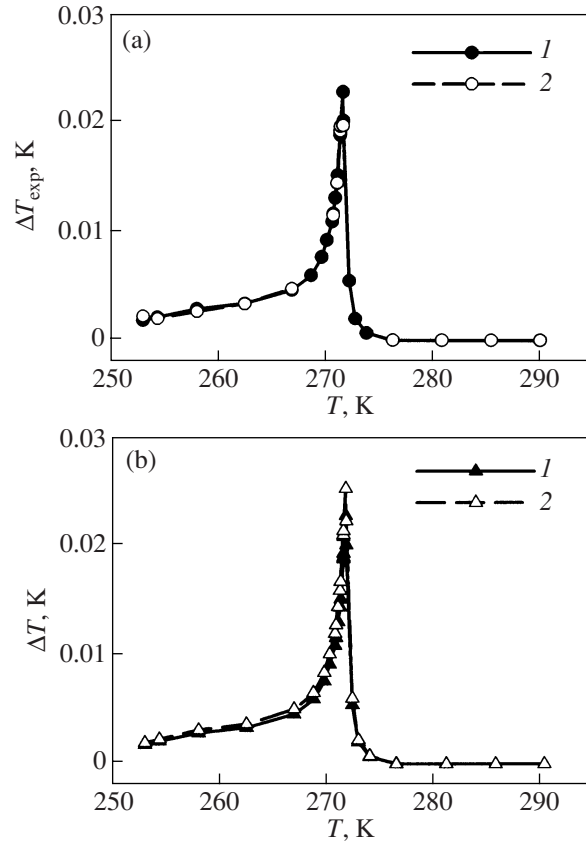

Fig. 2. (a) Temperature dependences of ΔT_{exp} measured upon (1) switching on the electric field and (2) switching off the electric field with a strength of 1.5 kV/cm. (b) Temperature dependences of (1) ΔT_{exp} and (2) ΔT_{ad} in the course of application of the electric field with a strength of 1.5 kV/cm.

fixture. Therefore, the heat liberated in the electrocaloric effect is spent in changing the temperature not only of the sample but of the sample + fixture system as well. Thus, the value of ΔT_{exp} observed in experiment is smaller than the theoretical value of ΔT_{ad}, but ΔT_{exp} and ΔT_{ad} approach one another the closer, the lower is the heat capacity of the fixture as compared to that of the sample.

The relation between ΔT_{exp} and ΔT_{ad} is given by the following equation:

$$\Delta T_{ad} = \Delta T_{exp}\left(1 + \frac{C_f}{C_{smp}}\right), \quad (1)$$

where C_f is the heat capacity of the fixture and C_{smp} is the heat capacity of the sample.

The heat capacity of the fixture was measured in a separate experiment, and its contribution to the total heat capacity of the sample + fixture system was found to be less than 10% within the temperature range covered by the study of the electrocaloric effect. The heat capacity of the 10-μm-thick silver electrodes was esti-
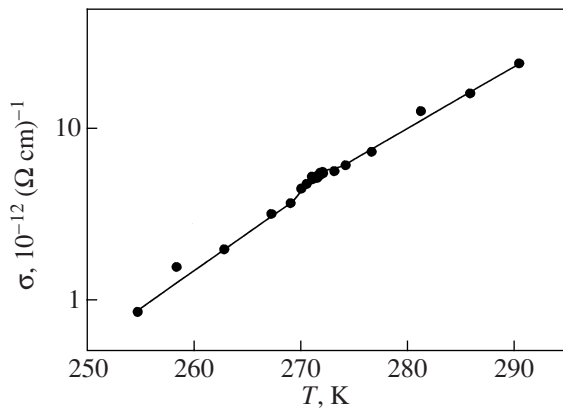
Fig. 3. Temperature dependence of the electrical conductivity of the NH_4HSO_4 crystal.

mated not to exceed 0.05% of that of the sample and, thus, could be neglected.

