SOVIET PHYSICS JETP VOLUME 32, NUMBER 4 APRIL, 1971

INVESTIGATION OF THE ANOMALOUS ELECTRIC SENFTLEBEN EFFECT

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Submitted March 26, 1970

Zh. Eksp. Teor. Fiz. 59, 1067–1079 (October, 1970)

We present the results of a theoretical and experimental investigation of the anomalous Senftleben effect in a number of polar gases. We study the theoretical expressions describing the dispersion (frequency dependence) of the effect assuming that the change of the thermal conductivity is due to the precession of the molecules in the external field, and that the positive part of the change of the thermal conductivity is in addition connected with the presence in the gas of collisions, for which the probabilities of the direct and inverse transitions are different. The anomalous effect was observed experimentally in the polar gases C_2H_5CN, C_2H_3CN, CH_3NO_2. It is shown that the relative change of ϵ, the coefficient of thermal conductivity of these gases, depends on the field E and on the pressure p via the ratio E/p. Results are presented of the investigation of the thermal conductivity of CH_3CN and $CHCl_3$ in an alternating electric field. It is observed that the dispersion of the anomalous Senftleben effect in CH_3CN gas is determined by the ratio f/p in the pressure range 0.07–1 mm Hg, in the frequency range 50 Hz–5 MHz, and at field amplitudes up to 100 V/cm, a fact that does not agree with the prediction of the theory based on the usual precession mechanism of the effect.

INTRODUCTION

It is known[1-10] that the transport coefficients of molecular gases decrease in magnetic and electric fields (the magnetic and electric Senftleben effects). The observable relative changes of the transport coefficient, for example of the thermal-conductivity coefficient ($\epsilon = \Delta\kappa/\kappa_0$) depend on the field (H or E) and on the pressure (p) via the ratio H/p (E/p). The $\epsilon(H/p)$ (or $\epsilon(E/p)$) function is monotonic and tends to a value ϵ_{sat} ($\epsilon_{sat} < 0$) with increasing ratio H/p (E/p).

It was observed in[9] that the $\epsilon(E/p)$ dependence observed in the gas CH_3CN has a nonmonotonic (anomalous) character. It was established there that ϵ in CH_3CN reaches a maximum value $\epsilon_{max} = 5 \times 10^{-4}$ at E/p = 280 V/cm-mm Hg and reverses sign at E/p = 380 V/cm-mm Hg. An analogous change of the thermal-conductivity coefficient of CH_3CN gas was observed in a magnetic field in[11].

The increase ($\epsilon > 0$) of the thermal conductivity coefficient of the gases CH_3CN, C_2H_5CN, C_6H_5CN in an electric field was noticed earlier[5,12]. The experimental procedure used by de Groot et al.[12] has made it possible to observe thermal-conductivity changes corresponding only to the initial section ($\epsilon < \epsilon_{max}$) of the $\epsilon(E/p)$ dependence. The obtained dependence was correctly extrapolated in[12] by means of a theoretical curve that yields in the limit as $E/p \to \infty$ a positive value of ϵ_{sat}.

A theory explaining the anomalous behavior of the transport coefficients of molecular gases in magnetic and electric fields was proposed by Levi, McCourt, and Tip[13,14]. They used a precession mechanism of the effect, namely, the change (increase or decrease) of the transport coefficient is due to the change (decrease or increase, respectively) of the cross section of the nonspherical molecules as a result of their precession in the field, the precession being due to the interaction of the magnetic (rotating) moment with the magnetic field, or of the dipole moment with the electric field. When the quantum equation is solved, they introduce a non-self-adjoint collision operator. In the high-temperature limit, when the rotation of the gas molecules can be described classically, such an operator describes collisions for which the probabilities of the direct and inverse transitions are not equal to each other. The presence of such collisions in the gas leads, as shown by a solution of the kinetic equation, to an increase of the thermal-conductivity coefficient in the external field, whereas the collisions described by a self-adjoint operator lead to its decrease.

The experimentally observed[9,11] $\epsilon(E/p)$ and $\epsilon_\perp(H/p)$ dependences for the CH_3CN gas ($\epsilon = (1/2)(\epsilon_\parallel + \epsilon_\perp)$, where $\epsilon_\parallel$ and $\epsilon_\perp$ are quantities corresponding to conditions when the field is parallel and perpendicular to the gradient of the temperature), are the sums of competing changes of the thermal-conductivity coefficient and are described satisfactorily by the theory proposed in[13,14].

The role in transport phenomena of collisions for which the probabilities of the direct and inverse transitions are not equal to each other have hardly been investigated. Since the anomalous behavior of the coefficients of thermal conductivity (the anomalous Senftleben effect) is directly connected with the presence of such collisions in the gas, further investigations of the anomalous Senftleben effect are of interest.

In this paper we present the results of a further investigation of the anomalous Senftleben effect. In Sec. 1, below, we present a theory of the dispersion (frequency dependence) of the anomalous effect in an alternating field. The Senftleben effect of dispersion was first observed experimentally with the thermal conductivity of NF_3 gas as an example[15], and the theory was developed in[16]. Investigations of the dispersions of the Senftleben effect have made it possible to confirm the precession mechanism of this effect, and also to determine the characteristic frequencies of the collisions responsible for the observed changes in the thermal-conductivity coefficient in an external field.

