Physics of the Solid State, 2025, Vol. 67, No. 6

07

Formation of a multi-link conductivity hysteresis loop during phase transition in vanadium dioxide films

© A.V. Ilinskiy[1], A.A. Kononov[2], E.B. Shadrin[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Herzen Russian State Pedagogical University,
St. Petersburg, Russia
E-mail: shadr.solid@mail.ioffe.ru

Received May 27, 2025
Revised May 27, 2025
Accepted May 29, 2025

It has been shown for the first time that in the dielectric spectra of a VO_2 nanocrystalline film, the Mott (electronic) component of the Mott-Peierls thermally stimulated phase transition manifests itself in the form of a monotonic increase in the frequencies of the features of the dielectric spectra on the heating branch and a decrease in their frequencies on the cooling branch of the thermal hysteresis loop. At the same time, the Peierls (structural) component manifests itself in the form of a redistribution of intensities between the monoclinic and tetragonal components of the fine structure of the dielectric spectra with a simultaneous monotonic change in the frequency position of the fine structure features, forming a multi-link nature of the hysteresis loop of the complex phase transition of conductivity.

Keywords: vanadium dioxide, semiconductor-metal phase transition, VO_2 nanocrystalline films, dielectric spectroscopy, specific conductivity.

DOI: 10.61011/PSS.2025.06.61692.147-25

1. Introduction

A semiconductor–metal phase transition (PT) in vanadium dioxide has a complex nature, which consists in the fact that with temperature growth the Mott's electron phase transition stimulates at $T_c = 340\,\mathrm{K}$ (67 °C) the Peierls' structural phase transition. After completion of the Peierls' structural PT, the crystalline lattice jumps from low-symmetry *m*-phase of monoclinic symmetry to high-symmetry *t*-phase of tetragonal symmetry [1–8]. The growth of symmetry is related to the thermal destabilization of V–V-dimers formed at $T < T_c = 340\,\mathrm{K}$ (67 °C) due to formation of σ-bonds in interaction of electrons of $3d_{x2-y2}$-shells of ions V, located in the centers of oxygen octahedrons.

Demonstration of the presence of multi-link nature of the hysteresis loop in the complex PT of conductivity, and the possibility to selectively control the physical parameters of VO_2 film nanocrystallite arrays at this T in various crystalline modifications, is the objective of this article. Gathering such essential information becomes possible due to unique possibilities provided by such study method as dielectric spectroscopy.

The analysis of the experimental results is carried out in this article by quite a promising variant of the method for theoretical elaboration of the experimental information that is obtained in the studies of dielectric spectra (DS), as the method of equivalent electrical circuits. That variety of the method is used, which is based on the detailed comparison of the equivalent electrical circuit parameters calculation results with the experimental results. The equivalent electrical circuits may adequately model the physical characteristics of combinations of nanocrystals that are accordingly in monoclinic and tetragonal phases. The conclusions drawn on the basis of such comparison make it possible to prove the validity of the statement on the possibility of selective observation of various experimental manifestations of Mott's electronic PT and Peierls' structural PT.

2. Dielectric spectra

Figure 1 shows DS of undoped vanadium dioxide film obtained in temperature interval (45–70 °C), i. e. in the area of semiconductor–metal PT. The spectra are characterized by the fact that they clearly show a fine structure of spectral features, which confirms the ability to selectively control the parameters of two combinations of VO_2 film nanocrystallites that coexist at every fixed temperature, being randomly mixed on the substrate surface.

Namely, the spectrum includes two adjacent *m*- and *t*-maxima of the function of frequency dependence of $\varepsilon''(f)$ imaginary part of dielectric permittivity (Figure 1, *a*), for which, as temperature increases, firstly, their resonance frequency increases, and secondly, mutual transfer of intensities takes place between the fine structure components. Indeed, at $T = 55\,^\circ\mathrm{C}$ the frequency dependence $\varepsilon''(f)$ has one well defined maximum at frequency $10^{4.5}$ Hz, and Cole-Cole diagram $\varepsilon''(\varepsilon')$ (Figure 1, *c*) contains one semi-circle which is slightly distorted compared to the typical one.

