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# Magnetic and resonance properties of the two-dimensional $S = 1$ compound $Ni_5(TeO_3)_4Cl_2$ with frustrated geometry

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The magnetic and magnetoresonance properties of a new single-crystal compound $Ni_5(TeO_3)_4Cl_2$ are studied. The measurements of the magnetization and magnetic susceptibility of the crystal in a wide temperature range (5–300 K) made it possible to conclude that $Ni_5(TeO_3)_4Cl_2$ is a quasi-two-dimensional antiferromagnet with the easy magnetization axis **a*** directed perpendicular crystallographic plane **bc** and a magnetic ordering temperature $T_N \approx 21$ K. The resonance measurements at 4.2 K in wide range of frequencies (25–105 GHz) and magnetic field (up to 200 kOe) permitted us to obtain the frequency–field dependence of AFMR spectrum for a field applied along the easy magnetization axis **a***. It is shown that the magnetic field directed along the antiferromagnetism axis (**H**||**a***) induces the magnetic phase transition of a spin-flop type which is found to be $H_{sf} \approx 120$ kOe. The magnetic resonance experimental data are described qualitatively in model of the biaxial antiferromagnet.

PACS: **76.50.+g** Ferromagnetic, antiferromagnetic, and ferrimagnetic resonances; spin-wave resonance;
75.50.Ee Antiferromagnetics.

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Recent increasing attention of scientists has been focused on «nonclassical» magnets in which of considerable importance are different kinds of topological inhomogeneities, spin fluctuations, competition and frustration of magnetic interactions, and so on. These peculiarities result in a number of specific features of magnetic properties, a new type of excitation, peculiar magnetic structures, nonlinear effects.

The above peculiarities are most pronounced for a system of reduced dimension. Hence, the investigation of two- and one-dimensional magnets is of obvious interest and way involve the development of new models for low-dimensional many-sublattice magnetic systems, especially as modern chemical technologies make it possible to produce new compounds of a given lattice symmetry and dimension.

The paper concerns study of magnetic and resonance properties of a new recent synthesized compound tellurium oxychloride $Ni_5(TeO_3)_4Cl_2$ [1], belong to the $Ni_5(TeO_3)_4X_2$ (X = Cl, Br, J).

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The x-ray diffraction analysis [1] shows that $Ni_5(TeO_3)_4Cl_2$ is of monoclinic symmetry with the space group $C2/c$. The cell parameters are as follows: $a$ = = 19.5674 Å, $b$ = 5.2457 Å, $c$ = 16.3084 Å, $\beta = 125°29'$, $z = 4$.

The compound has a clearly pronounced layered structure formed by the connected corners of $[Ni_5O_{17}Cl_2]$ blocks that consist of five face-coupled octahedrons of nickel. Nickel layers lie in **bc** plane and form complicated three angular structure. In such geometry effects of magnetic frustration may play significant role.

The previous studies of temperature dependences of magnetic susceptibility $\chi(T)$ and optical far IR spectra (10–100 $cm^{-1}$) of $Ni_5(TeO_3)_4Cl_2$ [1,2] demonstrate that at rather high temperatures the susceptibility can be described by the Curie–Weiss law with a negative constant $\Theta \approx -50$ K. This suggests that exchange interaction is of antiferromagnetic character. The temperature dependence of susceptibility at $T \approx 23$ K exhibits an anomaly which the authors relate to the transition to an antiferromagnetic state. The effective $g$ factor determined from the dependence $\chi(T)$ was 2.21. In addition, at temperatures below 23 K the authors of Ref. 1 observed the pronounced dependence of magnetic susceptibility on experimental conditions (ZFC and FC dependences $\chi(T)$). The investigation of magnetic susceptibility $\chi(T)$ was carried out on powdered samples. The optical measurements in magnetic fields made it possible to recognize absorption electron bands and to calculate the value of spin-flop transition field that appeared to be equal 100 kOe. It must be noted, that magnetic and resonant properties of isostructural single crystal $Ni_5(TeO_3)_4Br_2$ were studied in Refs. 3, 4.

The aim of the work under consideration was to study comprehensively the static magnetic properties $Ni_5(TeO_3)_4Cl_2$ single crystal in wide temperature range, as well as magnetoresonance properties investigation of this compound in a low-frequency diapason (25–100 GHz) at helium temperatures to determine the values of typical magnetic interaction.

