05,11

Nonlinearity and harmonics of the magnetic susceptibility of a Co^{2+} single-ion magnet in the paramagnetic region above the magnetic ordering temperature

© O.V. Koplak[1,2], E.V. Dvoretskaya[1,2], E.I. Kunitsyna[1], R.B. Morgunov[1,2]

[1] Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS, Chernogolovka, Russia
[2] I.M. Sechenov First Moscow State Medical University, Moscow, Russia

E-mail: Spintronics2022@yandex.ru

Received October 13, 2022
Revised October 13, 2022
Accepted October 19, 2022

In single-ion complexes based on Co^{2+} ions, the second and third harmonics of the magnetic susceptibility were found at temperatures of 2−4 K, which exceed the Neel temperature. The maxima of the second and third harmonics of the magnetic susceptibility are observed at a frequency of ∼ 1 Hz, at which the maximum of the first harmonic is observed in a field of 3.2 kOe. An analysis of the dependences of the second and third harmonics of the magnetic susceptibility on the field and temperature showed that the nonlinearity arises as a result of the formation of a spin glass state at temperatures slightly higher than the Neel temperature. In this state, there is no long-range spin order, but there are spin clusters in the spin glass state. The spin-glass state in a compound with a Co^{2+} ion with a high magnetic anisotropy is unusual in that the exchange interaction is much smaller than the single-ion anisotropy energy.

Keywords: molecular magnets, nonlinear magnetic susceptibility, nanostructures, spin dynamics, spin glass.

DOI: 10.21883/PSS.2023.01.54983.497

1. Introduction

A lot of relatively recent work has been devoted to nonlinear magnetic susceptibility in ferromagnets, where the low-frequency dynamics of domain walls leads to a resonant response to an external alternating magnetic field and makes it possible to obtain data on the mobility of domain boundaries [1–5]. The presence of second, third and higher-order harmonics in the study of ferromagnets does not seem unusual because the domain walls themselves are solitons, and their dynamics are always significantly nonlinear.

More intriguing is the fact that higher-order magnetic susceptibility harmonics are also observed at temperatures exceeding the magnetic ordering temperature. In [6] it is established that in a cubic CdCrSe ferromagnet, higher-order harmonics occur at $T > T_C$. It is assumed that these harmonics and nonlinearity arise because above the temperature of the magnetic ordering (Curie or Neel), local correlations of spins grouping into clusters with nonlinear susceptibility still persist. At the same time, the state of such a medium can be described within the framework of the theory of spin glasses [7,8]. For the case of rare-earth ions and transition metal ions with high values of single-ion anisotropy, anomalous states of spin glasses are well known, in which the energy of the exchange interaction between the spins E_{ex} is significantly less than the energy of single-ion magnetic anisotropy E_{anis}. In such magnetic states, the randomness of the spin distribution is supported by the random orientation of the main axis of magnetization of individual ions, and not by variations in the inter-spin distances. Therefore, the spin glass state can be realized in atomically ordered structures, and not only in amorphous alloys. For the first time, the theory of such spin Ising glasses with a high anisotropy value was developed in [9,10] and experimentally confirmed in the works of Almeida and Taules for DyFeB, PrFeB [11–14] alloys.

Recently, a new very active field of research has emerged for molecular or ionic metal-organic crystals, which use metal ions with high spin-orbit energy and, accordingly, with high single-ion anisotropy. They are called single-molecular magnets (SMM) with conditionally long relaxation times limited by the single-ion anisotropy barrier, or single-ion magnets (SIM) with faster magnetic relaxation provided by quantum spin tunneling and other types of relaxation. Such materials are metal-organic complexes containing a single paramagnetic ion capable of exhibiting slow spin relaxation due, as a rule, to the presence of strong magnetic anisotropy of the type „light axis“ [1,15–18]. These ions are separated by a significant distance in the crystal lattice ∼ 1−2 nm, which weakens the exchange and magnetic dipole interactions between them, leading to the fulfillment of the above condition $E_{ex} \ll E_{anis}$. The frequency of magnetic relaxation in such ions sometimes falls into the frequency window $f = 0.1-1000$ Hz, which

is available for studies in SQUID magnetometers at low temperatures $\sim 2\,\mathrm{K}$. In this case, the ion states with different magnetic moment projections are separated by an energy barrier, which leads to a long-term conservation of spin coherence and makes such ions suitable for quantum computing [19,20]. The prospect of storing magnetization inside just one molecule or one ion arouses wide interest in SMM and SIM, which can be used as platforms for quantum computing.

