MAGNETIC PROPERTIES OF FERROMAGNETIC DIELECTRICS (SPINELS) AT LOW TEMPERATURES

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The temperature dependence of the spontaneous moment of manganese and nickel ferrite samples is measured at temperatures between 2° and 30°K. It is found that the magnetic moment of a number of samples reaches its maximal value at a finite temperature Θ' and decreases with further decrease of the temperature. A possible cause of this anomalous variation of the moment is the existence of two close-lying energy levels of the Fe^{2+} ions in the octahedral ferrite sublattice. In the temperature range in which the anomalous magnetic moment is not manifest, the measured dependence of the spontaneous magnetic moment M_s on temperature and external magnetic field strength is in good agreement with a spin-wave theory calculation of the $M_s(T, H)$ dependence.

THIS paper is devoted to a study of magnetic properties of manganese and nickel ferrites in the low-temperature region. These ferrites have a structure analogous to that of the mineral spinel ($MgAl_2O_4$). The chemical formula for ferromagnetic spinels is $MeFe_2O_4$, where Me is usually a divalent metallic ion or a combination of metallic ions. The spinel unit cell is made up of eight such "molecules." The relatively large oxygen ions O^{2-} form a face-centered cubic lattice. The voids between the oxygen ions are occupied by the metal ions. The metal ions surrounded by four O^{2-} ions form the tetrahedral spinel sublattice A with magnetic moment M_A. The ions surrounded by six oxygen ions form the octahedral sublattice B with magnetic moment M_B. The total magnetic moment of the ferrite is

$$M = M_B - M_A.$$

At sufficiently low temperatures, ferromagnetic spinels are dielectric and it might appear that they could serve as an unusually favorable object of investigation from the point of view of a check on spin-wave theory.

There have been very few investigations of spinels at low temperatures. Kouvel [1] measured the specific heat of natural magnetite crystal Fe_3O_4 in the interval from 1.8 to 4.2°K. The magnetic part of the specific heat of the sample varied like $T^{3/2}$, in agreement with the deductions of a theory based on the spin-wave model. Belov and Nikitin [2] measured the magnetization of a single crystal of manganese ferrite. In the interval from 4.2 to 320°K, the magnetization varied like $T^{3/2}$. We measured the magnetization M of ferrites in the interval from 2.0 to 30°K. Unlike the aforementioned investigations, we measured the quantity dM/dT directly. The measurements were made in magnetic fields up to 22 kOe.

MEASUREMENT PROCEDURE

The measurement procedure employed was similar to that described in [3]. During the course of the experiment we measured dM/dT by determining the oscillations of the magnetic moment of a sample, resulting from oscillations in its temperature. The samples S in the form of a cylinder 0.4 cm in diameter and 2.5-3 cm long were placed in a container of nonmagnetic bronze B (Fig. 1). A heater H of nonmagnetic bronze wire 30 μ in diameter was wound bifilarly over the entire sample. The amplitude of the temperature oscillations was measured with a film-type carbon thermometer T. The container B together with the measuring coil A which was fastened on it were placed in a vessel with liquid helium. The container was filled with gaseous helium through a pipe P. Thus, the heat was removed from the sample S through the gas from the entire surface of the sample, and not from the ends only, as was done in the investigation of the metals before [3]. This was necessary in view of the low thermal conductivity of the ferrite.

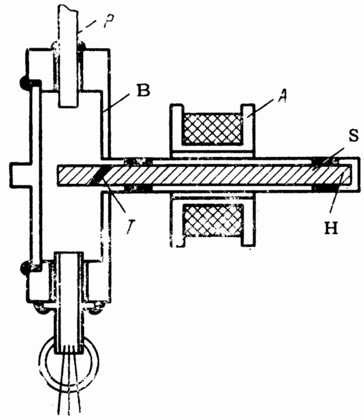

FIG. 1. Diagram of the instrument.