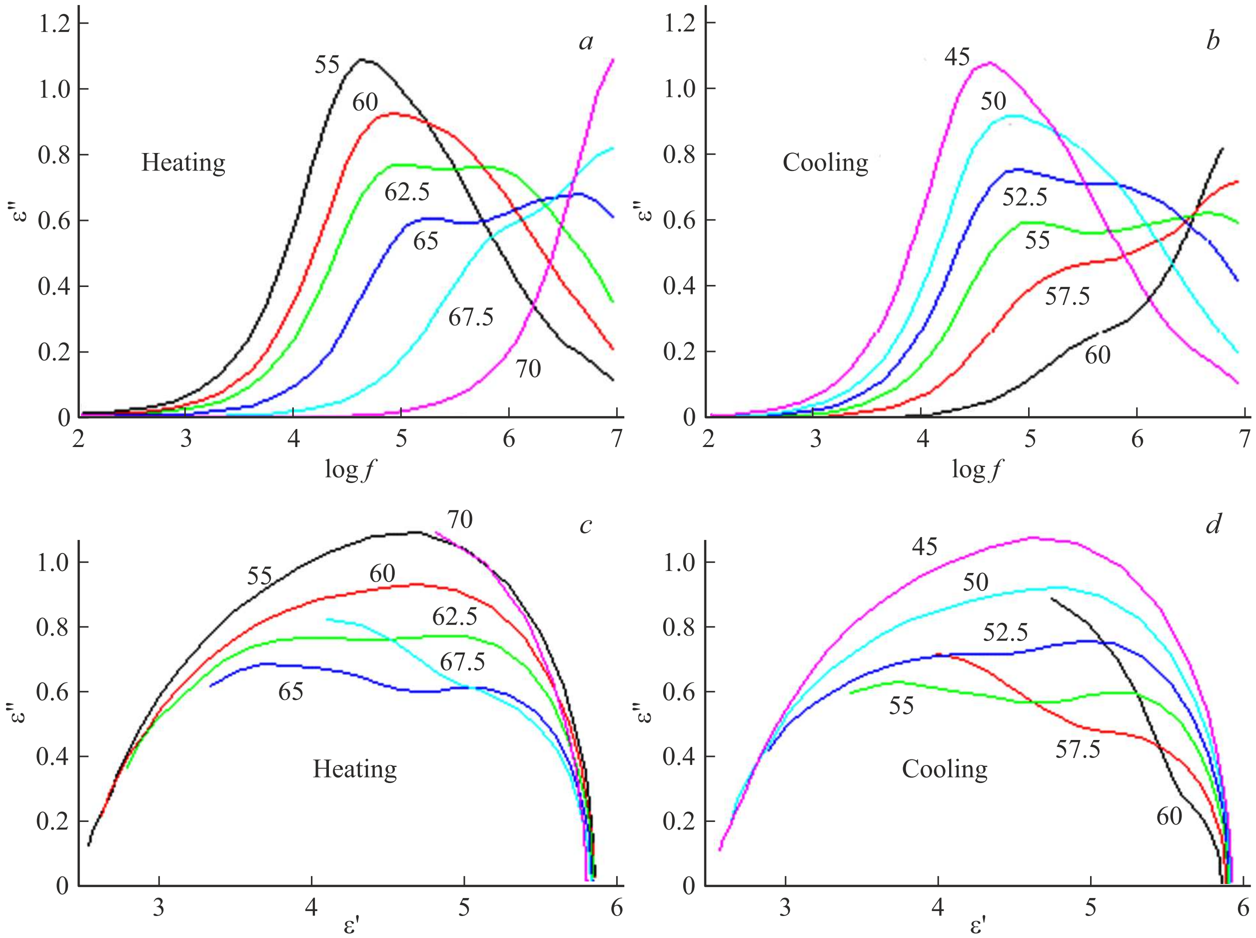

Figure 1. Fine structure of DS (a, b) and redistribution of intensities of (c, d) m- and t-maxima $\varepsilon''(f)$ while heating (a, c) and cooling (b, d) the undoped film of vanadium dioxide. Numbers — specimen temperatures in °C.

As temperature increases, m-maximum $\varepsilon''(f)$ moves to the area of high frequencies, its amplitude drops, and a well defined t-maximum appears on a high-frequency sloe of m-maximum. At the same time the shape of the semicircle of the Cole-Cole diagram $\varepsilon''(\varepsilon')$ turns out to be much more distorted. Note that at $T = 62.5\,^\circ$C and $T = 65\,^\circ$C a well defined fine structure is observed in the form of a frequency m–t-doublet. The Cole-Cole diagram $\varepsilon''(\varepsilon')$ shows the doublet structure in the form of two semi-circles partially imposed upon each other. With subsequent growth of temperature from 65 to 70 °C, again only t-maximum of function $\varepsilon''(f)$ is observed, being now located at frequency $f = 10^7$ Hz, besides, further heating is accompanied by the decrease in the frequency half-width of this maximum and growth of its intensity.

When the specimen is cooled from 70 to 45 °C, the described changes of DS fine structure recur in the reverse order, but with a delay in temperature by 10 °C (Figure 1, b). The fact of delay indicates the presence of thermal hysteresis of frequency characteristics of DS features.