In Sec. 2 we describe certain results of experiments in which the anomalous Senftleben effect was observed in the gases C_2H_5CN, C_2H_3CN, CH_3NO_2. The results of the experimental investigation of the thermal conductivity of the polar gases CH_3CN and $CHCl_3$ in an alternating field and their discussion are given in Sec. 3.

1. THEORY

Let us consider the dispersion of the anomalous Senftleben effect in polar gases in an alternating electric field $\mathbf{E} = E_0 \cos\omega t$. We shall use the classic kinetic equation for gases with rotational degrees of freedom, introduced in[2]. In the case of a polar gas with molecules of the symmetrical-top type, the equation is

$$\frac{\partial\chi}{\partial t} + N + \gamma\cos\omega t\,\frac{\partial\chi}{\partial\varphi_M} = -\hat{I}\chi, \tag{1}$$

where $f = f_0(1 + \chi)$ is the distribution function, $\gamma = dE_0\sigma/M$, $\sigma = \cos(\mathbf{dM})$, d is the dipole moment, φ_M is the angle variable in the space of the momenta M, and N is the inhomogeneous part of the kinetic equation and is given in[2]. Eq. (1) is written in a spherical coordinate system, in which the direction of the z axis coincides with the direction of the field **E**. The third term on the left in (1) takes into account the change of the non-equilibrium distribution function χ as a result of the precession of M in the electric field, due to the interaction of the dipole moment with the field.

The linearized collision operator in (1) is given by

$$\hat{I}\chi = \int f_{01}[(\chi + \chi_1)W - (\chi' + \chi_1')W']\,d\Gamma_1'\,d\Gamma_1\,d\Gamma'; \tag{2}$$

Here $d\Gamma = dv\,dM\,d\sigma$ is the phase volume, **v** the velocity of the molecules, and W and W' are the scattering probabilities:

$$\begin{gathered} W = W(\mathbf{v}, \mathbf{M}, \sigma;\ \mathbf{v}_1, \mathbf{M}_1, \sigma_1 \to \mathbf{v}', \mathbf{M}', \sigma';\ \mathbf{v}_1', \mathbf{M}_1', \sigma_1'), \\ W' = W'(\mathbf{v}', \mathbf{M}', \sigma'; \mathbf{v}_1', \mathbf{M}_1', \sigma_1' \to \mathbf{v}, \mathbf{M}, \sigma; \mathbf{v}_1, \mathbf{M}_1, \sigma_1). \end{gathered} \tag{3}$$

The prime denotes the dependence of the functions on the v, M, and σ of the molecule after the collision, and the subscript unity denotes the dependence on the same parameters of the partner molecule in the collision.

It was noted above that the anomalous behavior of the thermal-conductivity coefficient can be described by introducing a non-self-adjoint collision operator[13] into the quantum-kinetic equation. As follows from[13], the absence of inverse collisions, in other words, non-satisfaction of the equation

$$W = W' \tag{4}$$

is equivalent to the non-self-adjoint property of the quantum collision operator. If we accept this statement, then for a theoretical description of the dispersion of the anomalous Senftleben effect it is necessary to solve a classical kinetic equation, in which the collision integral takes into account the presence of collisions for which $W \neq W'$.

We shall solve the kinetic equation (1) by the perturbation-theory method developed in[2]. We subdivide the collision operator (2) into two parts

$$I = I^{(0)} + \varepsilon I^{(1)}, \tag{5}$$

where ϵ is a small parameter. As noted eariler in[2], and also in[17], such a breakdown is ambiguous and can therefore be carried out in such a way as to make $I^{(0)}$ an operator that is diagonal in the functional space ψ_n:

$$\begin{gathered} I^{(0)}\psi_n = \lambda_n\psi_n, \qquad \lambda_n = \lambda_{l_1 r_1 l_2 r_2 s}, \\ \psi_n = \sum_{m_1+m_2=m} C^{lm}_{l_1 m_1 l_2 m_2} Y_{l_1 m_1}(\mathbf{v})\,Y_{l_2 m_2}(\mathbf{M})\,T^{l_1}_{r_1}(v^2)\,L^{l_2}_{r_2}(M^2)\,\varphi(\sigma). \end{gathered} \tag{6}$$

In the general case the values of λ_n are determined by the set of numbers $l_1 r_1 l_2 r_2 s$.

The breakdown of the collision operator $\hat{I}^{(0)}$ (5) can be set in correspondence with the equality

$$W = W_{(0)} + \varepsilon W_{(1)}, \tag{7}$$

where $W_{(0)}$ satisfies the relation

$$W_{(0)} = W'_{(0)}. \tag{8}$$

In the function $W_{(1)}$ it is possible to separate two parts, W_s and W_a, which are respectively symmetrical and antisymmetrical against permutation of the variables v, M, and σ of the colliding molecules before and after the collision:

$$\begin{gathered} W_{(1)} = W_s + W_a, \\ W_s = {}^1\!/_2(W_{(1)} + W_{(1)}'), \qquad W_a = {}^1\!/_2(W_{(1)} - W_{(1)}'), \end{gathered} \tag{9}$$