Figure 2b plots the temperature dependences of the experimental quantity ΔT_{exp} and the quantity ΔT_{ad} calculated from Eq. (1) for the process of the field application.

Let us turn now to the remarkable experimental observation of a monotonic heating that a NH_4HSO_4 sample exhibited, apart from the electrocaloric effect-associated reversible temperature change ΔT_{exp}, under application of an electric field. For this reason, the temperature of the sample did not drop to the initial level after withdrawal of the external field. The rate of this heating depends on the field strength and crystal heat capacity $C_E(T)$. This observation suggests a high electrical conductivity of the crystal under study, which caused liberation of Joule heat in its internal resistance.

The data amassed in this study and in [6] were used to determine the temperature dependence of the electrical conductivity (Fig. 3) from the following equation:

$$\sigma(T) = \frac{C_{p,E} dT}{U^2} \frac{l}{d\tau} \frac{l}{F}, \qquad (2)$$

where U is the voltage at the sample electrodes, l is the electrode separation, and F is the electrode area.

The conductivity of NH_4HSO_4 in the temperature range 253–290 K was found to be substantially higher than that of other ferroelectrics. For instance, the conductivities of the Seignette salt and triglycine sulfate vary typically within the range $\sigma = 10^{-16}-10^{-13}$ (Ω cm)$^{-1}$ [9].

4. ANALYSIS AND DISCUSSION

The extensive and intensive electrocaloric effects are related through the ratio of the sample heat capacity to the corresponding temperature; in other words, the isothermal change in entropy as a characteristic of a crystal can, in a first approximation, be defined as

$$\Delta S(T) = -\frac{c_{smp}}{T} \frac{\Delta T_{ad}}{m_{smp}}. \qquad (3)$$

Here, m_{smp} is the sample mass.

Obviously, in the case of transitions close to the tricritical point where the heat capacity of the sample can change in the vicinity of the phase transition by several factors [15], the dependences $\Delta S(T)$ and $\Delta T_{ad}(T)$ can differ substantially. The heat capacity of NH_4HSO_4 upon the second-order transformation at T_1 changes by only ~10% [6] and, thus, cannot contribute noticeably to the behavior of the entropy as compared to that of the intensive electrocaloric effect. This is why we do not present here the temperature dependence $\Delta S(T)$ of ammonium hydrosulfate. The maximum value of ΔS was found for it to be ~0.1 J/(mol K).

At first glance, a comparison of NH_4HSO_4 with perovskite-like crystals (see table) does not show any merits of the former as regards the magnitude of the intensive electrocaloric effect they reveal. We note, however, that the investigation of ΔT_{ad} in PST and PZT [3, 4] was performed in markedly higher fields.

Studies of the electrocaloric effect have been recently focusing on the development of electrocaloric elements based on not only large-volume (bulk) samples but on ~100-µm-thick ceramics and even thin films as well. The latter approach would understandably permit reaching high electric field strengths at comparatively low applied voltages, which, in turn, would reduce the risk of electric breakdown.

Thermodynamic parameters of NH_4HSO_4 and some perovskite-like ferroelectric materials

Material	T_{PT}, K	δ, cm	E, kV/cm	ΔT_{ad}, K	References
PST	290	0.005	30	2.3	[3]
PZT	425	0.025	20	2	[4]
	500	3×10^{-5}	500	15	[5]
NH_4HSO_4	271	0.5	1.5	0.025	
		3×10^{-5}	500	8	

Note: T_{PT} is the phase transition temperature, and δ is the thickness of the element.

One of the first studies of ceramic samples of small thickness [4] was conducted with the composition $Pb_{0.99}Nb_{0.92}[(Zr_{0.73}Sn_{0.27})_{0.93}Ti_{0.07})]_{0.98}O_3$ based on the PZT ceramic enjoying presently wide use in electronics. For this composition, one succeeded in demonstrating an intensive electrocaloric effect in comparatively weak electric fields (see table), which was only a few times inferior to the values characteristic of the magnetocaloric effect ($\Delta T_{ad} \approx 10$–15 K) in magnetic fields of 5–10 T [8]. The complexity of the composition originates from the search for the possibility of reducing the ferroelectric transition point to room temperatures.