SMM studies using the example of multi-spin SMM complexes based on manganese acetate $Mn_{12}Ac$ by measuring magnetic susceptibility in an alternating magnetic field were intensively carried out and yielded important results, which consist in the appearance of maxima of magnetic susceptibility components during resonant tunnel transitions in magnetic fields determined by the difference in the Zeeman energies of the spin states of the complexes [21,22]. Although the study of linear susceptibility to an alternating field has become a standard tool for determining whether a molecular cluster has magnetic memory, the analysis of nonlinear susceptibility provides additional information about the relaxation process with little time and complexity of the experiment. The nonlinear dynamics of susceptibility depends not only on the relaxation time, as linear susceptibility, but also on how sensitive the relaxation is to an external magnetic field. In [22,23] it was shown that the presence of spin quantum tunneling and its strong dependence on the external field, which upsets the tunneling levels, makes a very large contribution to the nonlinear response of clusters Mn_{12}. This „quantum nonlinearity" can „be turned off and turned on" by external magnetic fields.

On the other hand, as will be shown in our work, SIM complexes are capable of exhibiting unusual magnetic properties at low temperatures, similar to those observed in spin glasses. Curie temperatures (T_C) or Neel temperatures (T_N) are often not achieved in real experiments in such compounds because the exchange interaction is quite small, and the temperature range of publicly available magnetometers is limited to temperatures of $1.6-1.8\,\mathrm{K}$. However, at quite accessible slightly higher temperatures $\sim 2\,\mathrm{K}$ in them, one can expect the occurrence of spin glass Ising states similar to what is observed in works [1,2,4,5]. One of the ways to detect the nonlinearity of magnetic properties is to register harmonics of the 2nd and 3rd orders when measuring magnetic susceptibility in an alternating magnetic field. In recent works [15,16], the first harmonic of magnetic susceptibility in metal-organic crystals based on $[CoLCl_2]\cdot H_2O$ complexes was studied in detail (L = the product of bis-condensation of diacetyl and 2-hydrazinyl-4,6-dimethylpyrimidine), in which the Co(II) ion is hexacoordinated [15,16]. The molecular and crystal structure of this compound is shown in Fig. 1. The crystal field parameters were set to [15,16] (axial crystal field parameter $\Delta_{ax} = -1252.15\,\mathrm{cm}^{-1}$, rhombic crystal field parameter $|\Delta_{rh}| = 183.65\,\mathrm{cm}^{-1}$, spin-orbit coupling parameter $\lambda = -148.6\,\mathrm{cm}^{-1}$, orbit reduction coefficient $\kappa = 0.775$, parameter of intermolecular exchange interaction $J = -0.085\,\mathrm{cm}^{-1}$). These parameters, calculated using the Griffith Hamiltonian, indicate the presence of a strong single-ion magnetic anisotropy of the light axis type with weak rhombic distortions. The complex demonstrates two relaxation processes that are 3.2 kOe in the magnetic field are recorded as maxima on the frequency dependence of the first harmonic of the imaginary part of the magnetic susceptibility $\chi^{(1)}_{\mathrm{Im}}(f)$, while the second maximum was observed only at 3.2 kOe at low frequencies ($< 1\,\mathrm{Hz}$) and temperatures ($< 5\,\mathrm{K}$) [15,16]. These complexes demonstrate antiferromagnetic correlations between ion spins and a Wess temperature of $-1.4\,\mathrm{K}$, close enough to the extremely low temperature available in a SQUID magnetometer based on helium-2.

The purpose of this work was to attempt experimental detection of the spin-glass state of the magnetic moments of ions Co^{2+} by registering 2nd and 3rd harmonics, as well as by establishing the influence of temperature and magnetic field on the signal corresponding to these harmonics.