W_s and W_a have the following properties:

$$W_s = W_s', \qquad W_a = -W_a'. \tag{10}$$

In the case of a gas whose molecules are not optical isomers, it follows from the principle of detailed balancing (invariance of the number of collisions in static equilibrium relative to inversion transformations (index s) and time reversal (index t)[18]) that

$$W_s' = W_s^{ts}, \qquad W_a' = -W_a^{ts}. \tag{11}$$

In accordance with (9) and (10), the operator $\hat{I}^{(1)}$ takes the form

$$\hat{I}^{(1)} = \hat{J}_s + \hat{J}_{sa} + \hat{J}_a. \tag{12}$$

The matrix elements of the operators $\hat{J}_s$, $\hat{J}_{sa}$, and $\hat{J}_a$ in the space ψ_n are written in the form

$$\begin{gathered} \langle\psi_m, \hat{J}_s\psi_n\rangle = \frac{1}{4}\int f_{01}[(\psi_m + \psi_{1m})^* - (\psi_m' + \psi_{1m}')^*][(\psi_n + \psi_{1n}) \\ - (\psi_n' + \psi_{1n}')]W_s\,d\Gamma\,d\Gamma_1\,d\Gamma_1'\,d\Gamma', \\ \langle\psi_m, \hat{J}_{sa}\psi_n\rangle = \frac{1}{4}\int f_{01}[(\psi_m + \psi_{1m})^*(\psi_n + \psi_{1n}) - (\psi_m' + \psi_{1m}')^* \cdot \\ \times (\psi_n' + \psi_{1n}')]W_a\,d\Gamma\,d\Gamma_1\,d\Gamma'\,d\Gamma_1', \\ \langle\psi_m, \hat{J}_a\psi_n\rangle = \frac{1}{4}\int f_{01}[(\psi_m + \psi_{1m})^*(\psi_n' + \psi_{1n}') - \\ - (\psi_m' + \psi_{1m}')^*(\psi_n + \psi_{1n})]W_a\,d\Gamma\,d\Gamma_1\,d\Gamma'\,d\Gamma_1' \end{gathered} \tag{13}$$

and, when account is taken of (9)—(11), have the following properties:

$$\begin{gathered} \langle\psi_m, \hat{J}_s\psi_n\rangle = \langle\psi_n, \hat{J}_s\psi_m\rangle, \quad \langle\psi_m, \hat{J}_{sa}\psi_n\rangle = \langle\psi_n, J_s\,\psi_m\rangle, \\ \langle\psi_m, \hat{J}_a\psi_n\rangle = -\langle\psi_n, \hat{J}_a\psi_m\rangle. \end{gathered} \tag{14}$$

From the fact that the operators $\hat{J}_{sa}$ and $\hat{J}_a$ are scalar and from (11) we get the following selection rules:

$$\langle n'|J_{sa}|n\rangle \neq 0,$$

If $l = l'$, $m = m'$, $l_2' - l_2$ is odd, $l_1' - l_1$ is even, and

$$\langle n'|\hat{J}_a|n\rangle \neq 0,$$

if $l' = l$, $m' = m$, $l_2' - l_2$ is odd, and $l_1' - l_1$ is even.

The selection rules for the operator $\hat{J}_s$ coincide with those obtained in[2], The solution of the kinetic equation (1) with allowance for the breakdown (5) and of equalities (12) and (13) can be obtained by repeating the procedure of[16]. The change of the thermal-conductivity coefficient then takes the form

$$\Delta\varkappa_{ik} = \delta_{ik}\Delta\,\mathrm{Re}\,C_{11,11} + e_i e_k(\Delta C_{10,10} - \Delta\,\mathrm{Re}\,C_{11,11}),$$

$$\Delta C_{lml'm'} = \sum_{nn'} B_n^{lm} B_{n'}^{l'm'} (\lambda_n)^{-1}$$

$$\times\left\langle \psi_n, \sum_{k=1}^{\infty} \frac{\omega^2 k^2}{\omega^2 k^2 + \lambda_n^2} J_k^2\left(\frac{m_2\gamma}{\omega}\right) \psi_{n'} \right\rangle \tag{15}$$

$$B_n^{lm} = \sum_{n_0} (\lambda_{n_0})^{-1} \langle A_{lm}, \psi_{n_0}\rangle \langle n_0 | \hat{I}^{(1)} | n\rangle. \tag{16}$$

Here $n_0 = \{lm, l_1 0, r_1 r_2, 0\}$, and J_k is a Bessel function.

Let us consider a non-spherical scattering model, when only the matrix elements for the operator $\hat{J}_c$ in transitions to states with $n_1 = \{lm, 12, 00, 0\}$ differ from zero, and for the operators $\hat{J}_{sa}$ and $\hat{J}_a$ they differ from zero only for transitions to the states with $n_2 = \{lm, 11, 00, 0\}$. In the case of the operator $\hat{J}_s$ this model coincides with the model introduced by Kagan and Maksimov[2], and corresponds to the approximation used by Levi and McCourt[13] in the solution of the kinetic equation by a variational method (the non-equilibrium distribution function is sought in the form of a finite series in irreducible tensors made up of the components of the velocity and angular momentum vectors, and the highest-order term in M contains a second-rank tensor). Expression (15) for this model has the form

