[6] V. H. Schmidt, A. B. Western, and A. G. Baker, Phys. Rev. Lett. 37, 839 (1976).
[7] R. Clarke and L. Benguigui, J. Phys. C 10, 1963 (1977).
[8] R. J. Birgeneau, G. Shirane, M. Blume, and W. C. Koehler, Phys. Rev. Lett. 33, 1098 (1974).
[9] A. N. Zisman, V. N. Kachinskiĭ, V. A. Lyakhovitskaya, and S. M. Stishov, Zh. Eksp. Teor. Fiz. 77, 640 (1979) [Sov. Phys. JETP 50, 322 (1979)].
[10] P. Bastie, M. Vallade, C. Vettier, and C. M. E. Zeyen, Phys. Rev. Lett. 40, 337 (1978).
[11] W. B. Yelon, D. E. Cox, P. J. Kortman, and W. B. Daniels, Phys. Rev. B 9, 4843 (1974).
[12] F. Borsa and A. Rigamonti, J. Magn. Reson. 20, 232 (1975).
[13] K. A. Muller, Structural Phase Transition and Soft Modes, Oslo University, 1971, 73.
[14] R. Blinc and B. Zekš, Soft Modes in Ferroelectrics and Antiferroelectrics, North-Holland, Amsterdam, 1974 (Russ. Transl., Mir, M., 1975, p. 301).
[15] V. L. Serebrennikov and A. K. Moskalev, Prib. Tekh. Eksp. No. 4, 183 (1977).
[16] V. L. Serebrennikov and I. P. Aleksandrova, Kompleksnye issledovaniya fazovykh perekhodov pod davleniem (Preprint: Comprehensive Investigations of Phase Transitions under Pressure), Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR, Krasnoyarsk, 1979.
[17] S. N. Popov, N. N. Krainik, and I. E. Mylnikova, J. Phys. Soc. Jpn. Suppl. 28, 120 (1970).
[18] T. V. Volk, E. I. Gerzanich, and V. M. Fridkin, Izv. Akad. Nauk SSSR Ser. Fiz. 33, 346 (1969).
[19] A. Kikuchi, Y. Oka, and E. Sawaguchi, J. Phys. Soc. Jpn. 23, 337 (1967).
[20] S. N. Koĭkov, N. N. Kraĭnik, V. G. Malinina, S. N. Popov, and M. N. Rozova, Izv. Akad. Nauk SSSR Ser Fiz. 35, 1790 (1971).
[21] A. K. Moskalev, I. P. Aleksandrova, and V. A. Lyakhovitskaya, Ferroelectrics 20, 221 (1978).
[22] G. A. Smolenskiĭ, V. A. Bokov, V. A. Isupov, N. N. Kraĭnik, R. E. Pasynkov, and M. S. Shur, Segnetoélektriki i antisegnetoélektriki (Ferroelectrics and Antiferroelectrics), Nauka, M., 1971, p. 30.
[23] K. S. Aleksandrov and I. N. Flerov, Fiz. Tverd. Tela (Leningrad) 21, 327 (1979) [Sov. Phys. Solid State 21, 195 (1979)].

Translated by A. Tybulewicz

Submillimeter dielectric spectra of Rochelle salt

A. A. Volkov, G. V. Kozlov, and S. P. Lebedev

P.N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted 2 April 1980)
Zh. Eksp. Teor. Fiz. 79, 1430–1437 (October 1980)

Submillimeter monochromatic spectroscopy in the frequency range 3–13 cm^{-1} and in the temperature interval 180–300 K were used to measure the dielectric spectra $\varepsilon^*(\nu,T)$ of Rochelle salt. It is shown that the singularities observed in the spectra are a continuation of the fundamental ferroelectric dispersion observed earlier at lower frequencies. It is established that in the low-temperature antipolar phase the reciprocal relaxation time obeys a cubic temperature dependence that is rather unusual for most ferroelectrics.