## Experimental technique

The magnetization measurements were performed in a temperature range 5–300 K at a constant magnetic field up to 50 kOe with the use of a SQUID magnetometer MPMS 5 Quantum Design. The resonance experiments were carried out with a pulsed tuned-frequency radiospectrometer in a magnetic field up to 200 kOe at helium temperature.

The sample of $Ni_5(TeO_3)_4Cl_2$ was a single crystal plate. The **b** and **c** axes lie in plate plane. The sample mass and the volume were $m$ = 13.927 mg and $V$ = = $2.6 \cdot 10^{-3}$ $cm^3$, respectively.

## Magnetic measurements

The experimental data on temperature dependence of magnetization in temperature range from 5 to 300 K are shown in Figs. 1–3. The measurements were carried out in magnetic fields of 100 and 1000 Oe.

The dependences $M(T)$ obtained for $Ni_5(TeO_3)_4Cl_2$ permitted us to determine the easy magnetization axis **a*** which is perpendicular to the **bc** plane layers. The high-temperature region of the temperature dependence of magnetic susceptibility for the easy magnetic axis from 80 to 300 K can be described by the Curie–Weiss law $\chi(T) = C/(T - \Theta)$ (see Fig. 2,*b*) with a negative constant $\Theta \approx -49$ K which is typical of antiferromagnetic exchange interaction. On further decreasing temperature below 80 K, $\chi$ continues its monotonic rise reaching its peak at $T_{max} \approx 30$ K and then it reduces (Figs. 1 and 2,*a*). The perpendicular susceptibility also have some peculiarity at temperature 30 K (see Fig. 3). At $T \approx 21$ K there is a kink in the parallel susceptibility curve (Fig. 1) while the perpendicular one exhibits a local minimum (Fig. 3). We associate in accordance with [1] anomaly at 21 K with phase transition in antiferromagnetic state. Anomalies at 30 K remain unclear. Most probably they related to low dimensionality of this system, but the ultimate answer calls for further investigation (for example specific heat).

As mentioned above, the experiments in Ref. 1 revealed that below the magnetic ordering temperature the temperature behavior of magnetic susceptibility was dependent on cooling method. The ZFC and FC dependences measured in fields of 100 Oe, 1 kOe and 10 kOe were substantially different. As for our similar studies (Fig. 1), we did not observe any dependence on cooling method. As is evident from the figure, the ZFC

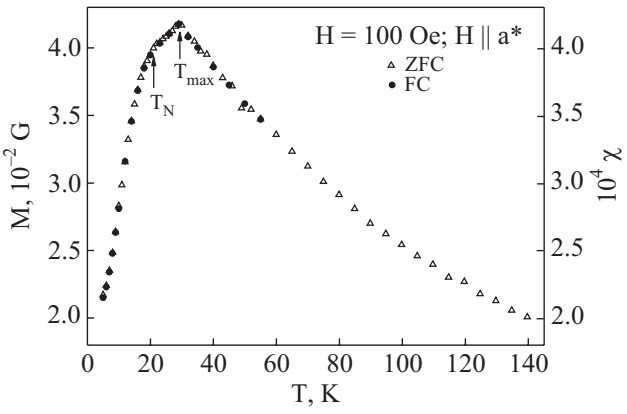


*Fig. 1.* The temperature dependence of magnetization and magnetic susceptibility of the single crystal $Ni_5(TeO_3)_4Cl_2$. The measurements were made in $H$ = 100 Oe directed along the easy magnetization axis **a*** after the sample cooling down to 5 K without magnetic field (the ZFC dependence) and in the field of 100 Oe (the FC dependence).