$$\begin{aligned}
\Delta C_{lml'm'} &= \Delta C^{-}_{lml'm'} + \Delta C^{+}_{lml'm'},\\
\Delta C^{-}_{lml'm'} &= -\sum_{n_0 n_0'} (\lambda_{n_0}\lambda_{n_0'})^{-1} \langle A_{lm}, \psi_{n_0}\rangle \langle \psi_{n_0'}, A_{l'm'}\rangle (\lambda_{n_1})^{-1}\cdot\\
&\times \langle n_0|J_c|n_1\rangle \langle n_0'|J_s|n_1\rangle \left\langle \psi_{n_1}, \sum_{k=1}^{\infty} \frac{\omega^2 k^2}{\omega^2 k^2 + \lambda_{n_1}^2} J_k^2\left(\frac{m_2\gamma}{\omega}\right) \psi_{n_1} \right\rangle\\
\Delta C^{+}_{lml'm'} &= \sum_{n_0 n_0'} (\lambda_{n_0}\lambda_{n_0'})^{-1} \langle A_{lm}, \psi_{n_0}\rangle \langle \psi_{n_0'}, A_{l'm'}\rangle\cdot\\
&\times [\langle n_0|\hat{J}_a|n_2\rangle \langle n_0'|\hat{J}_a|n_2\rangle - \langle n_0|\hat{J}_{sa}|n_2\rangle \langle n_0'|\hat{J}_{sa}|n_2\rangle]\cdot\\
&\times (\lambda_{n_2})^{-1} \left\langle \psi_{n_2}, \sum_{k=1}^{\infty} \frac{\omega^2 k^2}{\omega^2 k^2 + \lambda_{n_2}^2} J_k^2\left(\frac{m_2\gamma}{\omega}\right) \psi_{n_2} \right\rangle.
\end{aligned} \tag{17}$$

Expression (17) together with (15) gives the sought dependence of the thermal-conductivity tensor on the amplitude, the field frequency, and the pressure, inasmuch as $\gamma \propto E_0$ and $\lambda_{n_1}, \lambda_{n_2} \propto p$. The quantity $\Delta C^{-}_{lml'm'}$ describes the dispersion of the negative change of the thermal conductivity.

It is seen from (17) that the positive change of the thermal-conductivity coefficient is connected with the presence of collisions for which $W \neq W'$, and takes place only if

$$(\langle n_0|\hat{J}_a|n_2\rangle \langle n_0'|\hat{J}_a|n_2\rangle - \langle n_0|\hat{J}_{sa}|n_2\rangle \langle n_2|\hat{J}_{sa}|n_2\rangle) > 0.$$

When $\omega \to 0$, the expression (17) together with (15) gives the dependence of the anomalous effect on the ratio E/p in a constant field. The dependence obtained in this manner coincides with that given in[14].

An analysis of relations (17) shows that the dependences of the dispersion of the positive and negative changes of the thermal conductivity on the parameters γ and λ_n differ little from each other. This is due to the fact that in the approximate integration in (17) the values of M and σ in γ ($\gamma = dE_0\sigma/M$) can be replaced by certain mean values, since the integration is carried out with a wave function of the type $\sigma M^p \exp(-M^2 - k\sigma^2)$ (p is equal to 6 or 4). It follows from this, in particular, that in the region of weak fields, when $\gamma < \lambda$, the dispersion of the positive change of the thermal conductivity, like the dispersion of the Senftleben effect[15], is determined by the parameter ω/λ_{n_2}, and consequently by the ratio ω/p. Such a behavior of the dispersion can be explained from simple physical considerations: if we start from the precession mechanism of the effect, at field frequencies larger than the precession frequency, the end of the vector executes rotational oscillations with a period $2\pi/\omega$. It can therefore be stated that only the ratio of the two temporal parameters—the field frequency and the collision frequency—determines the dispersion of the effect.

An analysis of expressions (17) and numerical calculations show also that in the case of a large field amplitude, when $\gamma \gg \lambda_{n_1}, \lambda_{n_2}$, the quantities $\epsilon_{\omega+}/\epsilon_{0+}$ and $\epsilon_{\omega-}/\epsilon_{0-}$ ($\epsilon_{\omega+}$, ϵ_{0+}, $\epsilon_{\omega-}$, ϵ_{0-} are the positive and negative parts of ϵ at the frequencies ω and zero, respectively; $\epsilon = \frac{1}{2}(\epsilon_{\parallel} + \epsilon_{\perp})$) is determined by the ratio ω/γ (ω/E_0), whereas the dependences of $\epsilon_{\omega+}/\epsilon_{0+}$ and $\epsilon_{\omega-}/\epsilon_{0-}$ on λ_n, and consequently on p, are weak.

This result can also be explained by starting from the precession mechanism: if the precession frequency is much larger than the collision frequency, then an appreciable change in the path traversed as a result of the precession by the end of the vector M with increasing field frequency will take place at field frequencies larger than the precession frequency. Therefore an appreciable change of ϵ should likewise be observed at field frequencies larger than the precession frequency.

2. ANOMALOUS SENFTLEBEN EFFECT IN THE GASES C_2H_5CN, C_2H_3CN, CH_3NO_2 IN A CONSTANT ELECTRIC FIELD

The measurements whose results are given below were made at room temperature with apparatus analogous to that described in[6,8,9] in the pressure range p = 0.1–2 mm Hg and in fields E up to 400 V/cm. The measured quantity was $\epsilon = \frac{1}{2}(\epsilon_{\parallel} + \epsilon_{\perp})$ ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the values of ϵ under conditions when the field is parallel and perpendicular to the temperature gradient). The absolute values of ϵ were obtained from calibration experiments using the known effect in $CHCl_3$[9], using the procedure described in[8,9]. The relative error in the determination of ϵ did not exceed 20% in all the measurements.