Figure 2 provides dependences on temperature of frequency position of resonance frequencies of m- and t-maxima of function $\varepsilon''(f)$ when heating and cooling the film VO_2 specimen in the interval of 40–70 °C, demonstrating the presence of thermal hysteresis loop of resonance frequencies of function $\varepsilon''(f)$ maxima. Since the high-frequency area of the hysteresis loop of the maxima position goes beyond the limits of the frequency range of the dielectric spectrometer permissible for measurements, the demonstration of the closed shape of the hysteresis loop was carried out in a manner, according to which the hysteresis loop was formed under the principle of control of the temperature dependence of the frequency position of low-frequency slopes of m- and t-maxima fixed at the level of 0.2 of the loop height. This made it possible to establish the fact of loop „closure“ at high temperatures tracked until 100 °C.

3. Results of calculations of equivalent electric circuit characteristics

For analysis of temperature transformation of the fine structure components in the DS features, both Debye formula and calculation of characteristics of the equiva-

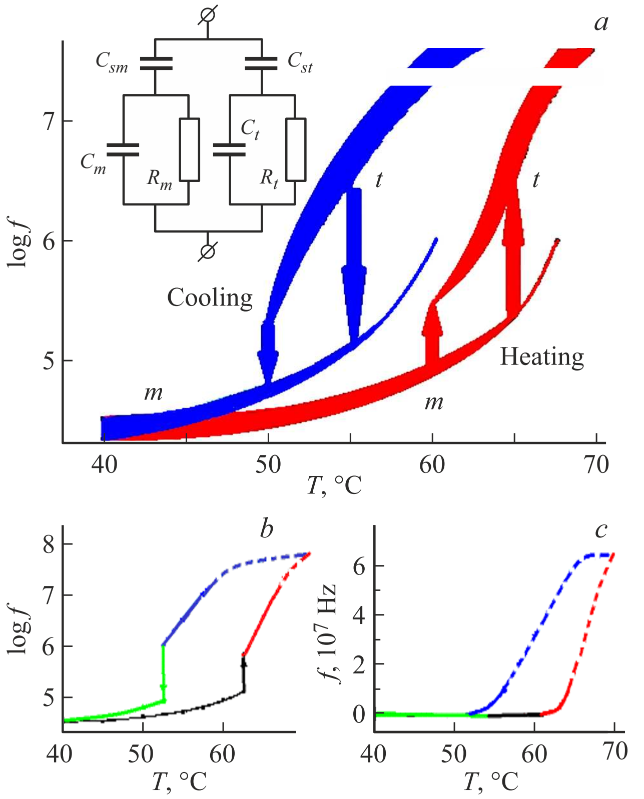

Figure 2. *a* — temperature hysteresis loop of resonance frequencies of *m*- and *t*-maxima $\varepsilon''(f)$; *b* — multi-link loop of temperature hysteresis of film grain VO_2 at a logarithmic scale; *c* — the same multi-link loop presented at a linear scale. The insert includes a two-contour equivalent circuit: C_m and C_t — capacitances and R_m and R_t — resistances of film parts made of monoclinic and tetragonal grains VO_2, accordingly. C_{sm} and C_{st} — capacitances of those parts of the insulating substrate, where crystalline grains VO_2 are arranged, corresponding to the monoclinic and tetragonal variants, accordingly.

lent electrical circuits may be used, with the parameters adequate to the set of the monoclinic and tetragonal combinations of thin-film specimen nanocrystallites that coexist on the surface. In the first case the Debye formula requires its complication by addition of two disperse members of relaxation oscillator distribution among their relaxation times, being presented as:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_m}{[1 + (i\omega\tau_{\mathrm{Dm}})]} + \frac{\Delta\varepsilon_t}{[1 + (i\omega\tau_{\mathrm{Dt}})]}.$$

However, such path does not seem to be meaningful in virtue of absence of a clear connection between mathematical parameters of the complicated Debye formula and measured parameters of DS in the studied specimen. The analysis method based on calculation of the parameters of the equivalent electrical circuits adequate to a thin-film specimen does not contain such a drawback. Therefore, in this article it was used in the variant, where a two-contour circuit presented in insert of Figure 2 was selected as an equivalent electrical circuit. The method to calculate the electrical parameters of this circuit is described in detail in paper [9].

Figure 3 presents the theoretical analogs of DS calculated in accordance with the equivalent circuit of Figure 2. Numerical values of constants ε_0 and ε_∞, resonance frequencies f_{m0}, f_{t0}, and values $\Delta\varepsilon''_m(f_{m0})$ and $\Delta\varepsilon''_t(f_{t0})$ in the curves, are selected using the principle of best agreement between the calculation results and the experiment results. The physical sense of the specified parameters reduces to the following: $\varepsilon^*(0) = \varepsilon'(0) = C_s/C_0$ — corresponds to the limit of $\varepsilon'(\omega)$ at $\omega \to 0$. $C_s = C_{sm} + C_{st}$ — electrical capacitance of the substrate, C_{sm} and C_{st} — total electrical capacitances of those substrate parts, which are occupied with *m*- and *t*-combinations of nanocrystallites, C_0 — electrical capacitance of the dielectric spectrometer cell, not containing the film specimen, i. e. $\varepsilon'(0)$ represents dielectric permittivity of the isolating substrate as such. This interpretation has the physical sense adequate to reality, since the corresponding estimates show that the drift of free electrons obtained as a result of their thermal generation ($R = \mathrm{const}$), fully displaces the probing electric field from the semiconductor film VO_2 to the mica dielectric substrate for all frequencies used in the experiment.