PACS numbers: 77.20. + y, 77.40. + i

1. INTRODUCTION

Phase transitions in Rochelle salt—the first known ferroelectric—have been comprehensively investigated for several decades, but some aspects of these phenomena and of the associated processes remain still debatable. No thorough investigation has been made, in particular, of the porlaization mechanisms that produce in the crystal, in a certain temperature interval (255–297 K), a state with spontaneous polarization.[1] As applied to this problem, the most informative experimental method turned out to be dielectric spectroscopy. At the frequencies 10^9–10^{11} Hz, the dielectric spectra of Rochelle salt have a clearly pronounced singularity in the form of a broad and rather intense absorption line, whose properties depend on temperature. The temperature behavior of this low-frequency (compared with the usual lattice vibrations) mode changes radically at the phase-transition points, and there is no doubt that it is most closely connected with the ferroelectric properties of the Rochelle salt.[2]

The study of the frequency and temperature dependences of the dielectric constant $\varepsilon^*(\nu, T)$ of this crystal has long been carried out practically simultaneously with the development and evolution of the necessary experimental procedures. Consequently some understanding of the character of the dispersion of $\varepsilon^*(\nu, T)$ was gained only in the early Seventies, when practical procedures were developed for the measurement of anomalously high values of the dielectric parameters of materials at radio and microwave frequencies. The $\varepsilon^*(\nu, T)$ dependences obtained for Rochelle salt[2] have become the classical example of relaxation dispersion of the dielectric constant in ferroelectrics. These dependences were the basis for the determination of the parameters of ferroelectrically active excitation of a crystal and of the determination of their temperature dependences near the phase transition points.

The present study followed the general plan of the investigation of the dielectric properties of ferroelectrics in the submillimeter band. Its purpose was the measurement of the temperature dependences of the real (ε') and imaginary (ε'') parts of the dielectric constant of Rochelle salt along the ferroelectric axis at frequencies ~10 cm^{-1} (3×10^{11} Hz). From the point of view of the study of the ferroelectric mode, this expansion of the region of the investigation of the dispersion of $\varepsilon^*(\nu, T)$ is of interest, since it can provide a better idea of the temperature dependence of the parameters of this mode the hitherto prevailing notion based on RF and microwave data.

Our investigation was stimulated also by the fact that Ushatkin *et al.*[3] reported observation of a new phase transition in Rochelle salt at 212 K, and reached their conclusion precisely on the basis of the submillimeter dielectric spectra.

2. EXPERIMENTAL TECHNIQUE

The dielectric spectra $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$ of Rochelle salt were measured by us with a spectrometer in which the radiation was generated by backward-wave tubes (BWT) (backward-wave spectrometer). Such instruments have already been used many times to solve similar problems, and have been described in the literature.[4,5] Up to now, however, they remained special measuring devices available only in laboratory models. Backward-wave spectrometers are close in their physical principles to the grating spectrometers of the IR band, but are intended for use exclusively in the submillimeter band, in which they are the most powerful tools for experimental research because they use special radiation sources, namely backward-wave tubes.[6]

The radiation is generated by a backward-wave tube and propagates from the source to the receiver in open space. Its frequency can be continuously tuned by varying the voltage supply to the BWT. By using a few of the oscillators now available commercially it is possible to cover a rather wide region of the spectrum, to ~40 cm^{-1}. This value can be regarded for the time being as the high-frequency limit of the operating range of the BWT spectrometers.

In our spectrometer we used a quasi-optical technique of channeling and recording the working radiation. On leaving the oscillator, prior to entering the measurement channel, the radiation is shaped into a paraxial beam of ~30 mm diameter with a strictly prescribed polarization. All the required additional focusing in the channel is effected by teflon lenses. The principal control elements in the channel (polarizer, beam splitters, semitransparent mirrors, etc.) are closely spaced wire grids.[7] The radiation receiver is an optical-acoustic detector. At a sensitivity 10^{-1} W/Hz$^{1/2}$, it ensures a useful signal/noise ratio ~10^6.

The spectometer is based on the single-channel principle of spectrum recording. Namely, regardless of the concrete measurement system used, the amplitude characteristic of the "empty" channel is recorded in individual points at specified frequency intervals (calibration), after which the same procedure is repeated but now with the investigated sample in the channel. Comparison of these two spectra determines the transfer function of the sample. The recording of the spectra is automatized and is effected with the air of the "Saratov-2" computer.