Figs. 1–3 show plots of ϵ(E/p) obtained for the gases C_2H_5CN, C_2H_3CN, CH_3NO_2 at different pressures. It is seen from the figures that within the limits of measurement error, ϵ depends on the field and on the pressure via the ratio E/p for all the investigated gases. At small E/p, ϵ is positive, and when this ratio increases it goes through a maximum ($\epsilon = \epsilon_{max}$). Further increase of this ratio leads to a reversal of the sign of ϵ. The values of ϵ_{max}, and also of $(E/p)_{max}$ and $(E/p)_0$, at which ϵ reaches the maximum value and is equal to zero are listed in the table.

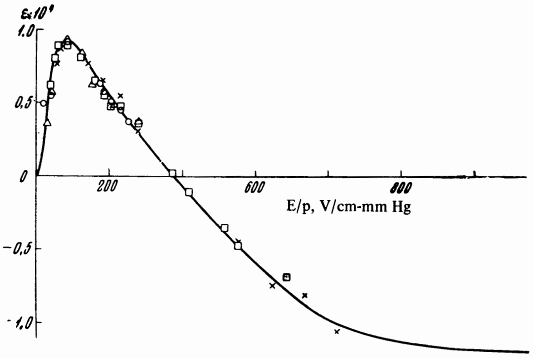

FIG. 1. Plot of $\epsilon(E/p)$ for the gas C_2H_5CN. The experimental points correspond to the following pressures (in millimeters of mercury): X–p = 0.33, □–0.66, Δ–1.00, O–1.33. The solid line corresponds to the theoretical relation (18).

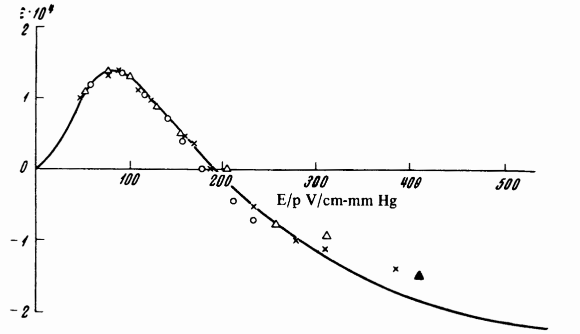

FIG. 2. Plot of $\epsilon(E/p)$ for the gas C_2H_3CN. The experimental points correspond to the following gas pressures (mm Hg): Δ–p = 0.60, X–p = 1.00, O–p = 1.33. The solid line corresponds to the theoretical relation (18).

The solid curves in the figures are the theoretical plots obtained from expressions derived in[14]:

$$\varepsilon = \varepsilon_+ + \varepsilon_-,$$
$$\varepsilon_+ = {}^3/_2\psi_+ c_1, \quad \varepsilon_- = -\psi_-(2c_2 + c_3),$$
$$c_1 = \frac{\xi'^2}{1+\xi'^2} \quad c_2 = \frac{\xi^2}{1+\xi^2} + \frac{8\xi^2}{1+4\xi^2}, \quad c_3 = \frac{\xi^2}{1+\xi^2} - \frac{8\xi^2}{1+4\xi^2},$$
$$\xi' = \Omega / \nu_+, \quad \xi = \Omega / \nu_-; \tag{18}$$

Here Ω is the average precession frequency, ν_+ and ν_- are the characteristic collision frequencies, $\nu_+ \sim \lambda_{n_1}$, $\nu_- \sim \lambda_{n_2}$ (see (17)), ψ_+ and ψ_- (larger than zero) determine respectively the limits of the values of the positive (ϵ_+) and negative (ϵ_-) changes of the thermal-conductivity coefficient. Expressions (18) give $\epsilon(E/p)$ values that coincide, as noted above, with those obtained from (17) in the limit as $\omega \to 0$.

As seen from the figures, the experimental data coincide with the theoretical relations within the limits of measurement errors. The table lists the values of the unknown parameters ψ_+, ψ_- and ν_-/ν_+ corresponding to the theoretical curves of Figs. 1–3.

In the review[10] it is indicated that de Groot et al. observed an increase of the coefficient of thermal conductivity of the gases CH_3NO_2 and C_2H_5CN. As in[12], these authors carried out their investigation in the electric field of a cylindrical capacitor. At the employed experiment geometry, they succeeded in observing a change in the thermal conductivity of these gases, corresponding only to the initial ($\epsilon_\perp < \epsilon_{max}$) sections of the $\epsilon_\perp(E/p)$ curve. The experimentally obtained plot of $\Delta T/T$ against V/p (T, ΔT–temperature of the pickup filament and its change when the field is turned on, V–voltage between the chamber wall and the filament) was incorrectly extrapolated by de Groot et al.[10] by means of a theoretical curve that gave a positive value of ϵ_{sat}.

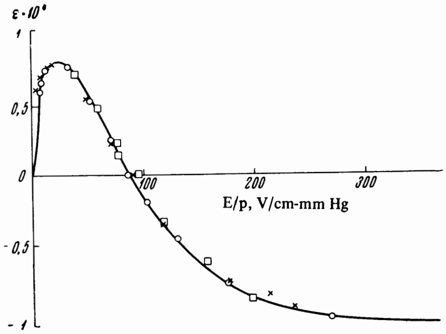

FIG. 3. Plot of $\epsilon(E/p)$ for CH_3NO_2 gas. The experimental points correspond to the following pressures (mm Hg): □–p = 0.80, X–1.33, O–1.80.