The value $\varepsilon^*(\infty) = \varepsilon'(\infty) = \varepsilon_\infty = CC_s/[(C + C_s)C_0]$ is determined by the limit of function $\varepsilon'(\omega)$ at $\omega \to \infty$. It corresponds to the theoretical combination of the serially connected electrical capacitances (here $C = C_m + C_t$ — capacitance of the semiconductor film, C_s — substrate capacitance) in those conditions, when the charger carrier in the thin film of the semiconductor, having their inherent mobility, are not capable to provide for any screening of the probing external field at high frequencies, i. e., in other words, „have no time to move".

$\tau_{\mathrm{Dm}} \approx R_mC_m = \varepsilon\varepsilon_0/\sigma_m$ ($\varepsilon_0 = 8.85 \cdot 10^{-12}\,\mathrm{mF/m}$) is the Maxwell relaxation time, σ_m — specific conductivity of a combination of nanocrystallites in the semiconductor state, i. e. a part of VO_2 film nanocrystallites in monoclinic symmetry.

$\tau_{\mathrm{Dt}} \approx R_tC_t = \varepsilon\varepsilon_0/\sigma_t$ represents the Maxwell relaxation time, and σ_t — specific conductivity of a combination of metallized nanocrystallites, i. e. a part of VO_2 film nanocrystallites of tetragonal symmetry.

It is necessary to emphasize that the numerical values of $\Delta\varepsilon_m$ and $\Delta\varepsilon_t$ do not depend, as the calculations confirmed, on the conductivity of the film material, but are determined exclusively by the numerical values of electrical capacitances corresponding to the combinations of nanocrystallites [9].

Thus, if the semiconductor film VO_2 consists of two types of nanocrystallites (grains) with specific conductivities ε_m and ε_t, DS will have resonance features at two frequencies f_{m0} and f_{t0}. Besides, the numerical values along the vertical axis of the curves of functions $\varepsilon''(f_{m0})$ and $\varepsilon''(f_{t0})$ will be determined by total areas of all grains of each type, adjacent to electrodes, beyond the connection to the degree of their mixing between each other on the substrate surface.