A quite recent study of a thin PZT film (~300 nm thick) culminated in the generation of a high field across the sample and demonstrated the possibility of realizing intensive (see table) and extensive electrocaloric effects comparable in magnitude to the magnetocaloric effect attained in the best presently available magnetocaloric materials [8].

One can expect publication of studies of PST-based film materials in the nearest future as well, in which the electrocaloric effect will most likely be comparable to ΔT_{ad} reached in PZT.

A comparison of the results obtained with NH_4HSO_4 in different fields at 271.46 K, a temperature adjoining closely that of the maximum in the dependence $\Delta T_{exp}(T)$, argues for a nonlinearity in the dependence $\Delta T_{exp}(E)$. An increase in the electric field strength by a factor 7.5 increased six times the intensive electrocaloric effect. Nevertheless, rough estimates suggest that, with a NH_4HSO_4 sample biased at 25–30 kV/cm, the strength used in PST and PZT studies [3, 4], the intensive electrocaloric effect can turn out quite significant, $\Delta T_{exp} \approx 0.4$–0.5 K.

At the same time, we have established that, even in fields of 1.5 kV/cm, the temperature of the sample exhibits irreversible changes caused by liberation of the Joule heat in its internal resistance. This factor is certainly an obstacle to complete reversibility of the electrocaloric effect, as well as to using crystalline NH_4HSO_4 as a solid-state cooling agent. The conductivity of such compounds as ammonium hydrosulfate is mediated, in particular, by the presence of protons in its structure. There are grounds to assume that even a partial substitution of hydrogen, for instance, with the Li atom, and the ammonium cations, with Rb, should substantially increase the electrical resistivity of the crystal. Successful solution of this problem would make the use of NH_4HSO_4 films a viable alternative. Indeed, it turns out that, for a sample ~10^{-5} cm thick, the intensive electrocaloric effect can become comparable to both the electrocaloric effect of PZT (see table) and the magnetocaloric effect reached in the best magnetic cooling agents [8].

More attractive, however, appears to be another approach involving investigation of the electrocaloric effect in NH_4HSO_4 in the vicinity of the first-order phase transition. There are grounds to believe that, by partial substitutions of atoms or their groups, one could not only reduce the conductivity of this compound but also, first, increase the temperature T_2 and, second, make this transition more diffuse to prevent destruction of the sample as a result of a large jump in its volume [6] while retaining a large derivative $\partial P/\partial T$, which determines, to not a small measure, the magnitude of ΔT_{exp}.

The potential of this approach is argued for by attempts at improving PST-based electrocaloric materials [3]. The degree of ordering (and, accordingly, the transition temperature and the magnitude of ΔT_{ad}) can be readily mediated in two ways. The first of them consists in thermal treatment of PST at 1590–1650°C, which brings about a change in the degree of ordering in the structure of Sc and Ta atoms and, accordingly, a change in the phase transition temperature in the range 273–291 K. The second way lies in changing the chemical pressure caused by a 10 mol % substitution of Sb^{5+} and Co^{3+} ions for Sc^{3+} and Ta^{5+} ions, which would modify the temperature of stability of the original phase over a wider temperature range (210–310 K) and increase the intensive electrocaloric effect to 2.3 K.

5. CONCLUSIONS

The effect of an electric field on the temperature of a NH_4HSO_4 crystal in the region of its high-temperature phase transition was studied by adiabatic calorimetry.

The magnitude of the zero-loss intensive electrocaloric effect and its temperature dependence are determined. This parameter has demonstrated its high reversibility under application and removal of an electric field. It has been found that the electrical conductivity of this crystal exceeds by far that of other ferroelectrics.

A comparison of the data obtained with the electrocaloric effect of presently promising materials has revealed that, if used as a film element, the NH_4HSO_4 ferroelectric can turn out a competitive cooling agent after its high conductivity has been suppressed.

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