

Logarithmic Relaxation of the Nonequilibrium State of the Charge Density Wave in TbTe_3 and HoTe_3 Compounds

A. V. Frolov^{a,*}, A. P. Orlov^{a,b}, D. M. Voropaev^{a,c}, A. Hadj-Azzem^d,
A. A. Sinchenko^a, and P. Monceau^d

^a Kotelnikov Institute of Radioengineering and Electronics of Russian Academy of Sciences, Moscow, 125009 Russia

^b Institute of Nanotechnology of Microelectronics of Russian Academy of Sciences, Moscow, 115487 Russia

^c Moscow Institute of Physics and Technology (National Search University), Dolgoprudnyi, Moscow region, 141701 Russia

^d Université Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, 38042 France

*e-mail: fralek@mail.ru

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The measurements of electronic transport including the dynamic properties of the charge density wave (CDW) in the quasi-two-dimensional compound HoTe_3 have been performed. The effects of the slow relaxation of the nonequilibrium state of the CDW during isothermal exposure in the zero current mode, previously observed in TbTe_3 , have been discovered and studied. A significant increase in the exposure time made it possible to clearly demonstrate that the relaxation is logarithmic. Relaxation features were studied in different temperature and time ranges. The data obtained indicate the glassy behavior of the CDW pinning centers in rare-earth tritellurides.

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INTRODUCTION

The charge density wave (CDW), which was studied for many years mainly in quasi-one-dimensional compounds [1], has recently found more and more new manifestations in quasi-two-dimensional systems [2]. The properties of the “two-dimensional” CDW, despite the similarities with one-dimensional systems, have quite a few differences that require deep studying and theoretical explanation [3]. Rare-earth tritellurides, RTe_3 (R: La, Ce, Pr, Nd, Gd, Tb, Dy, Er, Tm), are one of the few quasi-two-dimensional systems in which almost all the main CDW effects are observed. Compounds of this group attract considerable attention due to the existence of various collective quantum states in them: superconductivity [4, 5], several CDW types [6, 7], magnetic ordering [8, 9], as well as their interaction/competition with each other [10, 11].

The compounds of the RTe_3 family listed above have the same crystal structure and a close band filling. The lattice parameters increase monotonically with the atomic number of a rare-earth element, which leads to the monotonicity of a number of properties: CDW transition temperature and wave vectors, anisotropy in the layer plane and even environmental stability. Thus, replacing a rare-earth atom with a lighter/heavier one is equivalent to creating a so-called chemical pressure in the system [6, 7] and allows to fine-tune its properties, including the parameters of the charge density wave.

In these compounds, the most interesting dynamic CDW effects are also clearly observed: collective charge transfer (CDW sliding) and rf-synchronization of the CDW (Shapiro steps) [12–14]. As in quasi-one-dimensional systems, the CDW sliding effect manifests itself in a sharp increase in conductivity when an electric field is applied above a certain threshold value E_l , which is determined by pinning, i.e., “coupling” of the charge density wave with defects.

Recently, a number of unusual effects of extremely slow relaxation (the relaxation time is tens of hours) associated with the CDW collective motion were discovered in the TbTe_3 compound: during isothermal exposure of the sample, an increase in the threshold field with saturation was observed [15, 16]. The change in the value of the threshold field could be controlled using external factors: current and temperature [17, 18]. The effects, apparently associated with the dynamics of pinning centers, have much in common with relaxation processes in glassy systems, but their nature is still unclear, especially at the microscopic level.

The next logical step in studying these relaxation processes is to search them in another compound of RTe_3 class, which was implemented in this work. HoTe_3 was chosen as such a compound. The choice is due to a number of factors:

1. Holmium is one of the elements closest in properties to terbium: their atomic numbers are 67 and 65, respectively, their molar masses differ by several percent, atomic radii—by fractions of a percent. Accordingly, similar properties of the compounds are expected, which makes it possible to use the sample fabrication and measurement techniques that have been developed for TbTe₃.

2. Also favorable is the fact that the CDW transition in the HoTe₃ compound occurs at $T_{CDW1} = 285$ K [7]—just below room temperature. This makes it possible to study samples that had never undergone a CDW transition prior to measurements. In the TbTe₃ ($T_{CDW1} = 336$ K [7]), storage of crystals at room temperature resulted in the formation of a state with increased pinning, which was observed in the temperature dependence of the threshold field as a maximum at 295–300 K, and traces of which remained even after a long sample annealing.