We investigated the distribution of the amplitude of the temperature oscillations along the ferrite rod in an experiment with three thermometers placed on the sample. The amplitude of the temperature oscillations remained constant within ~3% over the entire length of the sample. The change in the amplitude of the temperature oscillations along the radius r of the cylinder is given by [4]

$$|\Delta T|_r / |\Delta T|_{r=a} = \Phi_0(\omega' r) / \Phi_0(\omega' a),$$

where

$$\Phi_0(z) = |\mathrm{ber}\, z + i\, \mathrm{bei}\, z|, \quad \omega' = (2\pi\nu / \chi)^{1/2}.$$

Here ν—frequency of the temperature wave, amounting to 9.2 cps; χ—temperature conductivity of the investigated ferrite samples, equal to ~1 cm^2/sec, and 2a—diameter of cylinder. Calculation shows that $|\Delta T|_{r=0}/|\Delta T|_{r=a} \sim 0.9$, that is, the change in the amplitude of the temperature wave along the diameter does not exceed ~10%. This correction remains practically constant in the temperature interval in which the main measurements were made. The gaseous helium in the container can cause a difference between the amplitude of the sample temperature oscillations ΔT and the thermometer oscillations ΔT^*. To determine the possible magnitude of this effect, we measured the dependence of dM/dT^* on the pressure of the helium in the container. When the pressure changed from 150 to 400 mm Hg at 300°K, the value of dM/dT increased by ~10%. With further decrease of pressure to 5 mm Hg, dM/dT^* remained practically constant. All the main measurements were made at a gas pressure ~20 mm Hg and at 300°K. In calculating the quantity $dM/dT \equiv M'$, we assumed that the amplitudes of the thermometer and sample temperature oscillations were equal.

The manganese and nickel ferrite samples investigated by us, which had different compositions,

Table I Investigated samples

	Composition of ferrite	Θ′, °K	10^5 C
I	$Mn_{0,84}Fe_{2,16}O_4$	14	7.3
II	$Mn_{0,84}Fe_{2,16}O_4$	~4	7,3
III	$Mn_{0,9}Fe_{2,1}O_4$	~4	7.3
IV	$Mn_{0,9}Fe_{2,1}O_4$	~2	7,3
V	$Mn_{0,43}Fe_{2,57}O_4$	⩽1	3,8
VI	$Ni_{0,78}Fe^{2+}_{0,12}Fe^{3+}_{2,07}O_4$	~4	—
VII	$Ni_{0,78}Fe^{2+}_{0,12}Fe^{3+}_{2,07}O_4$	~3.5	—

were single crystals grown by T. M. Perekalina by the Verneuil method in the Crystallography Institute of the U.S.S.R. Academy of Sciences. The [111] axes of the single crystals were close to the axes of the samples. The chemical composition of the samples is listed in Table I.

MEASUREMENT RESULTS

An unusual temperature dependence of M′ was observed in most investigated samples of the manganese ferrites (Fig. 2). Whereas in the temperature range 20—30°K the variation of M′(T) was close to that following from Bloch's $T^{3/2}$ law, as is the case for all ferromagnets, at lower temperatures the absolute value of M′ decreased sharply, went through zero, reversed sign, and became positive. Such a variation of M′(T) denotes that the curve of the spontaneous moment vs. temperature has a maximum. The insert in the upper right of Fig. 2 shows the results of the integration of the M′(T) curves for two samples (the dashed line in the figure represents Bloch's law).

The temperature Θ′ corresponding to the max-

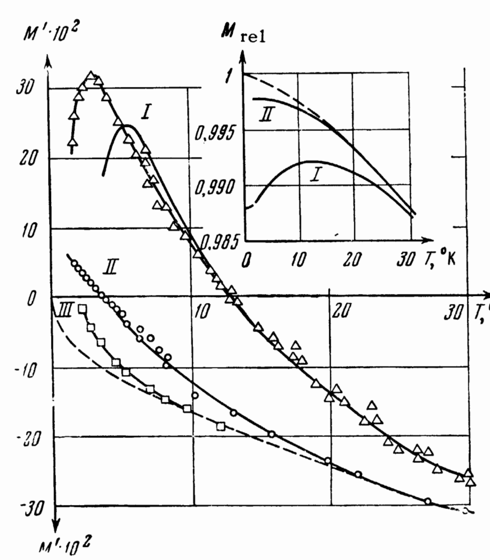

FIG. 2. Temperature dependence of M′ for manganese ferrite samples I, II, and III.