The investigated sample is placed in a cryostat that sets and maintains the temperature accurate to 0.05 K in the range 80–330 K.

Our approach to the study of the dielectric properties of matter with the aid of BWT spectrometers was analyzed in detail and described earlier.[8,9] Its main premises, which were adhered to in the present study, are the following.

1) The investigated sample is a plane-parallel plate with ~10 × 10 mm surface. 2) The sample thickness is chosen such that its transmission coefficient is not less than 10^{-3}–10^{-4}. 3) The linearly polarized wave is normally incident on the sample. 4) The measured quantities are the sample transmission coefficient t and the corresponding phase shift φ. 5) The refractive indices (n) and the extinction coefficients (k) of the sample are calculated from the following relations that describe the passage of a plane electromagnetic wave through a dielectric layer:

$$\begin{gathered} t=\exp(-4\pi kd/\lambda) \\ \cdot\frac{(1-R)^2+4R\sin^2\psi}{[1-R\exp(-4\pi kd/\lambda)]^2+4R\exp(-4\pi kd/\lambda)\sin^2(2\pi nd/\lambda+\psi)}, \\ \varphi=\frac{2\pi nd}{\lambda}-\operatorname{arctg}\frac{k(n^2+k^2-1)}{(k^2+n^2)(2+n)+n} \\ +\operatorname{arctg}\frac{R\exp(-4\pi kd/\lambda)\sin 2(2\pi nd/\lambda+\psi)}{1-R\exp(-4\pi kd/\lambda)\cos 2(2\pi nd/\lambda+\psi)}, \end{gathered} \tag{1}$$

where

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \quad \psi=\operatorname{arctg}\frac{2k}{n^2+k^2-1}$$

are the reflection coefficient and the phase shift of the wave and describe its reflection from an infinite layer, λ is the wavelength, and d is the sample thickness.

A diagram of the quasi-optical part of the setup is shown in Fig. 1. When measurements are made of the transmission coefficients of the samples, the elements in the dashed box (6, 7, 10, 11) are not used, and the quasi-optical channel is used in its simplest obvious modification. Figure 2 shows by way of example the transmission spectrum $t(\nu)$ of a Rochelle salt sample plotted in the tuning range of one BWT. A set of such spectra, obtained at various temperatures, makes it possible to establish the temperature dependence of t for individual fixed frequencies (Fig. 3a).

When the phase spectra $\varphi(\nu, T)$ are measured, the entire system illustrated in Fig. 1 is used. In this case

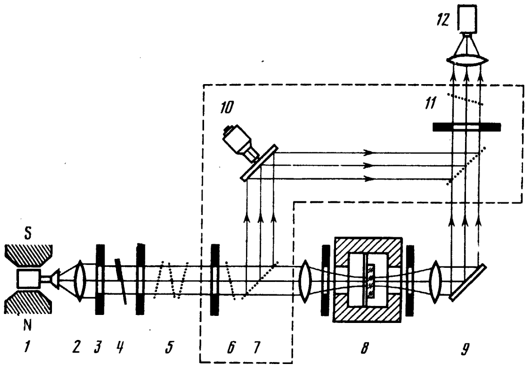

FIG. 1. Diagram of quasi-optical part of the BWT spectrometer: 1—radiation source, 2—teflon lenses, 3—absorbing diaphragms, 4—modulators, 5—grid attenuator, 6—polarizer, 7—beam-splitting grids, 8—thermostat with sample in it, 9—mirror, 10—phase-shift compensator, 11—analyzer, 12—radiation receiver.