In both TbTe₃ and HoTe₃ compounds, both high- and low-temperature CDWs in orthogonal directions in the layer plane are observed: $\mathbf{Q}_{CDW1} = (0, 0, 0.296)$, $\mathbf{Q}_{CDW2} = (0.32, 0, 0)$. Transition temperatures of low-temperature CDW are as follows: $T_{CDW2} = 41$ K [19] in TbTe₃ and 110 K in HoTe₃ [7].

EXPERIMENT

Transport measurements (resistance, current-voltage characteristics) of HoTe₃ microbridges were carried out in the temperature range of 77–350 K. The samples were prepared as follows [17, 20]: HoTe₃ single crystals were grown using the self-flux method [12] and attached to a sapphire substrate with a thin layer of Stycast epoxy, then submicron films were fabricated by micromechanical splitting. The quality of the crystals was controlled using X-ray diffraction, the smoothness and uniformity of the detached films were controlled using a Carl Zeiss Axio Imager A2 optical microscope in the differential interference contrast mode. The use of double-sided polished sapphire as a substrate turned out to be extremely successful for samples of this type, firstly, due to its high thermal conductivity, and secondly, because of the possibility to control optically the quality of the surface on both sides of the film. We also managed to reduce the thickness of the adhesive layer to fractions of a micron, as evidenced by the presence of a Newton's ring type structure when observing the sample surface from the side of the substrate.

Using focused ion beam (FIB) etching, bridge-like structures 20–250 μm long and 8–100 μm wide, oriented along the direction of the \mathbf{Q}_{CDW1} wave vector were milled. After this operation the bridge area was encapsulated with a thin layer of polymer. The electrical contacts were fabricated by laser ablation and indium cold soldering. HoTe₃ is less stable at room

conditions than TbTe₃: after a few hours, signs of surface degradation can be evidenced by optical imaging. The method of sample preparation described above using vacuum systems (FIB, laser deposition, desiccators) and encapsulation made it possible to reduce the time of exposure to air on the working area of the sample to tens of minutes.

Conductivity and current–voltage characteristics (CVCs) of the structures were measured by the four-terminal method using a Keithley 2400 precision current source and a Keysight 34420A nanovoltmeter. All measurements were carried out in an inert helium atmosphere.

Within the framework of this experiment, 11 bridge structures were fabricated and measured. The effects described below were observed on all samples. This paper presents the results obtained on a sample with the lowest values of resistivity and threshold field—a bridge with a length $l = 100$ μm, a width $w = 23.5$ μm, and a thickness $t = 800$ nm.

In HoTe₃, as in TbTe₃, when the sample is exposed at a certain temperature below the CDW transition, the threshold field changes with time. In this work, series of CVCs were successively measured during long-time exposure at temperatures of 200, 220, 240, 260, and 280 K, similarly to [16]. Within one series, the sample was cooled from a temperature $T_{ann} > T_{CDW1}$ to a given exposure temperature T_{exp} and then isothermally kept at T_{exp} for a long time, up to 210 h. During exposure, the threshold CVCs were measured at certain time intervals, from 10 to 120 min. Between measurements of CVCs, to control the exposure process, the time dependence of the sample resistance at a current of $I_{exp} = 10$ μA was recorded. Passing through the sample a current much lower than the CDW sliding threshold current ($I_{CDW} > 300$ μA) does not affect the time evolution of the I–V characteristics [17]; thus, it is equivalent to exposure in the zero current mode. The value of the threshold field $E_t = V_t/l$, corresponding to the beginning of the CDW sliding, was determined from a sharp break in the dependence $dV/dI(V)$ obtained by numerical differentiation.

RESULTS AND DISCUSSION

A typical change in the threshold CVCs at different temperatures before and after a long isothermal exposure is shown in Fig. 1a. The threshold field after exposure increased from two to five times, depending on temperature (Fig. 1b). During exposure, the resistance value corresponding to the static CDW regime remained unchanged (Fig. 1a). After the completion of the series, the sample was briefly heated to $T_{ann} = 300$ K $> T_{CDW1}$ followed by cooling to the next exposure temperature T_{exp} . It is noteworthy that after short-term heating and cooling of the sample to the