imum value of the magnetic moment M_{max} depends little on the external magnetic field. For example, when the field changed from 2 to 10 kOe, the temperature Θ′ of sample II changed only from 3.5 to 3.9°K. The values of Θ′ for the samples investigated by us are listed in Table I. The very weak dependence M′(H) is characteristic of all the samples in the temperature region where $M' > 0$. Thus, for example, in sample I the possible change in the field from 2 to 10 kOe does not exceed the measurement error (~10%). In the temperature region where $M' < 0$, the influence of the external field is usually more clearly pronounced, and $|M'|$ decreases here with increasing field. The function M′(T) probably has a similar character for nickel ferrite as well (Fig. 3). In this case, however, the reliability of the data we obtained at temperatures below 5°K is low, and we were unable to determine with certainty the change in the sign of M′ or to evaluate the exact value of Θ′.

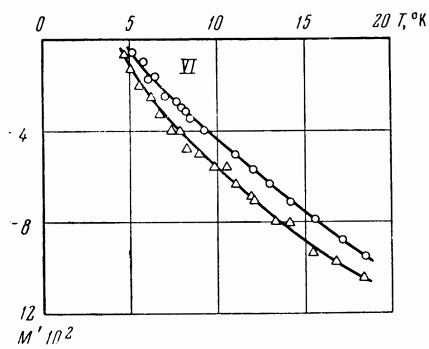

FIG. 3. Temperature dependence of M′ for nickel ferrite sample IV: Δ – in external magnetic field H = 2 kOe, o – in field H = 18 kOe.

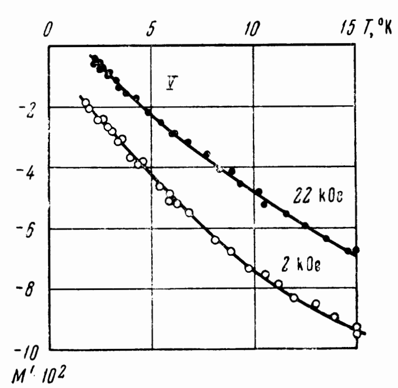

FIG. 4. Temperature dependence of M′ for manganese ferrite sample V: o – in field H = 2 kOe, • – in field H = 22 kOe.

Figures 4 and 5 show the results of the measurement of M′ for sample V of manganese ferrite, in which the change in the sign of M′, if it occurs at all, takes place at temperatures $T \lesssim 1$°K. The magnitude of M′ of this sample depends on the external field for the entire temperature interval investigated. A similar character of the temperature dependence and the dependence on the external magnetic field was observed by us earlier in a study of ferromagnetic metals[3,5].

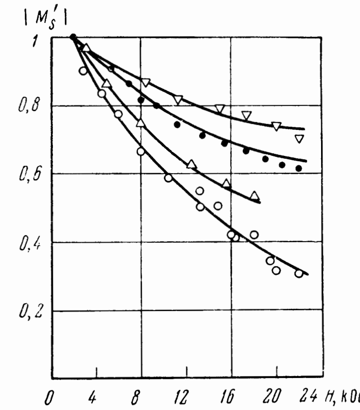

FIG. 5. Dependence of $|M'_s|$ on the magnetic field for sample V of manganese ferrite in relative units (unity is the value of M'_s at H = 2kOe): o – at 2.2°K, Δ – 3.5°K, • – 8°K, ∇ – 15°K. Continuous lines – theoretical plots based on Eq. (3a).

DISCUSSION OF RESULTS

a) Anomalous variation of the spontaneous moment of many ferrite samples. The presence of a maximum on the plot of the magnetic moment against the temperature is one of the most interesting features of the behavior of many ferromagnetic spinel samples at low temperatures. Measurement of the susceptibility of these samples has shown that the relative change in the susceptibility in a constant external magnetic field does not exceed 10% when the temperature is varied from 2 to 30°K. As indicated above, the value of M′ depends little on the external field near Θ′ at lower temperatures as well. This allows us to assume that the anisotropic constant of these samples has no anomalous properties that would explain the unusual variation of the magnetic moment. We see that in this case there is an anomalous temperature variation of the saturation magnetic moment of the ferrite samples.

We can propose the following explanation for this magnetic anomaly of spinels. For concreteness we consider a manganese ferrite.

