Low-frequency noise in vanadium dioxide undergoing a metal–semiconductor phase transition

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(Submitted 5 March 1980)
Zh. Eksp. Teor. Fiz. **79**, 1353–1362 (October 1980)

An investigation was made of the $1/f$ noise in vanadium dioxide. It was found that studies of the $1/f$ noise should be made using relatively small currents in order to ensure that the normalized noise power is independent of the current. The frequency dependence of the noise was studied in a wide range of temperatures. Far from phase transitions the noise spectrum obeyed the $f^{-\alpha}$ law, whereas near phase transitions the spectrum became more complex. Near these transitions there were also high-amplitude peaks in the temperature dependence of the noise intensity and these were clearly associated with the crossing of the metal–semiconductor phase boundary and also of the boundaries of the various modifications of semiconducting phases. The results show that a study of noise can provide a very sensitive method for constructing the phase diagrams of a wide range of materials undergoing the metal–semiconductor phase transition.

PACS numbers: 72.60. + g, 72.70. + m

In spite of the fact that the excess low-frequency noise of the $1/f$ type[1)] has been studied for a long time, there is as yet no clear idea of its nature. This has arisen because such noise is observed in a "catastrophically" wide range of phenomena in live and dead matter,[1] and the explanations of its partial manifestations published from time to time (see, for example, Ref. 2) have failed to give a complete solution to the problem.

Most of the investigations of the $1/f$ noise have been explained by equilibrium fluctuations of the resistance in a specially constructed inhomogeneous system. According to a different point of view, the $1/f$ noise is a consequence of transient phenomena in the current-conducting system or in the material as a whole.[3] This hypothesis is used in estimating the service life of electronic devices. Finally, there is another point of view according to which the $1/f$ noise is due to the non-equilibrium in the current-conducting system during the actual flow of the current. However, no work has been done on this aspect because of the difficulties encountered in theoretical descriptions.

The $1/f$ noise has been investigated in metals, insulators, and semiconductors with the aim of covering the widest possible range of states in the electron subsystem.[4] Therefore, it seemed of interest to study the $1/f$ noise in a material (such as vanadium dioxide) undergoing metal–semiconductor and semiconductor–semiconductor phase transitions, i.e., those phase transitions which cause very great changes in the electron subsystem. This provides a unique opportunity to investigate not only the manifestations of the noise in various electron states of matter but also on transition from one state to another.

Our interest in the noise in vanadium dioxide has been also stimulated greatly by the investigations published in Refs. 5 and 6, and also that in Ref. 7 dealing with the current noise in a two-contact switching device made of a vanadium dioxide single crystal.

EXPERIMENTAL METHOD

Our experiments were carried out on VO_2 single crystals grown by the gas-transport reaction method[8] and also by electrolysis of molten vanadium pentoxide. Samples were usually needle-shaped; their length was several millimeters and their cross section was 0.1 $\times$ 0.1 mm. Measurements were carried out under given-current conditions, as in Ref. 7, but in contrast to that study, use was made of a potentiometric four-contact circuit.

The spectrum of mean-square fluctuations of the voltage $\overline{\Delta U^2}$ was investigated using a real-time analyzer of the S4-73 type, which enabled us to record the spectrum simultaneously at 200 equidistant points on a frequency scale ranging from 2 Hz (resolution 0.01 Hz/channel) to 20 kHz (resolution 100 Hz/channel). Independent realizations of the spectrum were averaged under linear (or exponential) accumulation conditions using an F-36 multichannel register; the averaging was continued for 4 min and this period was the same at all the analyzed frequencies. The whole spectrum from 0.1 Hz to 20 kHz was recorded by measurements in four analyzer ranges: 20 Hz, 200 Hz, 2 kHz, and 20 kHz. We thus found that the total time for recording a single spectrogram was of the order of 16 min (the number of experimental points was then about 800). Naturally, in this procedure the precision deteriorated at lower frequencies (Fig. 1). The matching of the spectra recorded in different ranges was achieved using channels 10–100 in any range. In the presence of the $1/f$ noise such matching reduced to simple multiplication of the content of the channels in each lower (on the frequency scale) analyzer range by the relative change in its resolution (i.e., the factor of 10, 100, and 1000). However, in any frequency dependence of the spectrum other than $f^{-\alpha}$ this procedure could not be used for any quantitative conclusions. One could only say that the form of the spectrum was more complex than $f^{-\alpha}$.