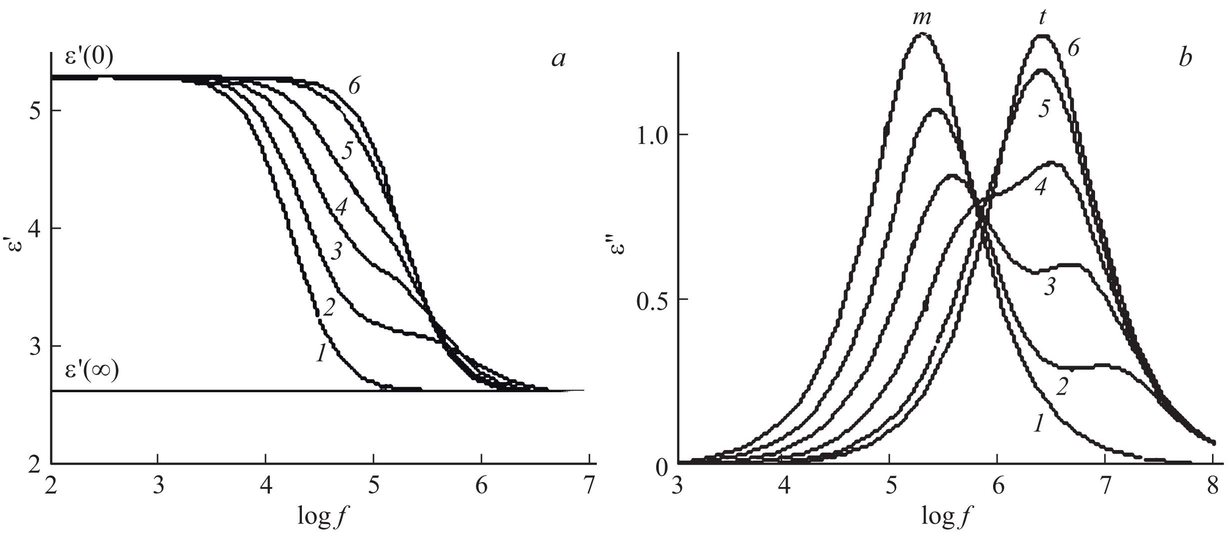

Figure 3. The results of calculation of the functions of frequency dependences $\varepsilon'(f)$ and $\varepsilon''(f)$, arranged in accordance with the two-contour circuit, with the demonstration of their transformation with the changing ratio between the areas, occupied by nanocrystallites of two different types, namely S_m and S_t: 1.0 and 0.0 (*1*), 0.8 and 0.2 (*2*), 0.6 and 0.4 (*3*), 0.4 and 0.6 (*4*), 0.2 and 0.8 (*5*), 0.0 and 1.0 (*6*). Besides, $C_0 = 38\,\mathrm{pF}$, $\varepsilon_s = 5.25$, $R_m = 2 \cdot 10^3\,\Omega$, $R_t = 2 \cdot 10^2\,\Omega$, $k = 1$, $C_m = kC_{sm}$, $C_t = kC_{st}$, $C_{sm} = \varepsilon_s C_0 - C_{st}$, where $C_{st} = 0$ (*1*), 40 (*2*), 80 (*3*), 120 (*4*), 160 (*5*) and 200 pF (*6*).

4. Interpretation of the experimental findings

In the temperature area $T < T_c$, i.e. in the interval from the room temperature to 55 °C, the specific conductivity σ_m increases monotonously in grains having monoclinic structure of the lattice and located in the semiconductor phase. I.e. the Mott's PT is implemented being extended in temperature, which experimentally manifests itself in the serial increase of the resonance frequency of $\varepsilon''(f)$ function maximum for one *m*-component of monoclinic symmetry only, provided for by one parameter only — semiconductor type of grains.

In the field of temperatures 55–65 °C the continuous growth of nanocrystalline grains specific conductivity continues, besides, at the same time the spasmodic transition occurs for some grains that reached the temperature point of Peierls (structural) PT, from the monoclinic phase to the tetragonal (metal) phase, which is supported by the spasmodic increase in specific conductivity in the part of the grains that changed to metal phase from the value σ_m to the value σ_t. I.e. together with the Mott's electronic PT in the part of grains that reached the temperature point of Peierls' PT, the Peierls' structural PT occurs being initiated by the Mott's transition. This PT manifests itself experimentally in the formation of DS, together with the preservation of the monoclinic — *m*-component, second — tetragonal — *t*-component provided for by the appearance of the combination of second-type grains with a shorter Maxwell relaxation time, which have the tetragonal structure of the lattice and find themselves in the metal phase. Coexistence of both combinations of grains in the field of temperatures 55–65 °C results in appearance of a fine structure of DS spectral features.

You can qualitatively describe Mott's PT as follows. Vanadium dioxide in the semiconductor monoclinic phase has V–V-dimers, which represent formations, where vanadium ions of the neighboring octahedrons are joined to each other in pairs with σ-bonds. According to Pauling [10], these bonds are bent due to the fact that two electrons forming the bond electrostatically push off of each other. However, according to the Pauling model, σ-bonds provided for by this electrostatic repulsion, are not finally damaged, because the drop in the electrostatic repulsion of pair electrons being squared by distance becomes compensated as the distance grows at a certain fixed distance between the bond electrons by attraction of magnetic moments of electrons, the force of attraction between which decreases in accordance with the linear, and not square law. When the film specimen is heated in the field of temperatures near T_c Peierls' phase transition, some σ-bonds of V–V-dimers determined by martensite properties of PT, is destabilized, turning from fully stable into periodically broken and reappearing dynamic σ-bonds. Such bonds are formed twice in one half-period of fully symmetrical phonon oscillations of V^{4+} ion chain along the lines that connect the centers of oxygen octahedrons. At the same time, thanks to cooperative nature of generalized Bloch functions describing the electron states of V ions in the crystalline lattice, the overall probability of free electron array appearance in the crystal is growing and, in particular, the density is higher for the probability of free electron appearance in σ-space between branches of bent (by Pauling), but still spared from destabilization, σ-bonds, which in general reduces their strength. On the other hand, increase in electron concentration in π^*-conduction band with their thermal diversion to this band from d_{bott} valence band causes, according to the MO theory [11], decrease in the total energy of both these bands, reducing the gaps between them due to the fact that their average energy approaches the level of vacuum energy at such decrease. Specifically for VO_2 the approach to the vacuum energy level happens due to strong exchange interaction of electrons, whose energy is in π^*-band that is narrow by energy and flat in k-space. The exchange interaction as such is both interaction of free conductivity electrons between each other and their interaction with the related valence electrons [12,13]. With the further continuous increase of film VO_2 temperature, the band gap of the semiconductor collapses, and closes by the energy of conduction band with the valence band, i.e. the Mott's insulator changes into Mott's metal.