2. Experimental procedure and samples

The magnetic properties of the Co^{2+} complexes were investigated using the MPMS XL SQUID magnetometer (Quantum Design), which has the option of measuring the real and imaginary parts of magnetic susceptibility in an alternating magnetic field. The frequency dependences of the real Re and imaginary Im parts of the magnetic susceptibility of the complex with Co^{2+} are obtained in the temperature range of $2-5\,\mathrm{K}$ and the magnetizing DC fields 1 kOe and 3.2 kOe with the amplitude of the alternating AC field 4 Oe. The samples were a powder of the synthesized compound SIM (Fig. 1) packed in a gelatin capsule in such a way that the capsule's contribution to the signal was negligible. The signal from the SIM sample at 2 K in an alternating magnetic field is shown in Fig. 2 (points *1*). This signal has a distorted shape and cannot be approximated by a pure harmonic function (see curve *2* in Fig. 2). Since these distortions, indicating the presence of higher-order harmonics, were small, in a separate series of experiments we were convinced that in ions in which there is no delayed relaxation at 2 K, distortion of the sinusoidal signal is not observed.

The magnetization of M in the variable field $H_{\mathrm{AC}} = h\sin\omega t$ is a function of time t, which can be decomposed as follows into a harmonic series [1,2,7]:

$$M(t) = M_{1\omega}\sin(\omega t + \theta_{1\omega}) + M_{2\omega}\sin(2\omega t + \theta_{2\omega}) + M_{3\omega}\sin(3\omega t + \theta_{3\omega}) + \ldots, \quad (1)$$

where ω — the angular frequency of the external field ($\omega = 2\pi f$), $M_{n\omega}$ — n-th harmonic component (where n — integer number), $\theta_{n\omega}$ — phase delay of the harmonic $M_{n\omega}$ relative to the external field H_{AC}. The alleged and real