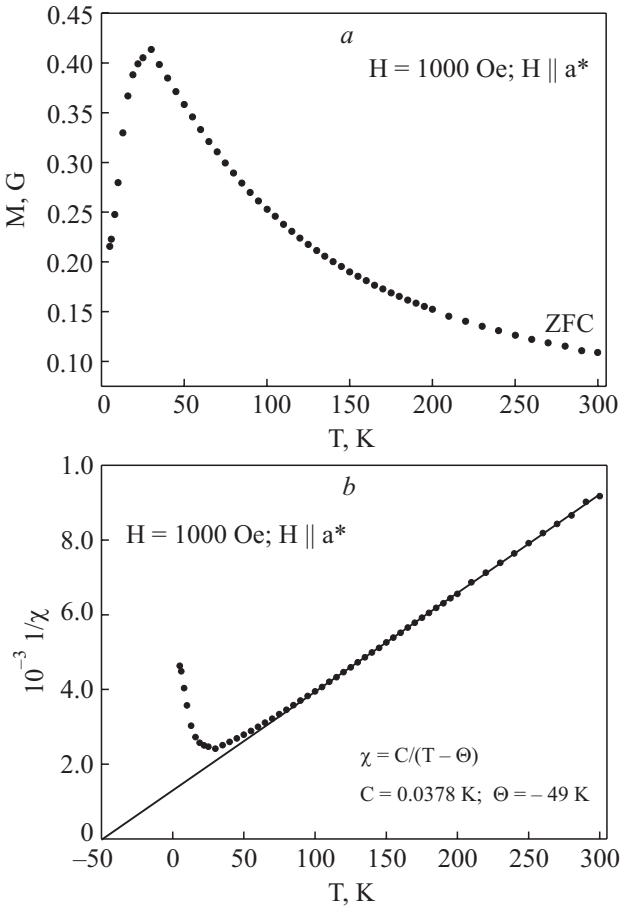


*Fig. 2*. (*a*) The temperature dependence of magnetization for $Ni_5(TeO_3)_4Cl_2$. The measurements were made in the magnetic field $H = 1000$ Oe directed along the easy magnetization axis **a*** after the sample cooling down to 5 K without magnetic field (the ZFC dependence). (*b*) The temperature dependence of inverse magnetic susceptibility calculated from the data shown in Fig. 2,*a*.

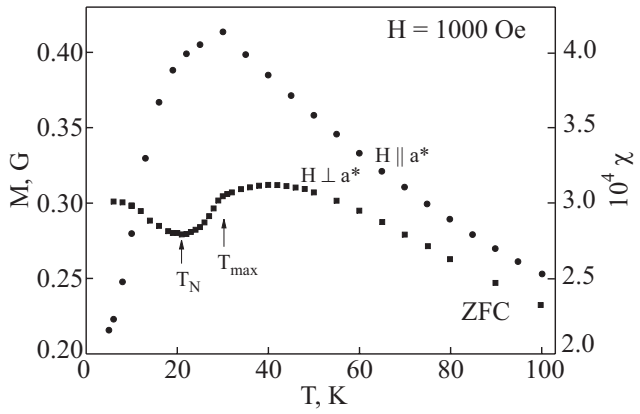


*Fig. 3*. The temperature dependence of magnetization and magnetic susceptibility for the $Ni_5(TeO_3)_4Cl_2$ single crystal measured at $H = 1000$ Oe parallel and perpendicular to the easy magnetization axis **a***. Prior to the measurements the sample was cooled down to 5 K without magnetic field (the ZFC dependence).

and FC dependences of parallel susceptibility of the $Ni_5(TeO_3)_4Cl_2$ single crystal measured in a field of 100 Oe show a good coincidence. It must be noted, that analogous measurements for isostructural $Ni_5(TeO_3)_4Br_2$ [4] don't display any dependence of results from cooling regime. It may be that the effect observed in Ref. 1 is related to the powdered sample structure.

Of particular importance for magnetic ordered systems is the existence of magnetic spin-reorientation phase transitions. For such transitions to be detected, the field dependences of magnetization were measured at different temperatures in an external magnetic field directed along the easy magnetization axis. The measurement data are illustrated in Fig. 4. As is seen, the field dependences $M(H)$ exhibit a slight nonlinearity. But at fields up to 50 kOe the dependences $M(H)$ do not demonstrate any dramatic changes in magnetization or kinks, suggesting that there are no magnetic phase transitions in $Ni_5(TeO_3)_4Cl_2$ within the magnetic field range studied. For comparison, Fig. 4 shows the dependence $M(H)$ measured at $T = 10$ K in a magnetic field perpendicular to the easy magnetic axis. This dependence is linear in a filed range of 0 to 50 kOe.

When treating the experimental data obtained on the powdered $Ni_5(TeO_3)_4Cl_2$ samples, the authors of Ref. 1 suggested that there was a weak ferromagnetic moment in the antiferromagnetic studies. For such a weak ferromagnetic moment to be detected in our single crystal $Ni_5(TeO_3)_4Cl_2$ the dependences $M(H)$ were measured in low magnetic field at $T = 5$ K with an external field applied along and perpendicular to the easy magnetization axis. The dependence $M(H)$ at a magnetic field directed