Therefore, under monotonous thermal destabilization of V−V-dimers, the critically small part of dimers that remained stable becomes incapable of holding the crystalline lattice of the grain in the low-symmetry monoclinic phase. As a result, a Peierls' structural PT of a crystal into a tetragonal phase takes place in a grain by a jump (by temperature) for the short time necessary for the phase interface spread at the velocity of sound from one grain surface to the other, and the part of dimers that remained stable is additionally destabilized at the same time, therefore the specific conductivity of each crystalline grain increases in a jump-like manner. In other words, Mott's electronic PT initiates Peierls' structural PT in all grains of the film, besides, initiation occurs at various temperatures defined by martensite nature of PT in VO_2 (according to martensite ideology of T_c Peierls' phase transition is inversely proportional to the square root of the middle size across of the grain). Upon completion of Peierls' PT, further temperature increase is accompanied with further development of Mott's PT, increasing the specific conductivity of the grain. Therefore, each elementary loop of the thermal hysteresis of a separate film nanocrystallie also turns out to be multi-link.

At temperatures exceeding 70 °C (in interval of 70−100 °C) the Peierls' PT is completed in all grains without exception, which experimentally manifests itself in disappearance of fine DS structure. Besides, Mott's PT continues developing, which finds its reflection in the continued monotonous growth of the resonance frequency of maxima of DS features.

As temperature drops from 100 to 30 °C, all processes are practically fully repeated in the reverse order, but with „delay" by temperature of 10 °C due to the presence of thermal hysteresis of PT in every separate crystalline grain.

The above makes it possible to interpret the branches of the temperature hysteresis loop of the frequency position of DS features in more detail.

Figure 2 shows that heating and cooling branches of the loop each consist of two components: monoclinic m (semiconductor) and tetragonal t (metal). At $T < 40\,^{\circ}\mathrm{C}$ all grains of the film, regardless of connection with their size, are in monoclinic phase, „respond" to one and the same resonance frequency of probing field $f_{m0}(T)$, signaling at the same time that they have the same specific conductivity $\sigma_m(T)$. At $T > 70\,^{\circ}\mathrm{C}$ all grains of the film, also regardless of the connection to their size, are in tetragonal phase, „respond" to one and the same resonance frequency $f_{t0}(T)$ and thus announce that here they have the specific conductivity $\sigma_t(T)$, which is the same for all.

This leads to the opportunity to build the elementary loop of thermal hysteresis in a separate crystalline grain (see Figure 2, b). This loop is characterized by two vertical intermittent transitions: from monoclinic m-branch to tetragonal t-branch with temperature increase and back from tetragonal t-branch to monoclinic m-branch with its decrease. The difference of the hysteresis loops of various grains from each other only consists in the temperature position of their transitions that are vertical by temperature (structural transitions). We will emphasize that the hysteresis loop looks much more deprived from the information point of view, having been built at the normal linear scale (Figure 2, c), compared to the same loop built at the logarithmic scale. The latter looks much more enriched from the information point of view (Figure 2, b). The reason for this phenomenon is the fact that the conductivity jump in structural transitions makes less than 1 % of the total conductivity change. Therefore, in the ordinary planar technology of electrodes at the linear registration of thermal hysteresis loop of VO_2 film conductivity that is generally accepted in the experiment, the structural changes are practically unseen, and mostly Mott's PT is recorded.

Note that the hysteresis loop of conductivity of an individual grain changes notably along its height with the change of the spatial geometry of the grain, even though the shape of the loop will remain unchanged. Moreover, the total conductivity hysteresis loops in serially (or) parallel joined grains also change in amplitude with the change of grain geometry, but remain unchanged in their shape.

To give a complete picture, it should be noted that a certain change in the shape of the total hysteresis loop could have caused the features in the processes of electric conductivity provoked by the presence of $p{-}n$-transitions or tunnel transitions between the contacting nanocrystallites of film VO_2, if the transition parameters depend on temperature. However, such have not yet been registered in vanadium dioxide.

Figure 2 shows that structural PTs that are intermittent by temperature occupy, as specified above, a part of branches that is minor in height in the total (main) hysteresis loop of specific conductivity of VO_2 film specimen. Therefore, it can be said that the multi-link shape of the thermal hysteresis loop is mainly formed by temperature dependence of specific conductivity determined by Mott's electronic transition extended by temperature. With the purpose to additionally test this statement, we performed three control experiments.