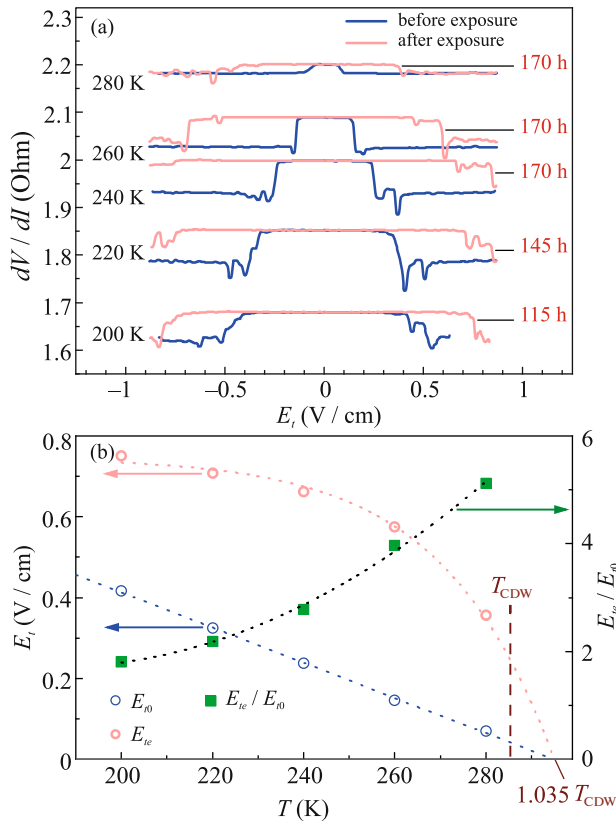


Fig. 1. (Color online) (a) Dependences of the differential resistance of the HoTe₃ microbridge on the magnitude of the electric field at different temperatures before and after a long isothermal exposure. (b) Temperature dependences of the threshold field before and after exposure, E_{i0} ($t = 0$) and E_{ie} ($t = t_{\text{exp}}$), and their ratio E_{ie}/E_{i0} showing how many times the threshold field increased during exposure. The dotted curves are drawn as an eye-guide.

same temperature T_{exp} , the threshold CVCs were completely reproduced, regardless of the temperature and duration of the exposure process preceding heating. Restoration of the original CVC shape by short-term heating was observed in both TbTe₃ and HoTe₃ compounds and indicates that the growth of the threshold field is not a diffusion process. An increase in pinning due to the diffusion of mobile defects has recently been observed in the quasi-one-dimensional compound TaS₃ [21, 22].

The evolution of the threshold field at different temperatures in the range of 200–280 K (Fig. 2a) has a form similar to that observed earlier [16]—the growth of the threshold field slows down with time. It was assumed in [16] that the dependence of the threshold field has the form $E_i(t) = E_0 - (E_0 - E_{i0(t=0)})e^{-t/\tau}$ —the value of E_i tends asymptotically to the saturation value E_0 (Fig. 2b). For a more accurate determination of E_0 , the exposure time was

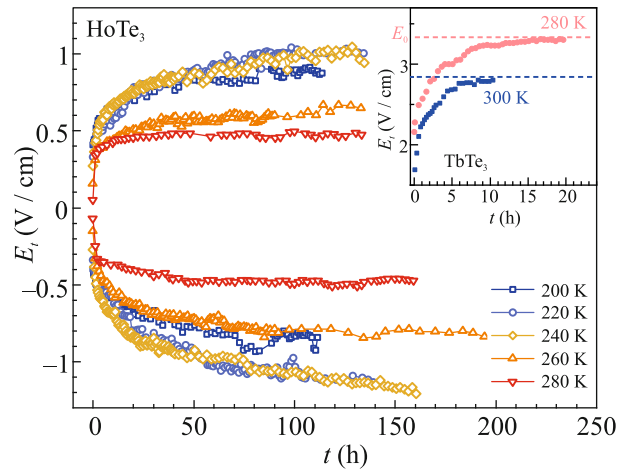


Fig. 2. (Color online) Time evolution of the threshold field of HoTe₃ sample during isothermal exposure at different T_{exp} . Inset: determination of the asymptotes of a similar process in the TbTe₃ compound in [16].

significantly increased. However, no saturation was observed even after 150–200 hours of exposure.

After rearranging the plots on a X -axis logarithmic scale, the dependences become linear (Fig. 3), that is, the threshold field changes with time according to the law $E_i(t) \sim \log(t/\tau)$. It can be seen in the inset to Fig. 2 that for TbTe₃ at 280 K the relaxation was very likely a logarithmic one, however, due to the limited exposure time, it was concluded that the decay of E_i to the saturation value is exponential for all T . New results for HoTe₃ made it possible to clearly demonstrate that the common case is more complex.

The logarithmic relaxation law is often found in complex highly disordered systems: ordinary [23] and spin glasses [24], Anderson dielectrics [25], as well as in biological objects, for example, in DNA [26] or in corn roots [27]. Elements in such systems, as a rule, interact intensively with each other at the micro level, while the interaction strongly depends on the history of the system. Neurons in the human brain, which are known to be closely interconnected with each other, also have a logarithmic distribution [28].