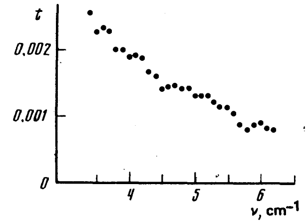

FIG. 2. Frequency dependence of the transmission coefficient of a plane-parallel Rochelle-salt sample 803 μm thick in the orientation **E** ∥ *a*, obtained at 217 K.

it constitutes a Rozhdestvenskiĭ two-beam polarization interferometer.[10] The measured quantity is the displacement of the moving mirror *10*, which compensate for the change in the length of the working arm of the interferometer when the investigated sample *8* is inserted. In the course of the measurement, the compensator mirror *10* follows-up the change in the length of the working arm, due to the change of the dielectric parameters of the sample when the radiation frequency or the sample temperature is changed. Figure 3b shows the temperature dependences of the displacement l of the mirror *10*, as obtained in one of our experiments. The phase shift φ is calculated from such curves by using the relation

$$\varphi=\frac{2\pi}{\lambda}(l\sqrt{2}+d).$$

The accuracy of the phase shift depends on t and amounts to 5–10 deg in the given example.[8]

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Numerical solution of the equations in (1) for n and k, based on the measured functions $t(\nu, T)$ and $\varphi(\nu, T)$, yielded the optical constants of the Rochelle salt, after which both components of its dielectric constants were calculated:

$$\varepsilon'=n^2-k^2,\quad \varepsilon''=2nk.$$

The results are shown in Fig. 4. As seen from the plots, both ε' and ε'' undergo appreciable dispersion at frequencies 3–13 cm^{-1} in a wide range of temperatures.

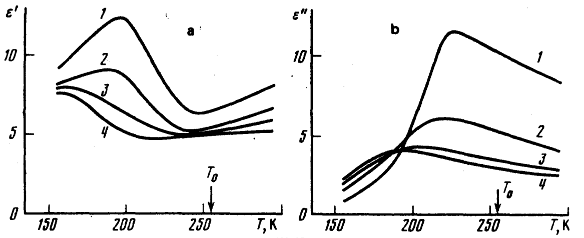

FIG. 4. Temperature dependences of the real (a) and imaginary (b) parts of the permittivity of Rochelle salt for the *a* axis at the frequencies 3.5 (1), 6.0 (2), 10.0 (3), and 12.7 (4) cm^{-1}.

The data on ε' and ε'' offer evidence that in the frequency range in which the measurements were made there is observed a broad absorption line with temperature-dependent parameters. In fact, the character of the frequency dependences of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ varies very strongly with temperature, and in a certain temperature region the functions $\varepsilon''(T)$ even exhibit a reversal in the sign of the dielectric dispersion: the $\varepsilon''(T)$ curves obtained for various frequencies intersect at temperatures 190–200 K. This peculiarity of the dielectric spectra, observed also by Poplavko *et al.*,[11] can be interpreted as indicating that at these temperatures the maximum of the temperature-unstable mode lies precisely in the frequency range 3–13 cm^{-1}.

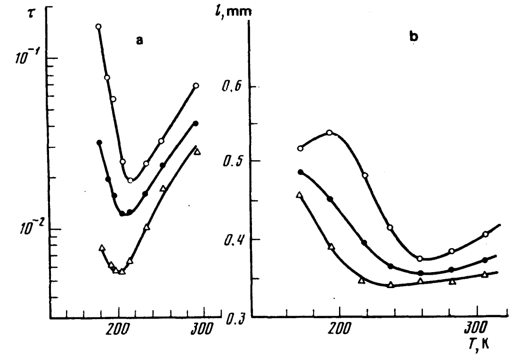

FIG. 3. Temperature dependences of the transmission coefficient (a) and of the compensator-mirror displacement (b) for a plane-parallel Rochelle salt plate 377 μm thick in the orientation **E** ∥ *a*, corresponding to the frequencies 6 (○), 10 (●), and 12.7 (△) cm^{-1}.

The data on $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$ were reduced by us on the basis of a simple dispersion relaxation model, i.e., the model used to describe the lower-frequency dielectric spectra[2]:

$$\varepsilon^*=\varepsilon_\infty+\frac{\Delta\varepsilon}{1+i2\pi\nu\tau}.$$

The three varied parameters of this model (the relaxation time τ, the dielectric contribution $\Delta\varepsilon$ of the relaxator, and the contribution ε_∞ of the high-frequency modes) were chosen by least squares at the individual temperature points to fit the experimental values of $\varepsilon^*=\varepsilon'-i\varepsilon''$ obtained at six frequencies. In the temperature range 180–230 K, i.e., where the characteristic frequencies of the investigated mode were close to those of the working band, we were able to choose τ, $\Delta\varepsilon$, and ε_∞ unambiguously without resorting to any assumptions whatever concerning τ, $\Delta\varepsilon$, and ε_∞. The average agreement between the calculated values of ε' and ε'' and the experimental data was of the order of 5%.