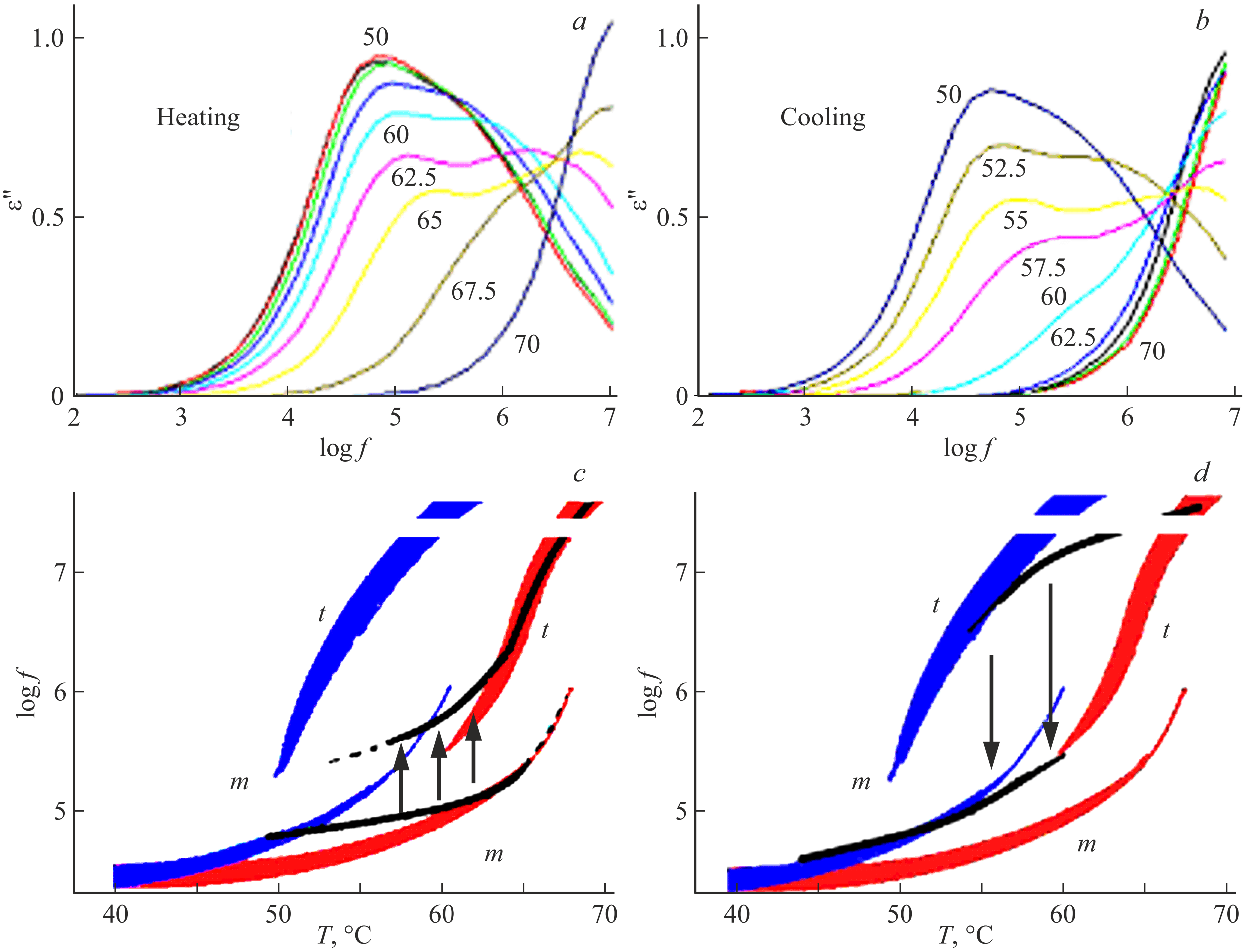

Figure 4. Dynamics of the DS fine structure (a, b) and its corresponding branches of minor hysteresis loops (c, d) inside the common loop of temperature hysteresis at heating (a, c) and cooling (b, d) of specimen t — tetragonal structure, m — monoclinic lattice structure.

5. Control experiments

1. Control of parameters of hysteresis minor loop heating branch. To obtain such, the specimen was first heated from 20 to 90 °C, then cooled down to 50 °C (i.e. not to the closure of the main loop branches), and then again heated to 70 °C with simultaneous registration of DS taken with step 2.5 °C. Figure 4, *a* shows that in the interval $50 < T < 60\,^\circ$C the thermal change of DS with temperature is insignificant, whereas in the interval $60 < T < 70\,^\circ$C structural PTs appear in some grains from monoclinic phase to tetragonal one. Besides, the minor loops as such close with the heating branch of the main hysteresis loop as the temperature increases to the high-temperature point of closure of both branches in the main loop.

2. Control of parameters of hysteresis minor loop cooling branch. To obtain such, the specimen pre-heated to 70 °C was cooled down from 70 to 50 °C at the simultaneous registration of DS with step 2.5 °C. Figure 4, *b* shows that in the interval $70 > T > 60\,^\circ$C the spectra hardly change, and in the interval $60 > T > 50\,^\circ$C the structural PTs appear from a certain part of grains from the tetragonal phase to the monoclinic one, besides, minor loops close with the cooling branch of the main loop of hysteresis as the temperature decreases to the low-temperature point of closure of both branches in the main loop.