Gas	d, dB	$10^4\epsilon_{max}$	$(E/p)_{max}$, $\frac{V/cm}{mm\ Hg}$	$(E/p)_0$, $\frac{V/cm}{mm\ Hg}$	$10^4\psi_+$	$10^4\psi_-$	ν_-/ν_+
C_2H_5CN	3,6	0,92	90	184	1,92	3,17	6,35
C_2H_3CN	3,89	1,42	82	370	4,2	7.5	3,73
CH_3NO_2	3.5	0.82	23	89	1,85	3.1	5.75

As follows from[13,14], the positive part ϵ_+ of the change of the thermal-conductivity coefficient is connected with the existence of anisotropy of the nonequilibrium distribution function χ in the moment space of the molecules, described by the vector term (M) in the expansion of χ in the irreducible tensors made up of the components of M, whereas ϵ_- is connected with the anisotropy of χ described in the M space by a divergence-free tensor of second rank. Using the formalism of the Senftleben-effect theory developed in[2], when the function χ is sought in the form of an expansion in the eigenfunctions of an "ideal" collision operator, it can be stated that ϵ_+ is connected with the anisotropy of χ described by the eigenfunction of this operator

$$\psi_1 \approx \sum_{\substack{m_1+m_2=m \\ m_2\neq 0}} C^{1m}_{1m_1 1m_2} \mathbf{Y}_{1m_1}(\mathbf{v}) \mathbf{Y}_{1m_2}(\mathbf{M}),$$

and ϵ_- with the anisotropy described by the function

$$\psi_2 \sim \sum_{\substack{m_1+m_2=m \\ m_2\neq 0}} C^{1m}_{1m_1 2m_2} Y_{1m_1}(\mathbf{v}) Y_{2m_2}(\mathbf{M})$$

(see the model of nonspherical scattering considered in Sec. 1).

The precession of polar molecules in an electric field leads to a change of the anisotropy in momentum space. Inasmuch as the molecule scattering cross section depends on the angle between the angular momentum and the relative velocity, the coefficient of thermal conductivity of the polar gas changes as a result in an electric field. The limiting values (ψ_+ and ψ_-) of the quantities ϵ_+ and ϵ_- as $E/p \to \infty$ (see (18)) are proportional to the squares of the matrix elements of the perturbed collision operator (the deviation of the total collision operator from the "ideal" one) describing the collisions that change the distribution χ in the M space from a spherically symmetrical one to the anisotropic one described by the functions ψ_+ and ψ_2.

It should be noted that the perturbed collision operator causing the "transitions" between the spherically symmetrical distribution and the distribution corresponding to the function ψ_1 describes collisions for which the probabilities of the direct and inverse transitions are different. It follows therefore that the quantities ψ_+ and ψ_- are connected precisely with this kind of difference in the molecule scattering. The data listed in the table show that for the investigated gases the values of ψ_+ and ψ_- are of the same order of magnitude, and therefore the contributions of the terms of the expansion of χ in terms of the functions ψ describing the indicated different types of anisotropy are comparable.

3. DISPERSION OF THE ANOMALOUS SENFTLEBEN EFFECT WITH THE THERMAL CONDUCTIVITY OF CH_3CN GAS AS AN EXAMPLE

The employed experimental setup and measurement procedure are analogous to those described in[6,8,9,15]. The measured quantity in these experiments was also $\epsilon = \frac{1}{2}(\epsilon_{\parallel} + \epsilon_{\perp})$. The experiments were performed at room temperature in the range of pressures p = 0.07–1 mm Hg and in fields up to 100 V/cm, in the frequency interval from 50 Hz to 5 MHz. The relative error in the determination of ϵ did not exceed 15% in all the measurements.

Fig. 4 shows experimental plots of $\epsilon(f/p)$ ($\omega = 2\pi f$) in CH_3CN gas, obtained at different E_0/p. As seen from the figure, ϵ is a constant quantity ($\epsilon = \epsilon_{LF}$) at a given E_0/p up to $f/p \approx 10$ kHz/mm Hg. Further increase of the ratio f/p leads to a noticeable decrease of ϵ. Starting with $f/p \approx 500$ kHz/mm Hg, ϵ becomes a constant quantity ($\epsilon = \epsilon_{HF}$) in the entire investigated region $f/p > 500$ kHz/mm Hg.

Let us explain the physical meaning of the experimentally obtained quantities ϵ_{LF} and ϵ_{HF}.

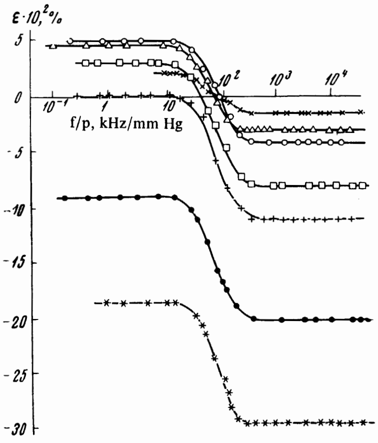

FIG. 4. Plot of $\epsilon(f/p)$ for the gas CH_3CN: X–E/p = 80.5, (E is in V/cm, and p is in mm Hg) (E = 80.5, p = 1), Δ–E/p = 154 (E = 77, p = 0.5). O–E/p = 160 (E = 40.5, p = 0.25 mm), □–E/p = 308 (E = 40, p = 0.13), +–E/p = 385 (E = 77, p = 0.20), ●–E/p = 592 (E = 77, p = 0.13), *–E/p = 1000 (E = 70, p = 0.07).