An accuracy of the same order can be obtained also for the spectra $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$ for temperatures above 230 K, but now by using additional data on the static permittivity.[2] In this case the following condition was added to the data-reduction program

$$\varepsilon_0=\Delta\varepsilon+\varepsilon_\infty$$

in order to eliminate the ambiguities in the values of $\Delta\varepsilon$ and τ determined by the described method when the dispersion region shifts towards a lower frequency relative to the working band, and the choice of the parameters becomes insensitive to the relation between $\Delta\varepsilon$ and τ. We note that in the temperature interval 180–230 K the cited relation between τ, $\Delta\varepsilon$, and ε_∞ is automatically satisfied with good accuracy.

Figure 5 shows, together with the data on τ obtained in Ref. 2 (dashed line), the results of our calculations of τ and $\Delta\varepsilon$. The corresponding values of ε_∞ in the temperature interval 180–250 K vary monotonically from 4.0 to 5.2. An analysis of the temperature dependence of these relaxator parameters indicates that the dispersion of $\varepsilon^*(\nu, T)$ observed at frequencies 3–13 cm^{-1} is a continuation, into the region of higher frequencies, of the same dispersion picture that was observed by Sandy and Jones[2] at relatively low frequencies.

As seen from Fig. 5, the results of the two studies, in which essentially different procedures were used to measure ε^*, are in good agreement. It must be mentioned, to be sure, that the values of ε_∞ assumed in the calculations differ greatly in the two cases. Sandy and Jones,[2] starting with the static values of ε' at low temperatures, assumed $\varepsilon_\infty = 9$, i.e., double the value used by us. Their choice of ε_∞, as already noted earlier,[4] is obviously incorrect: direct measurements, starting with 6 cm^{-1}, yield $\varepsilon' < 9$ at any temperature. In the case of relaxation dispersion, however, ε_∞ should be less than ε'. This error in the choice of ε_∞, however, is not significant at temperatures close to the phase transition point (225 K), inasmuch as under these conditions $\Delta\varepsilon$ becomes much larger than ε_∞ and assumes the decisive role in the model.

An interesting result of our investigation is, in our opinion, the observation of an unusual temperature dependence of τ in the low-temperature paraelectric region. The peculiarity of this dependence is that the quantity $1/2\pi\tau$ increases very rapidly with decreasing temperature, and this is patently different from the linear or near-linear variation of $1/2\pi\tau$ usually observed in ferroelectrics. The correct expression for Rochelle salt in the temperature interval 180–250 K is substantially different, viz.,

This behavior of $\tau(T)$ is apparently due to the fact that, in contrast to most ferroelectrics with a relaxation ferroelectric dispersion of $\varepsilon^*(\nu)$, in which the structure becomes disordered with increasing deviation of the temperature from the point of the phase transition in the paraphase, in Rochelle salt under similar conditions, on the contrary, an antipolar ordering of the ferroelectrically active subsystem of the crystal takes place.[1] The strong decrease of τ observed by us when the crystal is cooled means that the potential barrier that determines the motion of the ordered particles is several times lower at low temperatures than its value near the phase transition.

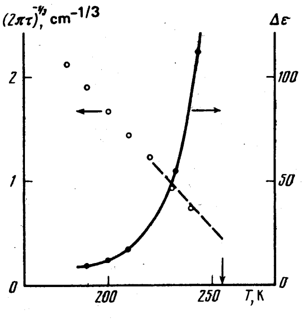

FIG. 5. Temperature dependences of the parameters of the relaxator that describes the dielectric dispersion of Rochelle salt. The arrow marks the phase-transition point 255 K.