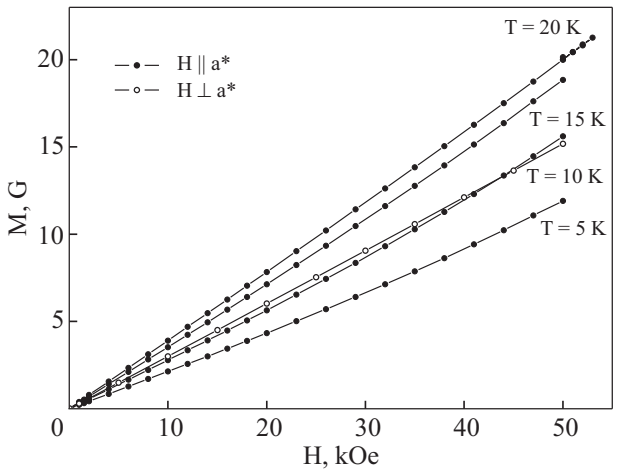


*Fig. 4*. The field dependences of magnetization for $Ni_5(TeO_3)_4Cl_2$ measured at temperatures of 5, 10, 15 and 20 K in the magnetic field applied along the easy magnetization axis **a***. For comparison, shown also is the dependence $M(H)$ measured at $T = 10$ K in the field perpendicular to the easy axis.

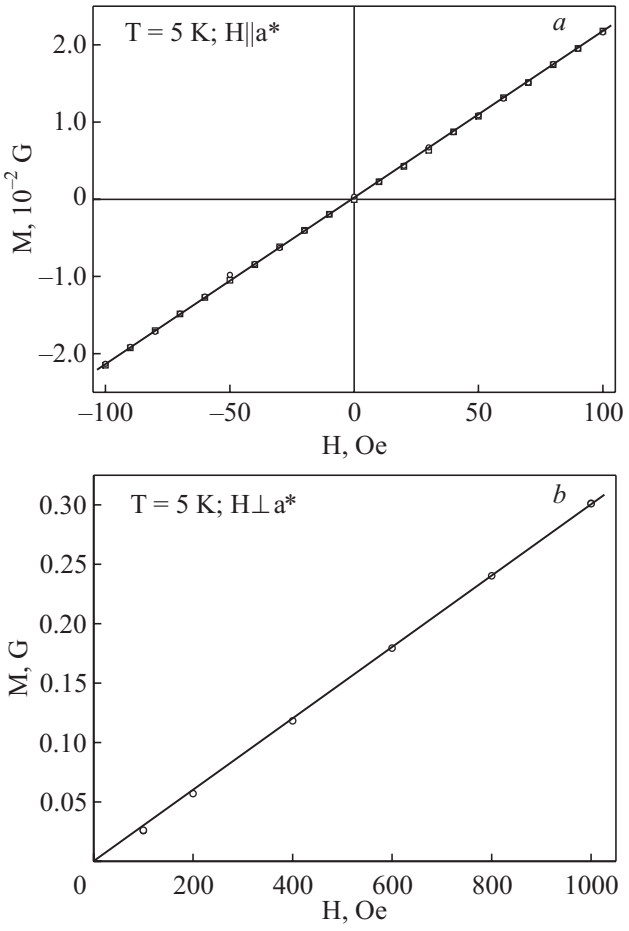


*Fig. 5*. (*a*) The field dependence of magnetization for the single crystal $Ni_5(TeO_3)_4Cl_2$ measured at $T = 5$ K in the magnetic field applied along the easy magnetization axis **a***. Points (○) and (□) correspond measuring with varying magnetic field from –100 to 100 Oe and from 100 to –100 Oe, respectively. (*b*) The field dependence of magnetization for $Ni_5(TeO_3)_4Cl_2$ measured at $T = 5$ K in the magnetic field normal to the easy magnetization axis.

along the easy magnetization axis is shown in Fig. 5,*a*. When measuring, the magnetic field was varied from –100 to 100 Oe and then from 100 to –100 Oe. As is evident from the figure, there is no magnetic hysteresis in the $M(H)$ curve. All the experimental points fit in well straight line that passes through the point $M = 0$ at $H = 0$. The dependence $M(H)$ measured at a magnetic field normal to the easy magnetization axis is illustrated in Fig. 5,*b*. In this case the field was varied from 0 to 1000 Oe, and the experimental points also fit in well the straight line that passes through the origin of coordinates. Thus, the magnetically ordered single crystal of $Ni_5(TeO_3)_4Cl_2$ did not display any weak ferromagnetic moment either along the easy magnetization axis **a*** or in the plane normal to it.