According to Harrison [6], Zaveta [7], and Miller [8], the distribution of metallic ions over the tetrahedral and octahedral sites in the lattice of manganese ferrite can be written in the form

$$Mn^{2+}_{1-x}Fe^{3+}_{x}[Mn^{3+}_{x}Fe^{2+}_{x}Fe^{3+}_{2-2x}]O_4.$$

The metallic ions outside the square brackets are located at the tetrahedral sites; the ions inside the square brackets form the octahedral sublattice B. Thus, in the B-sublattice of manganese ferrite, apparently as in the B-sublattice of nickel ferrite, there is always a certain number of Fe^{2+} ions. Let us assume that the gap between the ground state and the first excited state of the Fe^{2+} ion is several degrees K. The average orbital momentum of the Fe^{2+} ion in an excited state can differ from the orbital momentum of the ion in the ground state, that is, a partial "freezing" of the orbital momentum should be observed when the Fe^{2+} ion goes over to the ground state at $T < \Theta'$, thus leading to a decrease in the total magnetic moment of the ferrite by an amount ΔM_{orb}.

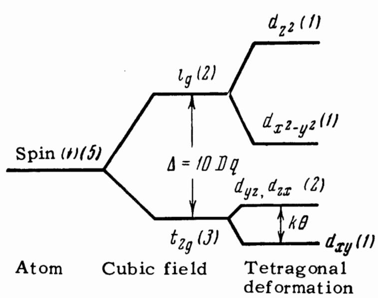

FIG. 6. Splitting of d-levels of Fe^{2+} ion.

A possible mechanism for the formation of two closely-lying levels is explained by the scheme shown in Fig. 6. The Fe^{2+} ion has an electron configuration d^6. Five of the d-electrons occupy completely the levels with spin (↑), forming a closed configuration not shown in the scheme. The sixth electron is at a level with spin (↓), which is five-fold degenerate in the atom. In the cubic field of the neighboring oxygen ions, this level splits into a doublet l_g and a lower-lying triplet t_{2g} (see, for example [9]). Consequently, the orbital ground state of the Fe^{2+} ion is triply degenerate in a field of cubic symmetry. According to the Jahn-Teller theorem [10], the deformation of the crystal lattice lifts the orbital degeneracy of the ground state. In particular, the tetragonal deformation splits the t_{2g} level into a doublet d_{yz}, d_{zx} and a lower singlet d_{xy}. Thus, the ground state of the Fe^{2+} ion in the octahedral sublattice is nondegenerate in this scheme (complete lifting of the degeneracy by an electric field is possible for the d^6 configuration in accordance with the Kramers theorem [11]). The first excited state of the Fe^{2+} ion is apparently degenerate, and therefore has, unlike the ground state, an average orbital momentum.

Allowance for the "freezing" of the orbital momentum leads to the following temperature dependence of the magnetic moment M of the sample

$$M = \left(M_0 + \frac{2\Delta M_{\text{orb}}}{1 + e^{\Theta/T}}\right)(1 - CT^{3/2}), \quad (1)$$

where Θ—distance between the ground and first excited levels.

Let us compare relation (1) with our results for manganese ferrite samples I and II (see Fig. 2). The magnetic moment of the samples, measured at T = 4.2°K, is $M_0 = 510 \pm 7$ cgs emu. The constant C, calculated from our data, is $C = 7.3 \times 10^{-5}$, so that it agrees within the limits of measurement accuracy with the value obtained by Belov and Nikitin [2]. We determine ΔM_{orb} by using the result of the integration of M′(T) (see insert in Fig. 2). For sample I we have $\Delta M_{orb} \approx 6$ cgs emu. A plot of M′(T), calculated from the foregoing data for sample I, is shown in Fig. 1 by a thick solid curve. The value of Θ was assumed to be 14°K. In the case of sample II, the values of Θ and ΔM_{orb}, estimated from (1), are Θ = 3.5—4.5°K and $\Delta M_{orb} \approx 2$ cgs emu.

The presence of two energy levels should lead to an anomalous behavior of the specific heat at temperatures comparable with the magnitude of their splitting. Measurement of the specific heat of manganese ferrite was recently made by Low [17]. According to the author's statement, this substance exhibits a specific-heat anomaly similar to the Schottky anomaly. Such a behavior of manganese ferrite is attributed by Low to the existence of valence transitions with activation energies 18—25°K.