In accordance with the generally accepted procedure,[9]

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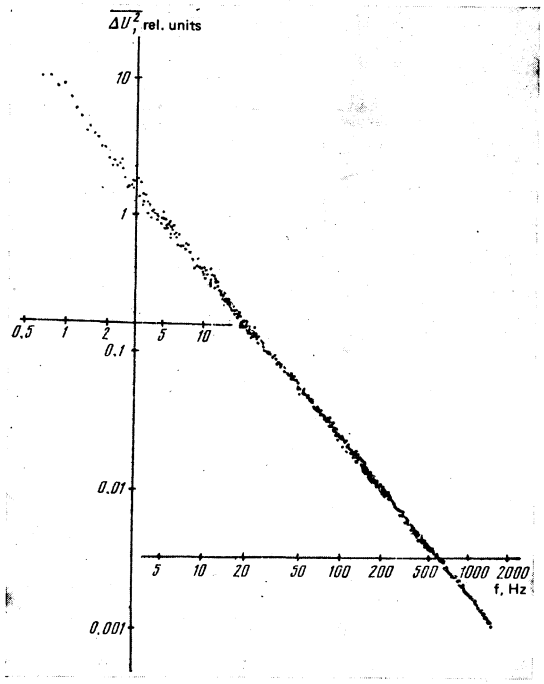

FIG. 1. Typical spectrogram of low-frequency noise. The noise power $\overline{\Delta U^2}$ is given in relative units and the procedure for matching the results obtained in different analyzer bands is described in text; $\alpha = 1.188 \pm 0.002$, $I = 8.5\,\mu$A.

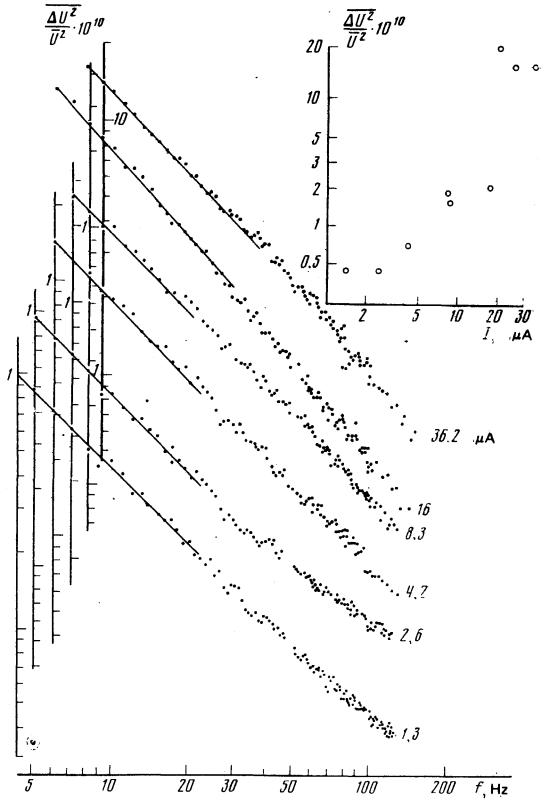

FIG. 2. Frequency dependences of the normalized noise power obtained for different currents through a sample. The ordinates of each lower spectrogram, recorded using the current given alongside the curve, are shifted relative to one another to the left and downward but the frequency scale is the same for all of them. The top right-hand corner gives the current dependence of the normalized noise power at 10 Hz in a band of 1 Hz.