Our experimental data on temperature dependence of magnetization $M(T)$ were used to estimate the value of exchange interaction. The exchange field $H_e$ may be estimated in the framework of the molecular field theory [5] from the phase transition temperature $T_N$. The exchange field $H_e$ can be calculated by the expression:

$$H_e = \frac{3k_B T_N}{g\mu_B S(S+1)}, \qquad (1)$$

where $k_B$ is the Bolzmann constant, $T_N = 21$ K is the Neel temperature, $S = 1$ is the spin, $\mu_B$ is the Bohr magneton, $g = 2.2$ is the $g$ factor. The calculation gives estimate value $H_e \approx 213$ kOe. This value is close to the estimation obtained in Ref. 2 by the same method.

The above experimental data indicate that the compound $Ni_5(TeO_3)_4Cl_2$ is a close realization of quasi-two-dimensional antiferromagnet.

### Magnetic resonance measurements

In the paramagnetic state the ground term of a $Ni^{2+}$ ion is $F$ ($S = 1$), and the lowest lying orbital level is a singlet. Therefore, for low-symmetry crystals there is a triplet structure with a large initial splitting (up to ten or even more inverse centimeters) at a zero magnetic field what is due to the single-ion anisotropy. Experimental study of magnetic resonance in such systems requires high frequencies and strong magnetic field both in paramagnetic and magnetically ordered states.

The resonance measurements of the magnetically ordered single crystal of $Ni_5(TeO_3)_4Cl_2$ were carried out in a frequency region of 25 to 105 GHz at helium temperatures in high magnetic fields. Magnetic fields up to 200 kOe produced by the pulsed technique were much higher than the magnetic anisotropy field. In our experiments the polarization **H**⊥**h** was used and the external magnetic field **H** was applied along the easy magnetization axis. These experimental conditions permitted us to observe two antiferromagnetic resonance (AFMR) lines corresponding to collinear and spin-flop magnetic phases and to study the frequency–field dependences of the spectrum. The behavior of the frequency–field dependence of the AFMR spectrum in an external magnetic field directed along the easy magnetization axis is shown in Fig. 6. As is evident from the figure, the AFMR lines moves forwards each other with decreasing frequency, and at $\nu = 30.8$ GHz and $H = (120 \pm 2)$ kOe they are coincident. The value of magnetic field corresponds to the experimental value of spin-flop transition field. The frequency–field dependence can be described by the theoretical relations for a biaxial antiferromagnet in collinear and spin-flop phases with an external magnetic field directed along antiferromagnet vector **L**.

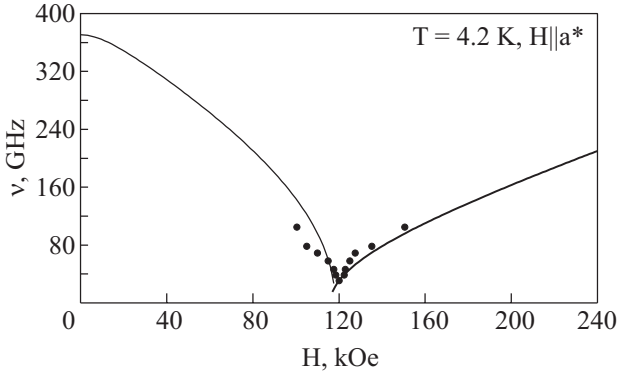


*Fig. 6*. The frequency–field dependence of AFMR spectrum for the external magnetic field applied along the easy magnetization axis **a*** of $Ni_5(TeO_3)_4Cl_2$, $T = 4.2$ K.

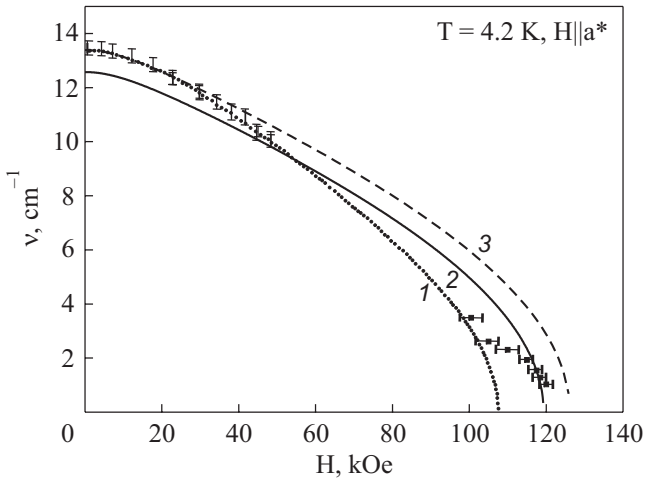


*Fig. 7*. Summary of our date and date of paper [2] for lowest resonant mode below the spin-flop field $H_{sf}$. The length of the vertical and horizontal bars indicates estimated error. The line *1* corresponds fitting curve from Ref. 2, the line *2* and *3* are obtained from our expression (2) with different parameters sets (explanation see in text).