3. In order to test the thermal stability of hysteresis states, the specimen was first heated from 20 to 90 °C, then cooled down to 60 °C, i.e. approximately to the middle of the cooling branch, and maintained at this temperature for an hour with the simultaneous registration of DS every 15 min. The obtained DS series is shown in Figure 1, *b*, which shows that the shape of the spectra remains unchanged with the course of time, if the temperature of their registration is fixed.

The given results of control experiments show that when temperature is reversed, the features of DS do not repeat their frequency positions corresponding to the heating (Figure 4, *a, c*) or cooling (Figure 4, *b, d*) branches of the main loop of thermal hysteresis, and in case of temperature change, they change their frequency position according to the movement of hysteresis minor loops in the branches, demonstrating the presence of the multi-link structure in the minor loops of hysteresis as well. This fact also means that the temperature hysteresis loop provided for by Mott's PT has steady-state, and not quasi-steady-state nature, as the third control experiment demonstrated with certainty.

The results of the completed studies show, therefore, that at the room temperature vanadium dioxide is first of all the Mott's insulator: as temperature grows from 20 to 100 °C, the specific conductivity of all nanocrystalline grains increases by more than three orders. Besides, in the corresponding temperature points different for grains of different middle sizes across, the Mott's electronic transition stimulates the Peierls' structural PT, besides, the specific conductivity of grains in the structural PT increases as in Mott's PT, but only by one order of its value, i. e. not so radically as at electronic PT. I. e. individual links of the loop differ drastically by their value.

6. Conclusion

Summing up the above, see below the main outcomes of this study, which consist in the following:

1. A fine structure of crystalline films VO_2 DS was found;

2. Redistribution of intensities of DS fine structure components with the growth of specimen temperature in the field of PT was established;

3. Physical parameters were identified for the temperature hysteresis loop in the frequency position of DS features;

4. The experimental results were interpreted, with the following statements:

1) the possibility was implemented to selectively watch the Mott's electronic transition and Peierls' structural transition;

2) the numerical value was assessed for the change in the specific conductivity of the film in process of Mott's PT (three orders of the value) and in process of Peierls' PT (one order of the value);

3) the experimentally confirmed conclusion was made that despite the generally accepted point of view, Mott's electronic PT has thermal hysteresis;

4) the nature of the factor was established, which forms the multi-link shape of the elementary loop of thermal hysteresis in an individual nanocrystallite of film VO_2: it is shown that the degree of effect of this factor at the shape of the loop is defined by 99 % with the physical characteristics of Mott's PT;

5) high probability is shown for the validity of the assumption that when measuring the parameters in the planar geometry for the thermal hysteresis loop of film VO_2 conductivity, the shape of the loop in axes (σ, T) also mainly depends on the physical characteristics of Mott's PT.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] W. Bruckner, H. Opperman, W. Reichelt, E.I. Terukov, F.A. Tschudnovskii. Vanadiumdioxide. Akademie-Verlag, Berlin (1983). 252 p.

[2] N.F. Mott. Perekhody metall-izolyator. Nauka, M. (1979). (in Russian).

[3] V.F. Gantmacher. Elektrony v neuporyadochennykh sredakh. Fizmatlit, M. (2013). p. 288 (in Russian).

[4] A.B. Migdal. UFN **147**, *10*, 210 (1985). (in Russian).

[5] E.B. Shadrin, A.V. Ilyinsky. FTT **42**, *6*, 1092 (2000). (in Russian).

[6] A.V. Ilinskiy, O.E. Kvashenkina, E.B. Shadrin. FTP **45**, *9*, 1197 (2011). (in Russian).

[7] A.V. Ilinskiy, O.E. Kvashenkina, E.B. Shadrin. FTP **46**, *9*, 1194 (2012). (in Russian).

[8] A.V. Ilinskiy, O.E. Kvashenkina, E.B. Shadrin. FTP **46**, *4*, 439 (2012). (in Russian).

[9] A.V. Ilinskiy, R.A. Kastro, M.E. Pashkevich, E.B. Shadrin. ZhTF **89**, *12*, 1885 (2019). (in Russian).

[10] L. Pauling. The nature of the chemical bond, 3rd Ed. Cornell Univ. Publishing, New York (1960).

[11] A.I. Volkov. Metod molekulyarnykh orbitaley. Novoe znanie, M. (2006). 136 s. (in Russian). ISBN 5-94735-107-2

[12] L.D. Landau, E.M. Lifshitz. Kvantovaya mekhanika, 5- e izd. stereotip. Fizmatlit, M. (2002). 808 s. (in Russian). ISBN 5-9221-0057-2

[13] M. Gatti, F. Bruneval, V. Olevano, L. Reining. Phys. Rev. Lett. **99**, 266402 (2007).

Translated by M.Verenikina