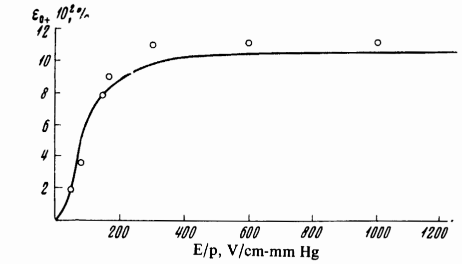

FIG. 5. Plot of $\epsilon_{0+}(E/p)$ for the gas CH_3CN. The solid line corresponds to the theoretical relation (18).

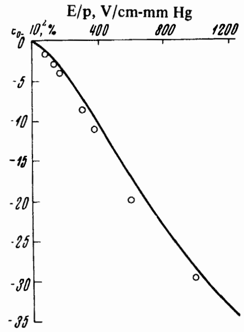

FIG. 6. The same as Fig. 5 but for $\epsilon_{0-}(E/p)$.

Expressions (18) obtained in[14] described the relative change of the coefficient of thermal conductivity in a constant field in the form of a sum of two effects, positive (ϵ_{0+}) and negative (ϵ_{0-}). The unknown parameters ψ_+, ψ_+, ν_-/ν_- in (18) were determined from experiments in a constant electric field and are given in[9]. They have the following values: $\psi_+ = 6.8 \times 10^{-4}$, $\psi_- = 2.3 \times 10^{-4}$ and $\nu_-/\nu_+ = 20$. Thus, expressions (18) give for a given gas the theoretical dependences of ϵ_{0+} and ϵ_{0-} on the ratio E/p. It is obvious that the experimentally obtained ϵ_{LF} and ϵ_{HF} should be connected with the quantities ϵ_{0+} and ϵ_{0-}.

Figs. 5 and 6 show a comparison of the experimentally obtained values of $\epsilon_{LF} - \epsilon_{HF}$ and ϵ_{HF} obtained for different E_0/p, with the theoretical plots of $\epsilon_{0+}(E/p)$, and $\epsilon_{0-}(E/p)$ (continuous curves). As seen from the figures, the measured values of $\epsilon_{LF} - \epsilon_{HF}$ and ϵ_{HF} coincide, within the limits of experimental error, with the theoretical ones. It follows therefore that apparently the difference $\epsilon_{LF} - \epsilon_{HF}$ is apparently the positive component of the relative change of the thermal conductivity of CH_3CN, and consequently

$$\varepsilon_{LF} - \varepsilon_{LF} = \varepsilon_{0+}, \tag{19}$$

and ϵ_{HF} is the negative component of the quantity in this gas:

$$\varepsilon_{HF} = \varepsilon_{0-}. \tag{20}$$

Thus, it can be assumed that the measurements in an alternating electric field make it possible to obtain directly in the investigated frequency band the dependences of the positive ϵ_{0+} and negative ϵ_{0-} changes of the thermal conductivity on the ratio E/p.

As follows from Fig. 4, no dispersion *of the negative* component of ϵ is observed in the investigated region of E_0, f, and p. This is apparently connected with the fact that at values of E_0 and p occurring in the experiments, the precession frequencies Ω are larger than the collision frequencies ν_- connected with the negative change

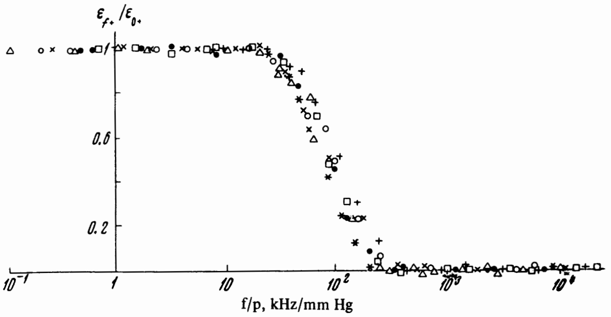

FIG. 7. Plot of $\epsilon_{f+}/\epsilon_{0+}$ against f/p for the gas CH_3CN: +–E/p = 80.5, ▲–E/p = 154, ○–E/p = 160, ■–E/p = 308, X–E/p = 385, ●–E/p = 592, ∗–E/p = 1000 (E/p is given in V/cm-mm Hg).

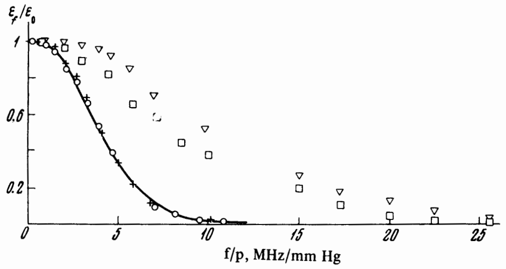

FIG. 8. Plot of ϵ_f/ϵ_0 against f/p for $CHCl_3$ (E is in V/cm and p is in 0.3 mm Hg): +–E/p = 150 (E = 45, p = 0.3), ○–E/p = 178 (E = 80, p = 0.45), □–E/p = 318 (E = 68, p = 0.21), ∇–E/p = 450 (E = 96.5, p = 0.21). The solid line corresponds to the theoretical relation (21).

of ϵ. Indeed, at E_0 = 40 V/cm and p = 0.5 mm Hg we have $\Omega = dE/\sqrt{kTI} \approx 20$ MHz and $\nu_- = 12$ MHz ($I = 2.7 \times 10^{-38}$ g/cm², d = 3.8 dB). Therefore, as was noted in the discussion of (17), a noticeable change of ϵ should be observed at field frequencies $f \gtrsim \Omega$. It follows therefore that the variation of ϵ as a function of f/p can be connected with the change of only the positive component.