a study was made of the dependence of the noise power on the current in the investigated sample. These measurements were carried out at temperatures far from the phase transition points where the $1/f$ law was obeyed. The reasons for this procedure were as follows. A large number of experiments indicated that the mean-square fluctuations (i.e., the spectral density of the noise) obeyed the empirical law

$$\overline{\Delta U^2} = \frac{\Delta f}{f} \frac{C_H}{N} I^2 R^2, \qquad (1)$$

where N is the number of carriers in the investigated system, I is the current through the sample, R is the resistance of the sample, and C_H is the Hooge constant.[9,10] It has been suggested[9,10] that C_H is a universal constant applicable to a large number of different materials and having a value of the order of 2×10^{-3}. However, other investigations have found that this constant has values three or four orders of magnitude greater[7] or three orders of magnitude less.[11] Therefore, the question of universality of this constant is still subject to discussion. In particular, we found that the semiconducting state of VO_2 is characterized by $C_H \approx 4$.

Figure 2 shows the results of a determination of the normalized noise power $\overline{\Delta U^2}/U^2$ as a function of the current I at a given frequency $f = 10$ Hz in a band of $\Delta f = 1$ Hz. The same figure includes the noise spectra recorded at fixed values of the current. We can see that variation of the current alters the noise power and the nature of the law $f^{-\alpha}$. Only in the limit of small currents ($I \leq 5\,\mu$A) is the spectrum close to $f^{-\alpha}$ ($\alpha = 1.05 \pm 0.01$) and there is a flat region in the dependence on the current. As the current is increased, the values of α and C_H change significantly. It is reported in Ref. 7 that when the current density is $j \approx 1.2 \times 10^4$ A/m^2, which is considerably greater than the values in our study (for $I = 5\,\mu$A the current density in our sample was $j \approx 5 \approx 10^2$ A/m^2), it is found that $\alpha = 1.25$ and $C_H \approx 100$, which can be regarded as extrapolation of our current dependences to the range of high currents.

RESULTS OF MEASUREMENTS

In view of the above discussion, we investigated the temperature dependence of the noise spectrum at low currents of the order of 2 μA. The results of this investigation are presented in Fig. 3. Near each curve we have given the temperature at which the measurements were carried out. Between room temperature and ~50 °C all the spectra obey the same $f^{-\alpha}$ law ($\alpha = 1.05 \pm 0.01$). By way of example, Fig. 3 includes a spectrogram recorded at $t = 49.4$ °C. Considerable changes in the spectra are observed at higher temperatures. Although at low frequencies ($f < 50$ Hz) all the spectra obey the same universal law $f^{-\alpha}$, there are considerable changes in the high-frequency parts of the spectra.

Even more interesting features on approach to the

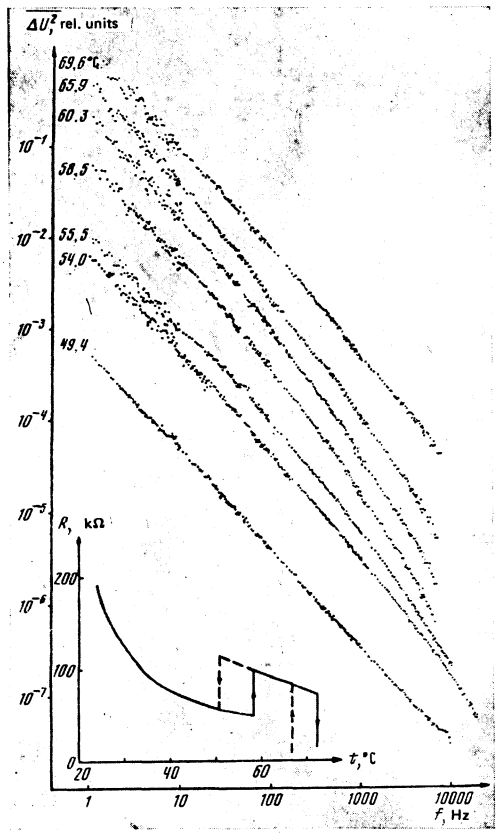

FIG. 3. Spectral dependences of the normalized noise power recorded at various temperatures. The lower left-hand corner shows the temperature dependence of the resistance of vanadium dioxide.