We consider now the question of the existence in Rochelle salt at 212 K of the phase transition whose symptoms Ushatkin *et al.*[3] have taken to be the singularities they observed in the submillimeter dielectric spectra. The crucial point of their study[3] is the conclusion that the shift of the maxima on the $\varepsilon''(T)$ plots at higher temperatures (Fig. 4b) upon decrease of the working frequency of the radiation takes place only so long as $\nu > 9.7$ cm^{-1}. Starting with this frequency, the position of the maximum of $\varepsilon''(T)$ in the temperature scale ceases to change, and they are observed at $\nu < 9.7$ cm^{-1} at one and the same temperature, namely 212 K. This pattern of the behavior of $\varepsilon''(\nu, T)$ together with the data on $\varepsilon'(\nu, T)$ obtained in the same study indicate, in their opinion, that a temperature-unstable resonant mode exists in the crystal, and that its behavior points to the presence of an hitherto unknown phase transition in Rochelle salt at the point $T = 212$ K.

Our experimental results point to a different behavior of ε' and ε'': the maxima on the plots of $\varepsilon''(T)$ as well as of $\varepsilon'(T)$ shift continuously, with decreasing frequency, towards higher temperatures and exhibit no anomalies whatever at 212 K. This process is due furthermore, as noted above, to the same relaxation phenomena which were observed earlier in the microwave and the RF dielectric spectra.

In our opinion, the submillimeter data on the permittivity of Rochelle salt crystals reveal no specific singularities at 212 K, and the conclusions of Ushatkin *et al.*[3] must be regarded as incorrect.

Thus, our investigation of the dielectric spectra of Rochelle salt has shown that the singularities observed in the frequency dependences of the dielectric constant at submillimeter wavelengths for the *a* axis are a continuation of the fundamental ferroelectric dispersion previously investigated at higher frequencies. It retains its relaxation character in a wide temperature interval. The reciprocal of the relaxation temperature in the low-temperature antipolar phase has furthermore a cubic temperature dependence that is unusual for most ferroelectrics.

In conclusion, the authors thank N. M. Shagina for supplying the Rochelle salt samples used in the measurement.

[1] F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.

[2] F. Sandy and R. V. Jones, Phys. Rev. **168**, 481 (1968).

[3] E. F. Ushatkin, V. V. Meriakri, and Yu. M. Poplavko, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 557 (1974) [JETP Lett. **19**, 293 (1974)].

[4] V. N. Aleshekin, V. V. Meriakri, E. F. Ushatkin, and V. G. Tsykalov, Izv. AN SSSR, Ser. Fiz. **35**, 1924 (1971).

[5] V. P. Bystrov, N. A. Irisova, G. V. Kozlov, A. V. Kutsenko, B. A. Polos'yants, and S. A. Terekhin, Élektronnaya tekhnika, élektronika SVCh (Electronic Engineering, Microwave Electronics) **11**, 83 (1975).

[6] M. B. Golant, Z. G. Alekseenko, Z. S. Korotkova, L. A. Lukina, A. A. Negirev, O. P. Petrova, T. B. Rebrova, and V. S. Savel'ev, Prib. Tekh. Eksp. No. 3, 231 (1969).
[7] N. A. Irisova, Vestnik AN SSSR **10**, 63 (1968).
[8] A. A. Volkov, G. V. Kozlov, and S. P. Lebedev, Radiotekh. i Élektron. **24**, 1405 (1979).
[9] A. A. Volkov, G. V. Kozlov, S. P. Lebedev, and A. M. Prokhorov, FIAN Preprint No. 23, 1980.
[10] G. V. Kozlov, Prib. Tekh. Eksp. 4, 152 (1971).
[11] Yu. M. Poplavko, V. V. Meriakri, L. P. Perverzeva, V. N. Aleshkin, and V. I. Molchanov, Fiz. Tverd. Tela (Leningrad) **15**, 2515 (1973) [Sov. Phys. Solid State **15**, 1672 (1974)].