For fields lower than the field of spin-flop transition $H_{sf}$ the observed AFMR can be given by the expression [6,7]

$$(\omega/\gamma)^2 = \frac{1}{2}\{H^2 + C_1 + C_2 - [H^4 + 2H^2(C_1 + C_2) + (C_2 - C_1)^2]^{1/2}\}, \quad (2)$$

where $\gamma = g\mu_B/\hbar$, $C_1 = 2H_eH_{a1}$, $C_2 = 2H_eH_{a2}$.

For the field $H = H_{sf} = (2H_eH_{a1})^{1/2} = 120$ kOe one can observe a spin-reorientation magnetic phase transition followed by the formation of the spin-flop phase. Our experimental value of the spin-flop transition is somewhat higher that calculated in Ref. 2, $H_{sf}$ = 100 kOe, because the authors of the Ref. 2 experienced difficulties with precise extrapolation of the transition field by the initial portion of the frequency–field dependence. For a biaxial antiferromagnetic the spin-flop transition field in the general case is equal to the low-frequency gap of magnon excitation $(\omega_1/\gamma)^2 = 2H_eH_{a1}$. Hence, knowing the value of exchange interaction effective field, one can estimate the magnetic anisotropy field $H_{a1}$ that equals 34 kOe. Using Eq. (2), we estimate the values of magnon high-frequency gap and magnetic anisotropy field $H_{a2}$ and obtain 434 GHz and 47 kOe, respectively. At fields higher than spin-flop transition the frequency–field dependence is of the form [6,7]

$$(\omega/\gamma)^2 = H^2 - H_{sf}^2 . \quad (3)$$

Equations (2) and (3) give the best fit of the experimental dependences $\nu(H)$ for the following parameters values: $H_e = 213$ kOe, $H_{a1} = 34$ kOe, $H_{a2} = 47$ kOe, $H_{sf} = 120$ kOe, $\nu_1 = 371$ GHz, $\nu_2 = 434$ GHz, $g = 2.21$. It is evident that description is rather qualitative.

Now we can try to compare our experimental data in 0.1–3.5 cm$^{-1}$ frequency range with optical far IR spectra (10–100 cm$^{-1}$) taken from paper [2]. Figure 7 represents these data for lowest resonant mode below the spin-flop field $H_{sf}$ . Line labeled as *1* is fitting curve from Ref. 2 based on assumption a collinear spin structure. It is seen that low-frequency region does not described and spin-flop field is too small comparing with the experiment. The line *2* corresponds to our expression (2) with mentioned above parameters. In this case we obtain energy gap 371 GHz (12.37 cm$^{-1}$) 9% less experimental value 405 GHz (13.5 cm$^{-1}$). The curve *3* also corresponds to Eq. (2) when constants are fitted so that we obtain experimental value of energy gap. In this case we must suppose the spin-flop field $H_{sf}$ = 130 kOe (8% more than experiment). As is seen in all cases there is rather qualitative agreement with experiment. Evidently the model of two-sublattice biaxial antiferromagnet is too simple for this compound to say nothing about rough estimated parameters.

Thus, the complex study of magnetic and resonance properties of the $Ni_5(TeO_3)_4Cl_2$ single crystal made it possible to obtain the following results:

1. The investigation of the magnetization of the $Ni_5(TeO_3)_4Cl_2$ single crystal in a wide temperature range demonstrates that the crystal is a quasi-two-dimensional antiferromagnetic with the easy magnetization axis **a*** directed perpendicular crystallographic plane **bc** and a magnetic ordering temperature $T_N \approx 21$ K. No a weak ferromagnetic moment has been observed in the $Ni_5(TeO_3)_4Cl_2$ single crystal.

2. The frequency–field dependence of the AFMR spectrum in $Ni_5(TeO_3)_4Cl_2$ in external magnetic field directed along the antiferromagnetism axis of the crystal

(**H**||**a***) was studied. It was shown that in **H**||**a*** there occurs a spin-flop magnetic phase transition at $H_{sf}$ = = 120 kOe.

3. The magnetic resonance experimental data can be described qualitatively in model of the biaxial antiferromagnet.

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