expected various phase transitions in vanadium dioxide were observed in the temperature dependence of the normalized spectral density. The measurement results are shown in Fig. 4a. The temperature dependence of the noise in the semiconducting phase was recorded at a fixed frequency allowing for the temperature dependence of the resistance and, consequently, for the temperature dependence of the carrier density. This was done by normalizing the power in the noise spectrum to the value of U^2R. In fact, according to Eq. (1),

$$\frac{\overline{\Delta U^2}}{U^2}=\frac{\Delta f}{f}C_H\frac{1}{N}\propto\frac{\Delta f}{f}C_HR,$$

and then for a fixed value of $\Delta f/f$, we have

$$\overline{\Delta U^2}/U^2R\propto C_H.$$

(It is assumed here that the mobility of carriers depends weakly on temperature, in agreement with the results of Ref. 12.)

The noise spectrum was also investigated in the metallic phase of vanadium dioxide. In this case, we found that the value of C_H was $\sim 10^{-8}$ and it was close to that given by Hooge. This value of C_H was 10^8 times less than that reported in Ref. 7, which was clearly due to the fact that the measurements in Ref. 7 were carried out by the two-contact method and in the metallic state the contact resistance was greater than the resistance of the sample.

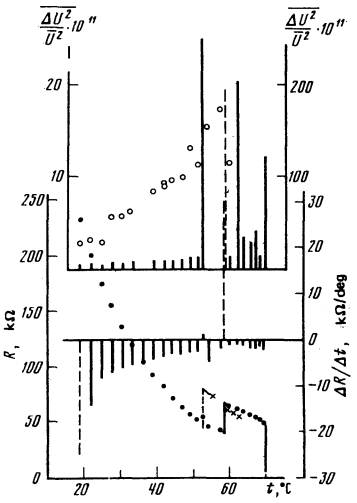

FIG. 4. Temperature dependences of the noise power (upper half) and of the resistance and the derivative of the resistance with respect to temperature (lower half). In the upper half the noise power is plotted in two scales (circles and continuous lines) differing by a factor of 10 in order to stress the smooth rise of the normalized power, which is difficult to detect on a scale of the peaks.

DISCUSSION OF RESULTS

1. A comparison of the temperature dependences of the normalized noise power and of the resistance of a sample (Figs. 4a and 4b) readily shows that the singularities in the dependence $R(t)$ are correlated with sharp peaks in the noise. The reason for this correlation can be established by considering the phase diagram of vanadium dioxide.[13]

Incorporation of trivalent impurities such as chromium, aluminum, iron, etc. in the lattice of vanadium dioxide stabilizes two new semiconducting phases with the monoclinic symmetry: M_2 and T. This is illustrated in the phase diagram shown in Fig. 5 for the $V_{1-x}Fe_xO_2$ system, which is taken as an example.[14] When temperature of this system is increased, three phase transitions are observed: $M_1 \rightleftarrows T$ (semiconductor–semiconductor), $T \rightleftarrows M_2$ (semiconductor–semiconductor), and $M_2 \rightleftarrows R$ (semiconductor–metal) instead of one transition $M_1 \rightleftarrows R$ which occurs in pure vanadium dioxide. Moreover, the transitions $T \rightleftarrows M_2$ and $M_2 \rightleftarrows R$ are observed readily because of the large jumps in the resistance, latent heat of phase transition, and other

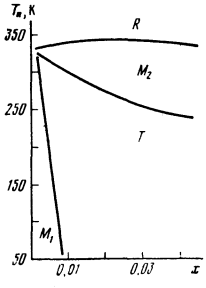

FIG. 5. Typical phase diagram of VO_2 doped with a divalent impurity.

properties, whereas the transition $M_1 \rightleftarrows T$ can be detected only by x-ray and NMR and ESR methods. It has not yet been possible to find any anomalies in the electrical resistance or to measure the latent heat of this last transition. Therefore, the order of this transition is not yet known reliably, but it is suggested in Ref. 15 that it should be of the first order.