Translated by J. G. Adashko

Nuclear magnetic relaxation and spin diffusion in the local fields of paramagnetic centers

V. A. Atsarkin and V. V. Demidov

Institute of Radio Engineering and Electronics, USSR Academy of Sciences

(Submitted 3 April 1980)
Zh. Eksp. Teor. Fiz. **79**, 1438–1450 (October 1980)

It is shown that the current theory of nuclear relaxation in solid dielectrics should be modified to take into account the spatial distribution of the paramagnetic impurity spin-flip rates. This results in some new dependences of the nuclear relaxation time on the inhomogeneous EPR broadening, on the magnetic field strength, etc. These predictions are confirmed experimentally in the case of relaxation of ^{183}W nuclei in ZnWO$_4$:Cr^{+3} crystals. The existence of effective nuclear spin diffusion under the conditions of a strong "diffusion barrier" is confirmed here for the first time ever with the same crystals. The results are shown to agree quantitatively with the theory of spin diffusion induced by paramagnetic centers, with the multiexponential nature of the electronic correlation function for $S > 1/2$ playing the decisive role.

PACS numbers: 76.60.Es

INTRODUCTION

It is well known that, as a rule, nuclear magnetic relaxation in solid dielectrics is due to dipole coupling of nuclear spins in the matrix with electron spins of paramagnetic impurities, the nuclear spin diffusion playing a substantial role (see, for example Refs, 1 and 2). In the last decade significant progress has been achieved in the study of these phenomena, mainly as a result of a consistent allowance for the role of electronic spin-spin interactions regarded as a quasi-equilibrium "electronic spin-spin reservoir" (ESSR).[3-5] At the same time, a deeper understanding of the physical mechanism of nuclear relaxation has generated new problems, three of which are the subject of this paper. These are: first, the question of the rate of transfer of nuclear Zeeman energy of the ESSR; second, the question (closely connected with the first) of the characteristic times of the mutual electron spin flips ("flip-flops"), particularly under conditions of inhomogeneous broadening of the EPR line; third, the problem of induced nuclear spin diffusion in the strong local fields of paramagnetic centers. In the first section of this paper, we consider several aspects of the theory of these phenomena; in the second section we present results of experiments carried out on ZnWO$_4$ crystals doped with paramagnetic Cr^{+3} ions.

1. THEORETICAL BASIS

1.1 Transfer of nuclear Zeeman energy to the electronic spin–spin reservoir (ESSR)

As is well known, direct relaxation of the nuclear spin I_i falling within the "sphere of influence" of the nearest electron spin S_j occurs under the action of the fluctuating local magnetic field generated by the z-component S_{jz} of the electronic spin (the z axis is directed along the external magnetic field **H**). Averaged over all angles, the rate of this relaxation is

$$(\tau_{ij}^{\text{dir}})^{-1}=C_j r_{ij}^{-6}, \tag{1}$$

where r_{ij} is the separation between I_i and S_j and

$$C_j={}^3/_5(\hbar\gamma_S\gamma_I)^2 J_j(\omega), \tag{2}$$

where γ_S, γ_I are the gyromagnetic ratios of the spins S and I, $\omega=\gamma_1 H$, and

$$J_j(\omega)=(\langle S_z^2\rangle-\langle S_z\rangle^2)\frac{2\tau_{cj}}{1+\omega^2\tau_{cj}^2} \tag{3}$$

is the Fourier transform of the correlation function

$$G_j(t)=\langle S_{jz}(0)S_{jz}(t)\rangle, \tag{4}$$

the variable part of which is assumed[1,2] to be exponential in the correlation time τ_{cj}.

If the function $G_j(t)$ is due to electronic spin-phonon interaction (as has usually been considered in earlier nuclear relaxation theories), then the Zeeman energy of the nucleus I_i is transferred directly to the lattice, and all τ_{cj} are the same and equal to the electronic spin-lattice relaxation time τ_{1e}. In this case, the subscript j in Eqs. (2)–(4) may be omitted and the parameter C, common to all the nuclei, is used in the calculation of the observable nuclear spin-lattice relaxation time τ_{1n}.

A more complicated situation arises when the correlator of Eq. (4) is due to electronic spin-spin interactions, leading to a flip-flop of the spins S. The first

0038-5646/80/100726-07$02.40