In both compounds, the presence of two time intervals on the relaxation dependence, Figs. 3a, 3b, with different slope is traced. In HoTe₃ the transition is clearly visible for most temperatures (Fig. 3b), and the break point for different temperatures is practically the same: $t_b \approx 10$ h.

A change in the slope of the logarithmic dependence is often observed in various glassy systems and is usually associated with the phenomenon of “aging” [29]—the dependence of the relaxation behavior of the system on the time t_w of being in a state that precedes the relaxation process. Moreover, the time t_b , at which

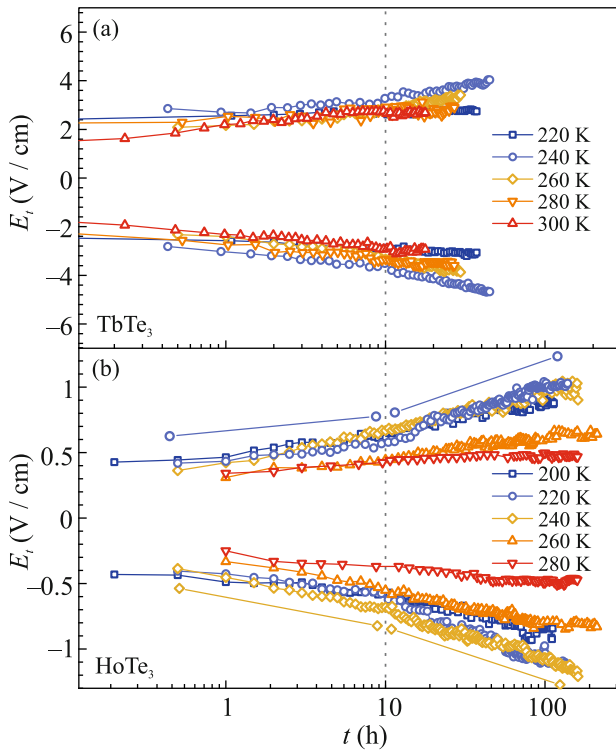


Fig. 3. (Color online) Dependences of the time evolution of the threshold field in the TbTe_3 and HoTe_3 compounds at different temperatures plotted on a logarithmic scale along the x axis. (a) Data from [16]. (b) Data from Fig. 2. The vertical dotted line shows the approximate boundary between two time intervals with different values of the slope, $t_b \approx 10$ h. Straight lines in (b) show how the slope angle changes in different time intervals for some dependences: 220 K, $E_t > 0$ and 240 K, $E_t < 0$.

a break is observed, as a rule, correlates with the aging time, $t_b \approx t_w$.

Within the framework of this experiment, there are no characteristic times on a scale of 10 h: the process of cooling to a given temperature T_{exp} takes no more than 30 min, and the temperature stabilization time before the start of a series of measurements does not exceed several minutes at all. Probably, the occurrence of a break in the relaxation dependence is not directly related to the aging process. At the same time, the question of the existence of aging effects in our system remains open. Aging is inextricably linked with glass systems, so its experimental detection could clarify the nature of the nonequilibrium state in RTe_3 compounds.

Another feature that can be observed in Fig. 3 is that the growth of the threshold field reaches its maximum at intermediate temperatures. For all relaxation curves in Figs. 3a, 3b, the slope angles $dE_t/d \log t$ were determined for both time ranges. As expected, the dependences of the obtained values on the exposure temperature (Fig. 4a) exhibit the maximum in the