Samples of vanadium dioxide investigated by us contained small (<1%) amounts of Cr and Fe impurities. The presence of such trivalent impurities gave rise on top of the metal-semiconductor transition ($M_2 \rightleftarrows R$), to an additional semiconductor–semiconductor transition ($T \rightleftarrows M_2$) at $T \sim 58$ °C (Fig. 4). In the case of discrete (point-by-point) determination of the thermogram in Fig. 4, there was naturally a possibility of missing some spectral singularity. Therefore, to obtain a complete picture of all the significant singularities (peaks) in such a thermogram, dynamic measurements were made, i.e., continuous recording of the total spectral noise ($\overline{\Delta U^2}$) at 10 Hz in a band 1 Hz wide during slow (at a rage of ~0.01 °C/sec) heating of the sample (Fig. 6).

We found that the two most pronounced groups of noise peaks in Fig. 6 near 69–70 and 57–61 °C corresponded exactly to the $M_2 \rightleftarrows R$ and $T \rightleftarrows M_2$ transitions. The noise peaks at $T \sim 46$–47 °C were, in our opinion, due to the $T \rightleftarrows M_1$ transition. In the same region we observed a slight kink in the temperature dependence of the resistance (Fig. 4b). The origin of a group of noise peaks near 65 °C was not clear but it was likely to be associated with deviations from stoichiometry in some parts of the sample, which could reduce the transition temperature from the semiconducting to the metallic state.[13]

Each of the groups of peaks in Fig. 6 had its own characteristic "fine-structure" which could naturally be attributed to the fact that the phase boundaries shown in Fig. 5 were not lines but had finite dimensions.[16]

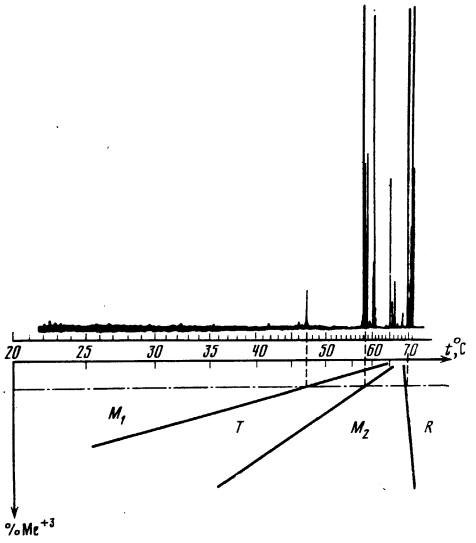

FIG. 6. Thermogram of the noise power recorded at 10 Hz in a band of 1 Hz (explanations in text). The lower part of the figure shows the phase diagram of VO_2 doped with a trivalent impurity.

We thus found that noise investigations can provide a very fine and sensitive method for constructing the phase diagrams of a wide range of materials undergoing the metal–semiconductor phase transition. One should stress here particularly that observation of the $T \rightleftarrows M_1$ transition in vanadium dioxide, which—as indicated by our measurements—is readily manifested by noise peaks, is a difficult experimental task, especially in the case of small single crystals. Unfortunately, doped vanadium dioxide is available only in the form of small single crystals.