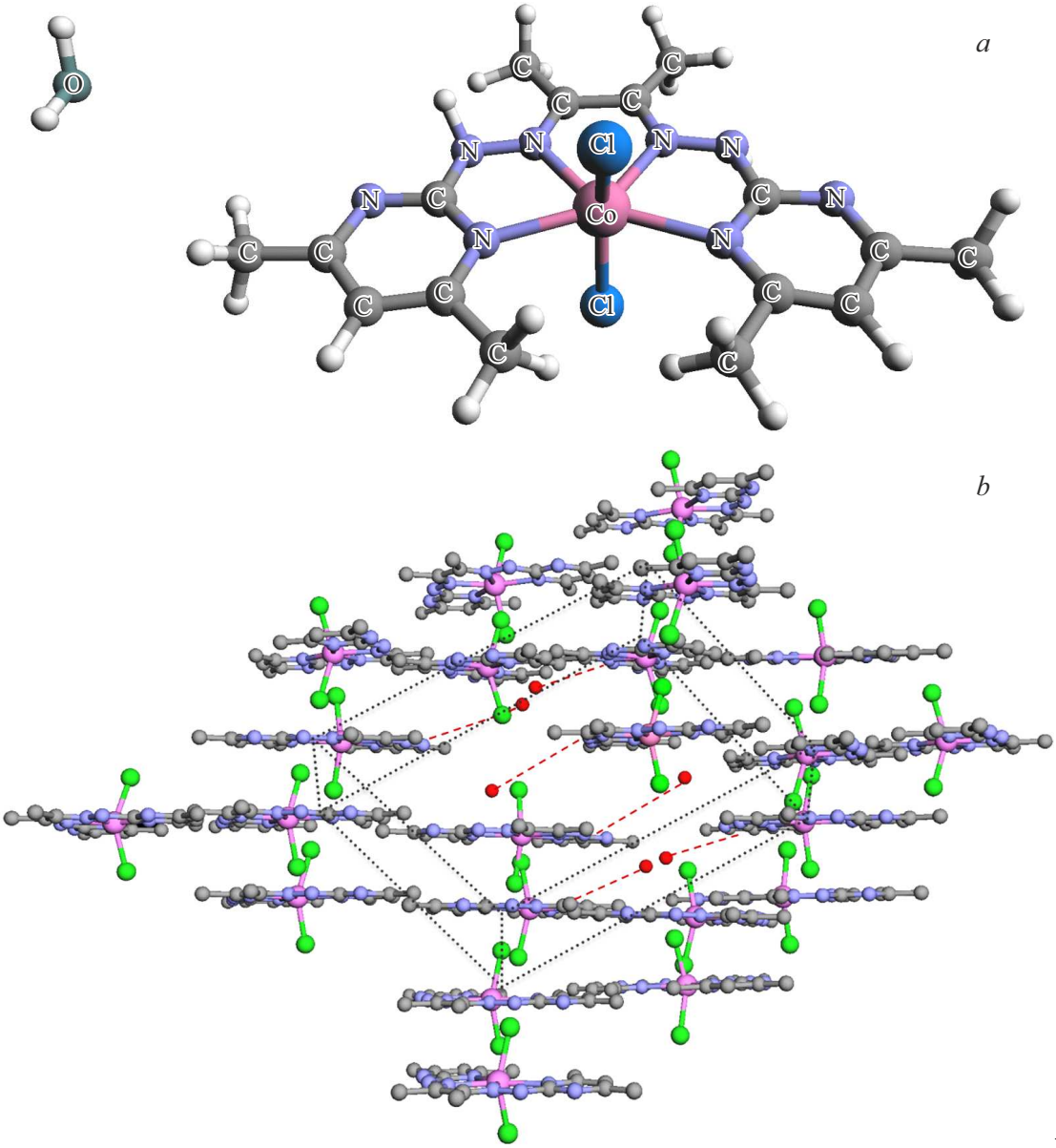

Figure 1. Molecular structure (a) and projection of a fragment of the crystal structure (b) of the complex $[CoLCl_2] \cdot H_2O$ (L = the bis-condensation product of diacetyl and 2-hydrazinyl-4,6-dimetilpyrimidine), according to [15,16].

and imaginary components of the magnetic moment of the sample can be written as

$$\chi_{\mathrm{Re}}^{(1)} = M_{1\omega} \cos\theta_{1\omega},$$

$$\chi_{(Im)}^{((1)} = -M_{1\omega} \sin\theta_{1\omega},$$

$$\chi_{\mathrm{Re}}^{(2)} = M_{2\omega} \cos\theta_{2\omega},$$

$$\chi_{\mathrm{Re}}^{(3)} = M_{3\omega} \cos\theta_{3\omega}. \qquad (2)$$

The first harmonic $\chi_{(1)}$ of the magnetic moment is directly proportional to the external magnetic field. Second harmonic $\chi^{(2)}$ is usually used to analyze materials that have spontaneous magnetization [1,2]. Finally the third harmonic $\chi^{(3)}$ is a relatively exotic characteristic, different from zero in relatively rare cases. One example of such situations is spin glasses, where there is a locally cooperative, but at the same time disordered on average, direction of spins [5]. Thus, a non-zero value of $\chi^{(3)}$ usually confirms the presence of a glassy state due to frustration of magnetic moments of magnetic domains (without phase transition) or weak ferromagnetism in antiferromagnets [1,2,5]. Therefore, to search for a possible spin-glass state, we used the real and imaginary parts of the third harmonic $\chi_{\mathrm{Re}}^{(3)}(f)$ and $\chi_{\mathrm{Im}}^{(3)}(f)$, in addition to the second $\chi_{\mathrm{Re}}^{(2)}(f)$ and $\chi_{\mathrm{Im}}^{(2)}(f)$ and the first $\chi_{\mathrm{Re}}^{(1)}(f)$ and $\chi_{\mathrm{Im}}^{(1)}(f)$ magnetic susceptibility.

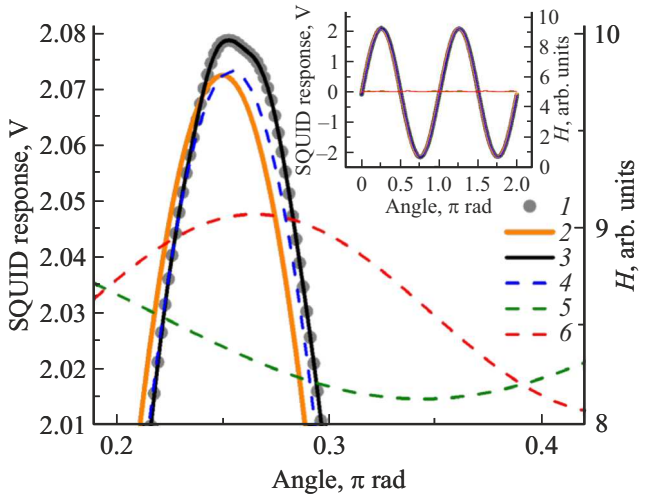

Figure 2. (*1*) Sample signal recorded by a SQUID magnetometer in an alternating magnetic field H_{AC}; (*2, 3*) — approximations by pure harmonic function and expression (1), respectively; (*4, 5, 6*) — contributions of the first, second and third harmonics to the signal, respectively. On the insert, the dependence of the signal The magnetization AC of the sample from the phase of the alternating field, measured in a constant magnetizing DC field $H_{DC} = 1000$ Oe. The amplitude AC of the field $h_{AC} = 4$ Oe.