Figure 7 shows a plot of $\epsilon_{f+}/\epsilon_{0+}$ ($\epsilon_{f+} = \epsilon - \epsilon_{HF}$) as a function of f/p. From the data given in the figure it is seen that the dispersion of ϵ_{f+} is determined by the ratio of the field frequency f to the collision frequency ν_+, and depends little on the field amplitude, and consequently also on the precession frequency in the entire range of the ratio E_0/p (or Ω/ν_+).

It must be emphasized that the character of the dispersion of ϵ_{f+} differs from the dispersion of the Senftleben effect, namely, the dispersion of ϵ_{f+} is determined by the ratio of the field frequency to the collision frequency ν_+, for an arbitrary ratio of the precession frequency to the frequency ν_+, whereas the dispersion of the Senftleben effect is determined by the ratio f/ν only when $\Omega < \nu$. The latter was shown in[15], which gives the results of an experimental investigation of the thermal conductivity of NF_3 in an alternating electric field. A similar behavior of the dispersion of the Senftleben effect was observed also for the gas $CHCl_3$.

Figure 8 shows the ratio of the Senftleben effect in $CHCl_3$ in an alternating field at a frequency f (ϵ_f) to the corresponding effect in a constant field (ϵ_0) against the ratio f/p for different values of E_0/p. It is seen from the figure that the experimental data obtained at E_0/p equal to 150 and 178 V/cm-mm Hg coincide, within the limits of experimental error, with the theoretical relation (solid line) given in[16]:

$$\varepsilon_f/\varepsilon_0 = [1 + (\omega/n\lambda'_{n_1})^2]^{-1}, \quad \lambda_{n_1} = n\lambda'_{n_1}, \quad \omega = 2\pi f \qquad (21)$$

(n—gas density).

Expression (21) follows from (17) if we put $\hat{J}_{sa} = \hat{J}_a = 0$ (in other words, $W = W'$) and use the relation $\gamma \ll \lambda_{n_1}$. The value of the parameter λ'_{n_1} was obtained by comparing the theoretical curve corresponding to formula (21) with the experimental data (Fig. 8) and is equal to $(6.5 \pm 0.6) \times 10^{-10}$ cm³/sec. This value coincides, within the limits of errors, with the value obtained in[9] by comparing the theoretical and experimental plots of $\epsilon(E/p)$ in a constant field: $\lambda'_{n_1} = (5.8 \pm 0.6) \times 10^{-10}$ cm³/sec. The agreement between (21) and the experimental data obtained at E_0/p = 150 and 178 V/cm-mm Hg is due to the fact that at $E_0 \le 80$ V/cm and p = 0.3 mm Hg the relation $\Omega < \lambda_{n_1}$ is satisfied. Indeed, for $CHCl_3$ ($I = 2.32 \times 10^{-38}$ g-cm², d = 1.02 dB) at E = 80 V/cm and p = 0.3 mm Hg we obtain $\Omega \approx 5.0$ MHz and $\lambda_{n_1} = 6.6$ MHz. A similar behavior of the dispersion of the Senftleben effect was observed earlier in the gas NF_3[16].

As seen from Fig. 8, at the values E_0/p = 318 and 415 V/cm-mm Hg one observes a change in the character of the dependence of ϵ_f/ϵ_0 on f/p with increasing E_0/p, the abscissa of the point $\epsilon_f/\epsilon_0 = 1/2$ shifting towards larger values of f/p. Such a behavior of ϵ_f/ϵ_0 as a function of f/p follows, as noted above, from expression (17).

Thus, we can conclude from the foregoing data that the dispersion of the Senftleben effect in $CHCl_3$ is described satisfactorily by a theory based on the precession mechanism of the effect.

Inasmuch as the experiments in CH_3CN gas were carried out at E_0 = 40–100 V/cm and $p \le 1$ mm Hg, the inequality $\Omega \gg \lambda_{n_2}$ was satisfied ($\Omega \ge 20$ MHz, $\lambda_{n_2} \le 0.6$ MHz). According to the foregoing analysis of expression (17), a dependence of $\epsilon_{f+}/\epsilon_{0+}$ on the ratio f/E_0 should be observed in this case. The obtained experimental data (Fig. 7) do not agree with this consequence of the foregoing theory of the dispersion of the anomalous Senftleben effect. To explain the anomalous effect it is apparently not sufficient to use only a theory based on the usual precession mechanism of the effect, even with allowance for the presence in the gas of collisions for which the probabilities of the direct and inverse transitions are different.

The authors are deeply grateful to L. L. Gorelik, Yu. M. Kagan, L. A. Maksimov, and V. V. Sinitsyn for fruitful discussions and valuable advice, to G. P. Sukhanov for help with the measurements, and to V. I. Rukavishnikov and D. L. Lemenovskiĭ for help with the work.

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Translated by J. G. Adashko
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