2. We cannot give any reasonable explanation for the $f^{-\alpha}$ noise observed in the semiconducting and metallic states of VO_2. This applies to the region close to the phase transitions, where there is a great variety of the vanadium dioxide structures and the spectrum deviates from the simple $f^{-\alpha}$ law. In this region it is difficult to investigate the true nature of the spectrum because the resolution varies with the band. Equally serious difficulties are encountered in the interpretation of such spectra. We do not know the answers to the seemingly simple questions: is the spectrum normalized (are the original $f^{-\alpha}$ and new spectra cumulative) or is it the result of two mechanisms (i.e., are the $f^{-\alpha}$ and new spectra additive)? However, it should be pointed out that the frequency range of the observed deviations of the spectra from the $f^{-\alpha}$ law is 1–1000 Hz (Fig. 3), i.e., these deviations may be attributed (if a suitable theory is available) to the appearance in the investigated system—at temperatures close to the phase transition—of some additional relaxation mechanism with a characteristic time scale from seconds to milliseconds. This conclusion is in qualitative agreement with the results of Ref. 17, where the nucleation time of ~1 sec was reported.

The change in the $f^{-\alpha}$ law is observed when the current is increased (Fig. 1). One should stress that the effects of heating of a sample by the maximum currents were small (within 1–1.5 °C), i.e., there is no question of any pretransition phenomena.

3. The normalized noise power increased on approach to the transition (Fig. 4). This may possibly be due to heterophase fluctuations near a first-order phase transition. However, to the best of our knowledge, there is no dynamic theory of heterophase fluctuations in a form suitable for the interpretation of the noise experiments. Such an overall rise of the normalized noise power and, possibly, its more rapid rise near phase inhomogeneities in vanadium dioxide is reported in Ref. 18. However, the higher range of frequencies employed in that study ($f \sim 40$ kHz) and the greater measuring currents prevent us from concluding that the results are comparable.

The influence of the switching regime on the noise spectrum of vanadium dioxide was investigated in Ref. 6 and, in particular, a report was given of spectral and current singularities resembling qualitatively those observed in the present study. However, the ranges of the frequency and currents where these singularities

were observed conflicted with the criteria in Ref. 6.

The authors regard it as their pleasant duty to thank A. G. Aronov, G. M. Drabkin, A. G. Lomakin, D. I. Khomskiĭ, B. I. Shklovskiĭ, and participants of a seminar of a team headed by V. L. Gurevich (A. F. Ioffe Physicotechnical Institute) for a valuable discussion of the results; A. A. Alekseyunas, V. A. Bareĭkis, V. M. Bondarenko, and Yu. S. Liberis advised us and discussed the measurement method; N. E. Timoshchenko supplied us with several vanadium dioxide crystals grown by the electrolytic method.

[1)]The $1/f$ noise includes also the noise obeying the law $1/f^{\alpha}$, where $\alpha = 1 \pm 0.3$.