Thus, the entire aggregate of the presently known experimental data does not contradict the explanation proposed above for the anomalous temperature variation of the magnetic moment of spinels. As can be seen from Table I, the temperature at which the anomaly takes place varies from sample to sample in a manner which cannot be controlled at all. This is not surprising, since the magnitude of the splitting of the low-lying levels of the Fe^{2+} ion is determined apparently by the random distortions of the crystal lattice.

b) Concerning the applicability of the theory of spin waves to ferrodielectrics. The anomaly of the magnetic properties of spinels at low temperatures makes it difficult to compare, their characteristics with the deductions of the theory of spin waves in a broad temperature interval. Such a comparison can apparently be made only in the temperature region $T \gg \Theta$, where the influence of the "freezing" of the orbital angular momentum on M′(T) is negligibly small. The most convenient for such a comparison is sample V, for which $\Theta \lesssim 1$°K. We shall use the experimental results obtained at temperatures below 2°K, where the appearance of the anomaly is known to be of low likelihood.

It follows from spin-wave theory (see, for example,[13]) that at sufficiently low temperatures the magnetic moment of a ferromagnet can be represented in the form (see the appendix)

$$M_s = M_0 - \frac{\mu T^{3/2}}{(2\pi)^2 a^{3/2}} J(\alpha, \beta);$$

$$\alpha = \mu H_i / T, \qquad \beta = 2\pi M_0 / H_i, \qquad H_i = H + H_a, \quad (2)$$

where H_a—effective anisotropy field. The values of the integral $J(\alpha, \beta)$ for concrete values of the parameters α and β have been tabulated in the appendix. The experimental results were compared with the relations

$$M_s = M_0 - CM_0 T^{3/2} \frac{J(\alpha, \beta)}{J(0)}; \quad (3)$$

$$M_s' = \frac{dM_s}{dT} = \frac{CM_0}{J(0)} T^{1/2} \left[\frac{3}{2} J(\alpha, \beta) + T \frac{dJ(\alpha, \beta)}{dT}\right]. \quad (3a)$$

Figure 5 shows (continuous lines) a plot of $M_s'(H)$ calculated from relation (3a). In the calculations we assumed $M_0 = 510$ cgs emu and $\mu = 2\mu_0$, (μ_0 = Bohr magneton); the anisotropy field was not taken into account, in view of the lack of reliable data. As can be seen from the figure, there is splendid agreement between the theoretical calculations and the experimental data in the entire temperature interval investigated. The experimental data and the calculated $M_s'(T)$ are compared in Fig. 7. We see that the results of the calculation are in satisfactory agreement with the experimental data in this case, too.

For the remaining samples, a direct comparison of the experimental data with relation (3a) is difficult. We can state nevertheless that for samples of manganese and nickel ferrite with

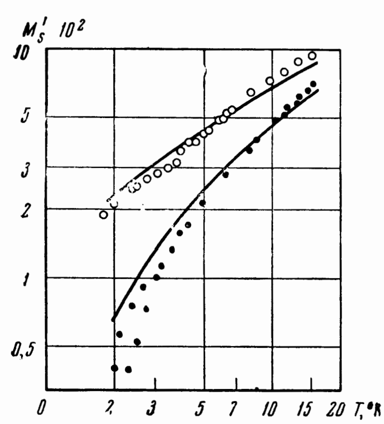

FIG. 7. Dependence of M_s' on the temperature for manganese ferrite sample V, logarithmic scale: o field H = 2 kOe, ● – field H = 22 kOe. The continuous lines – theoretical plots of relation (3a).

$\Theta \sim 2$–4°K in the temperature region T > 10°K the behavior of $M'(T)$ (see, for example, Fig. 3) is close to that predicted theoretically.

Thus, our results show that, unlike ferromagnetic materials[3,4], the dependence of the spontaneous moment of ferro-dielectrics on the temperature and on the external magnetic field, in the absence of anomaly, is fully explained by spin-wave theory.

The authors thank T. L. Kapitza and A. I. Shal'nikov for continuous interest in the work, I. E. Dzyaloshinskiĭ for useful discussions, and T. M. Perekalina for graciously supplying the ferrite single crystals prepared in her laboratory.