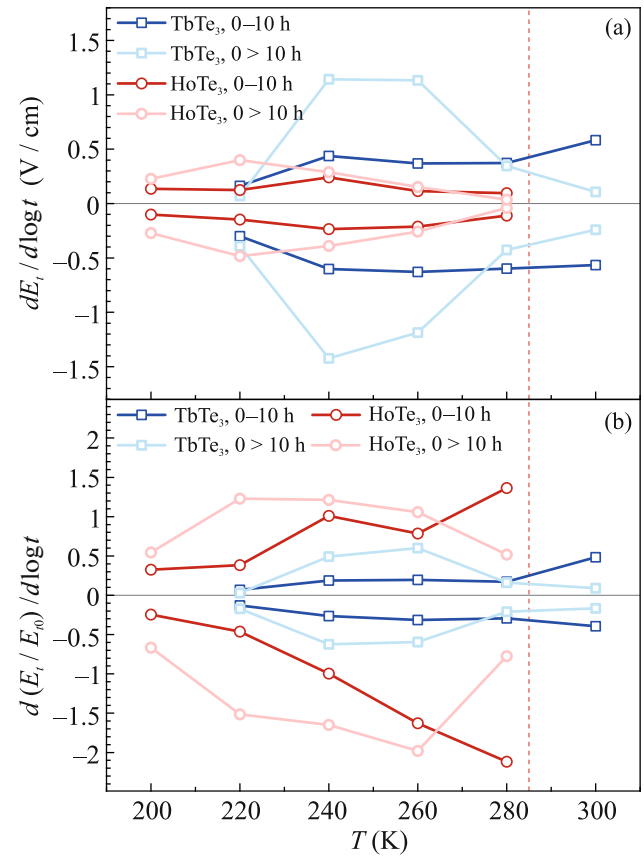


Fig. 4. (Color online) Dependence of slope angles extracted from plots 3a, 3b for TbTe_3 and HoTe_3 compounds for two time ranges. The dotted line shows the CDW transition temperature in HoTe_3 , $T_{\text{CDW1}} = 285$ K (in TbTe_3 $T_{\text{CDW1}} = 336$ K is outside the graph).

central part, 50–80 K lower than the CDW transition temperature T_{CDW1} . For the TbTe_3 compound, the maximum is located approximately 30 K higher in temperature.

The appearance of the maximum in the temperature dependence of the threshold field growth rate, despite the fact that other parameters of the RTe_3 compounds (resistance, threshold field) behave monotonically in this temperature range, may seem unexpected. However, there are several possible reasons for the slowdown in the growth rate of E_t as at high as well as at low temperatures.

During cooling, a slowdown of thermal processes occurs, including one in the CDW system. If we assume that the system of pinning centers is in a highly disordered glassy state, which, as is known, is non-equilibrium, and the system slowly relaxes to the equilibrium state, then a decrease in temperature leads to an increase in the transition time between metastable pinning states and, thereby, a strong deceleration of the relaxation process. The slowdown in the growth of

E_t at high temperatures is probably due to the proximity to the CDW transition—fluctuations destroy the nonequilibrium state (similar phenomena were also observed in spin glasses).

In $R\text{Te}_3$ compounds, in contrast to one-dimensional CDW materials, the temperature dependence of the threshold field, $E_{t0}(T)$, has a strict linear form (Fig. 1b) [13], despite the fact that the value of E_{t0} is nonequilibrium. At the moment there is no theoretical model that explains this linear relationship. It is noteworthy that the temperature dependence of the threshold field after a long exposure $E_{te}(T)$ in Fig. 1b corresponding a strong decay of the relaxation process has a completely different form, resembling a typical temperature dependence of the CDW gap. We also note that if both dependences are interpolated to low temperatures, they can intersect at a temperature of $100 < T < 120$ K, near $T_{\text{CDW}2} = 110$ K.

Considering that in HoTe_3 the values of E_{t0} at 200 and 280 K differ by almost an order of magnitude, it was decided to analyze how not only the absolute value of the threshold field changes with temperature, but also its ratio to the initial nonequilibrium value, E_t/E_{t0} . Figure 4b shows the dependence of $d(E_t/E_{t0})/d \log t$ at different temperatures for both compounds. In the initial time interval, the growth rate of E_t/E_{t0} increases monotonically with increasing exposure temperature, while at T_{exp} close to T_{CDW} , after ~ 10 h the growth of E_t/E_{t0} practically stops. Perhaps, at temperatures close to the CDW transition, the formation of a completely ordered structure of pinning centers is impossible due to fluctuations, as a result of which, during relaxation, a quasi-equilibrium state with pinning close to the maximum value for a given exposure temperature is formed. The dependences in Fig. 4b are similar for both compounds.

One of the main questions related to the discovery of a nonequilibrium CDW state in $R\text{Te}_3$ compounds is whether the evolution of E_t is a change in the pinning parameters that determine E_{t0} value or a new type of pinning is formed. The results obtained show that the rate of growth of the threshold field during relaxation correlates weakly with the initial value of the threshold field E_{t0} , which is an indication of the formation and evolution of a special type of pinning in $R\text{Te}_3$ compounds. Since the conductivity of the samples and the CDW transition temperature do not change during isothermal exposure, the observed changes in the threshold field can be due to changes only in the CDW subsystem. Most likely, these may be the rearrangement of the CDW macrostructure, for example, the formation and evolution of a specific domain structure as suggested in [16]. Elucidation of the nature of the observed effect requires further research.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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