[1]Sh. M. Kogan, Usp. Fiz. Nauk **123**, 131 (1977) [Sov. Phys. Usp. **20**, 763 (1977)].
[2]B. I. Shklovskii, Solid State Commun. **33**, 273 (1980).
[3]A. N. Malakhov and A. V. Yakimov, Radiotekh. Elektron. **19**, 2435 (1974).
[4]Tezisy dokladov II konferentsii po fluktuatsionnym yavleniyam v fizicheskikh sistemakh (Abstracts of Papers presented at Second Conf. on Fluctuation Phenomena in Physical Systems), Vilnius, 1979, pp. 66–89.
[5]E. C. Jelks, R. M. Walser, R. W. Bene, and W. H. Neal, Appl. Phys. Lett. **26**, 355 (1975).
[6]A. A. Kokin and G. B. Mikhaĭlov, Fiz. Tverd. Tela (Leningrad) **18**, 3384 (1976) [Sov. Phys. Solid State **18**, 1970 (1976)].
[7]A. Alekseyunas, V. Bareĭkis, V. Bondarenko, and Yu. Liberis, Fiz. Tverd. Tela (Leningrad) **20**, 1980 (1978) [Sov. Phys. Solid State **20**, 1143 (1978)].
[8]K. Nagasawa, Mater. Res. Bull. **6**, 853 (1971).
[9]F. N. Hooge, Phys. Lett. A **29**, 139 (1969).
[10]F. N. Hooge, Physica (Utrecht) **60**, 130 (1972).
[11]V. P. Palenskis and Z. L. Shoblitskas, Tezisy dokladov II konferentsii po fluktuatsionnym yavleniyam v fizicheskikh sistemakh (Abstracts of Papers presented at Second Conf. on Fluctuation Phenomena in Physical Systems), Vilnius, 1979, p. 70.
[12]W. H. Rosevear and W. Paul, Phys. Rev. B **7**, 2109 (1973).
[13]A. A. Bugaev, B. P. Zakharchenya, and F. A. Chudnovskiĭ, Fazovyĭ perekhod metall-poluprovodnik i ego primenenie (Metal–Semiconductor Phase Transition and Its Applications), Nauka, M., 1979.
[14]W. Brückner, U. Gerlach, W. Moldenhauer, H. P. Brückner, B. Thuss, H. Oppermann, E. Wolf, and I. Storbeck, J. Phys. (Paris) **37**, Colloq. 4, C4-63 (1976).
[15]M. Marezio, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B **5**, 2541 (1972).
[16]J. M. Reyes, S. L. Segel, and M. Sayer, Can. J. Phys. **54**, 1 (1976).
[17]T. G. Lanskaya, I. A. Merkulov, and F. A. Chudnovskiĭ, Fiz. Tverd. Tela (Leningrad) **20**, 336 (1978) [Sov. Phys. Solid State **20**, 193 (1978)].
[18]A. Alekseyunas, V. A. Bareĭkis, V. M. Bondarenko, Yu. S. Liberis, V. I. Miller, V. A. Perelyaev, and G. P. Shveĭkin, Tezisy dokladov II Vsesoyuznogo soveshchaniya po khimii tverdogo tela (Abstracts of Papers presented at Second All-Union Conf. on Solid-State Chemistry), Sverdlovsk, 1978.

Translated by A. Tybulewicz

Theory of tunnel relaxation in a photon field

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(Submitted 12 March 1980)
Zh. Eksp. Teor. Fiz. **79**, 1363–1375 (October 1980)

The subbarrier relaxation of a particle located in a nonsymmetric double-well potential is considered. The phonon subsystem plays the role of a thermostat. It is shown that the tunnel kinetics of the particle is characterized by two relaxation times. The relaxation of the occupation numbers is proportional to the square of the overlap integral, whereas the relaxation of the phase correlation is of zero order with respect to the overlap integral and generally proceeds at a faster rate than the relaxation of the occupation numbers. The relative roles of two-phonon and one-phonon relaxation mechanisms are elucidated. Experiments on sound absorption in amorphous media and on tunnel diffusion of mesons are discussed within the framework of the proposed model.

PACS numbers: 43.35.Fj, 43.35.Gk, 63.10. + a

1. INTRODUCTION

In recent years, a whole group of problems has arisen which can in pattern be reduced to sub-barrier tunneling between two potential wells with slightly displaced energy levels, in the presence of an arbitrary interaction with the phonon field. This group includes quantum diffusion of light particles in crystals with defects, the class of low-frequency excitations in amorphous media, orientational transitions, and so on. A characteristic feature of these problems is the presence of a small parameter, such as the overlap integral J of the wave functions belonging to states in different wells. This leads to the result that two-well tunnel kinetics differs in principle from the well-known picture of relaxation of two-level systems (spin relaxation). As will be shown below, even in the presence of only one dissipation mechanism—the interaction of the "particle" with the phonon field—a property of two-well kinetics is the simultaneous presence of fast and slow relaxations that differ strongly in magnitude. Using the language of spin kinetics and introducing approximately the concept of longitudinal T_1 and transverse T_2 relaxation times, we can verify that the relaxation of the occupation numbers (longitudinal relaxation) is due to transitions from one well to the other, and the probability of this transition is pro-

 0038-5646/80/100688-07$02.40