APPENDIX

CALCULATION OF THE SPONTANEOUS MOMENT OF A FERROMAGNET BY SPIN-WAVE THEORY

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At low temperatures, in accordance with the spin wave theory (see, for example,[13]), the magnetic moment of a ferromagnet M is of the form

$$M = M_0 - \frac{1}{(2\pi)^2} \int_0^\pi \sin\varphi\, d\varphi \int_0 \frac{k^2 dk}{e^{\varepsilon/T} - 1} \frac{\partial \varepsilon}{\partial H}. \quad (A.I)$$

Here M_0—spontaneous moment at absolute zero, T—temperature, k—wave vector of the spin wave, ϵ—spin-wave energy:

$$\varepsilon = [(ak^2 + \mu H_i + 4\pi M_0 \mu \sin^2\varphi)(ak^2 + \mu H_i)]^{1/2}, \quad (A.2)$$

where $H_i = H + H_a$ (H—external magnetic field, H_a—anisotropy field); φ—angle between the vector k and the direction of the external magnetic field.

From (2) we easily obtain

$$\frac{\partial \varepsilon}{\partial H} = \frac{\mu}{\varepsilon}(ak^2 + \mu H_i + 2\pi M_0 \mu \sin^2\varphi),$$

$$d\varepsilon = \frac{2ak\,dk}{\varepsilon}(ak^2 + \mu H_i + 2\pi\mu M_0 \sin^2\varphi),$$

$$k\,dk\, \partial\varepsilon/\partial H = \mu\, d\varepsilon / 2a.$$

Substituting these expressions in (1) we get

$$M = M_0 - \frac{\mu}{8\pi^2 a} \int_0^\pi \sin\varphi\, d\varphi \int_{\varepsilon_{min}}^\infty \frac{k(\varepsilon, \varphi)}{e^{\varepsilon/T} - 1} d\varepsilon, \; .$$

$$\varepsilon_{min} = \sqrt{\mu H_i(\mu H_i + 4\pi\mu M_0 \sin^2\varphi)},$$

$$k = \frac{1}{\sqrt{a}}\left[-\mu H_i - 2\pi\mu M_0 \sin^2\varphi + \sqrt{\varepsilon^2 + 4\pi^2\mu^2 M_0^2 \sin^4\varphi}\right]^{1/2}.$$

Introducing the notation

Table II

α	J (β=10)	J (β=5.5)	J (β=1.5)	α	J (β=0.5)	J (β=0.15)
0.02	1.46	1.58	1.76	0.2	1.04	1.12
0.06	1.01	1.17	1.42	0.3	0,847	0.930
0.10	0.779	0,94	1.22	0.6	0.500	0.580
0.14	0.624	0,781	1.06	1.0	0,273	0.340
0.18	0.512	0.661	0.945	1.4	0.157	0.208
0.20	0.466	0.612	0.894	1.8	0,0925	0.130
0.22	0.426	0.567	0.847	2.2	0.0551	0.0827
0.26	0.359	0.491	0.764	2.4	0,0427	0.0660
0.30	0.305	0.428	0.693			

$$\alpha = \mu H_i / T, \quad \beta = 2\pi M_0 / H_i, \quad \varepsilon / T = z,$$

we obtain the following expression for the magnetic moment:

$$M = M_0 - \frac{\mu}{(2\pi)^2} \frac{T^{3/2}}{\alpha^{3/2}} J(\alpha, \beta),$$

$$J(\alpha, \beta) = \int_0^{\pi/2} \sin\varphi \, d\varphi \int_{x(y)}^{\infty} \frac{\sqrt{z^2 - x^2(\varphi)}}{y(z, \varphi)} \frac{dz}{e^z - 1},$$

$$x(\varphi) = \alpha\sqrt{1 + 2\beta \sin^2\varphi},$$

$$y(z, \varphi) = [\sqrt{z^2 + \alpha^2\beta^2 \sin^4\varphi} + \alpha(1 + \beta \sin^2\varphi)]^{1/2}. \quad \text{(A.3)}$$

Thus, the problem reduces to calculating the definite integral $J(\alpha, \beta)$. The integral $J(\alpha, \beta)$ was calculated with a computer for values of α and β corresponding to the ranges of temperatures and magnetic fields that are most frequently encountered in experiments. Table II shows the results of the calculation for several values of α and β and illustrates the character of the variation of $J(\alpha, \beta)$.

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