3. Experimental results

3.1. The magnetic moment of complexes in a constant magnetic field

The dependences of the molar magnetization M on the field H at temperatures 2–10 K are shown in Fig. 3, *a*. There is no hysteresis on these dependences, which indicates the absence of a long-range ferromagnetic order in the samples. Saturation magnetization at 50 kOe corresponds to the effective magnetic moment of the ion $\mu_{eff} = 4.2\mu_B$, which is in good agreement with the data for Co^{2+} obtained by other authors and is explained by mixing the orbital moment of the ion L with the spin moment $S = 1/2$. As a result, the total angular momentum of the ion is J higher than would be expected for a purely spin moment. This mixing occurs because the freezing of the orbital moment by the crystal field in such ions occurs only partially.

The temperature dependences of the molar magnetization M multiplied by the temperature T in external fields $H = 1$–4 kOe are shown in Fig. 3, *b*. The value of MT for a paramagnet is convenient because in the high-temperature region it should be independent of temperature, according to Curie's law $M \sim C/T$. In the low-temperature region, even in a paramagnet with non-interacting spins, this value decreases as a result of the transition from classical to quantum statistics of filling Zeeman energy levels. The dependences are compared with the predictions of the theory for a paramagnet with non-interacting moments of ions and taking into account the interaction (solid lines in Fig. 3, *b*). This will be discussed in detail further. In this paper, in contrast to [15], where the full temperature dependences of magnetization up to 300 K are given, we were interested only in the low-temperature part, the deviation of which from the Brillouin function gives information about the interactions between the magnetic moments of individual ions.

In addition to dynamic magnetic susceptibility, static magnetic susceptibility is often used in the literature, which, instead of the derivative $\chi = dM/dH$, is defined as the ratio $\chi_S = M/H$. This value is equal to the dynamic susceptibility in the temperature range where the magnetization is directly proportional to the magnetic field $M \sim H$, i.e. in those conditions when there are no nonlinear contributions of various interactions to the magnetization. Fig. 3, *c* points represent the experimental temperature dependence $\chi_S(T)$ and its comparison with Curie's law (solid line). It can be seen that below 10 K there is a significant decrease in the value of χ_S compared to its values for an ideal paramagnetic.

The presented results of studies of complexes in a constant magnetic field indicate that at low temperatures less than 5–10 K, ionic magnetic interactions between ions occur in the sample, which cannot be explained by the magnetic dipole interaction, which is ~ 0.1 K.

3.2. Nonlinear magnetic susceptibility in alternating magnetic field

Two relaxation processes were detected in [15], one of which is low-frequency) was detected at 1 Hz, and other (high frequency) — at 1000 Hz. A detailed analysis of the temperature dependences of these maxima was presented in [15]. In this paper, the emphasis is placed only on the low-temperature region 2–5 K, where cooperative spin phenomena are expected. Therefore, in this work, the frequency dependences of various harmonics of magnetic susceptibility were obtained in the fields 1 kOe and 3.2 kOe in [15].

Fig. 4, *a–f* shows the frequency dependences of the real Re and imaginary Im parts of the magnetic susceptibility for the first harmonic $\chi^{(1)}_{Re}(f)$ and $\chi^{(1)}_{Im}(f)$ (*a, b*), for the second harmonic $\chi^{(2)}_{Re}(f)$ and $\chi^{(2)}_{Im}(f)$ (*c, d*) and for the third harmonic $\chi^{(3)}_{Re}(f)$ and $\chi^{(3)}_{Im}(f)$ (*e,f*) at 2–5 K in a constant magnetic field $H_{DC} = 1$ kOe. Frequency dependences of the real and imaginary parts of the first harmonic $\chi^{(1)}_{Re}(f)$ and $\chi^{(1)}_{Im}(f)$ (*a, b*) are similar to the dependencies obtained in [15]. Dependency $\chi^{(1)}_{Re}(f)$ represents a step, and dependency $\chi^{(1)}_{Im}(f)$ — maximum. Both of these features shift with an increase in temperature from 2 to 5 K in the direction of high frequencies.

The amplitudes of the second and third harmonics are expected to be small, but their frequency dependences indicate the nonlinearity of magnetic susceptibility. The real part and imaginary parts of the sec-

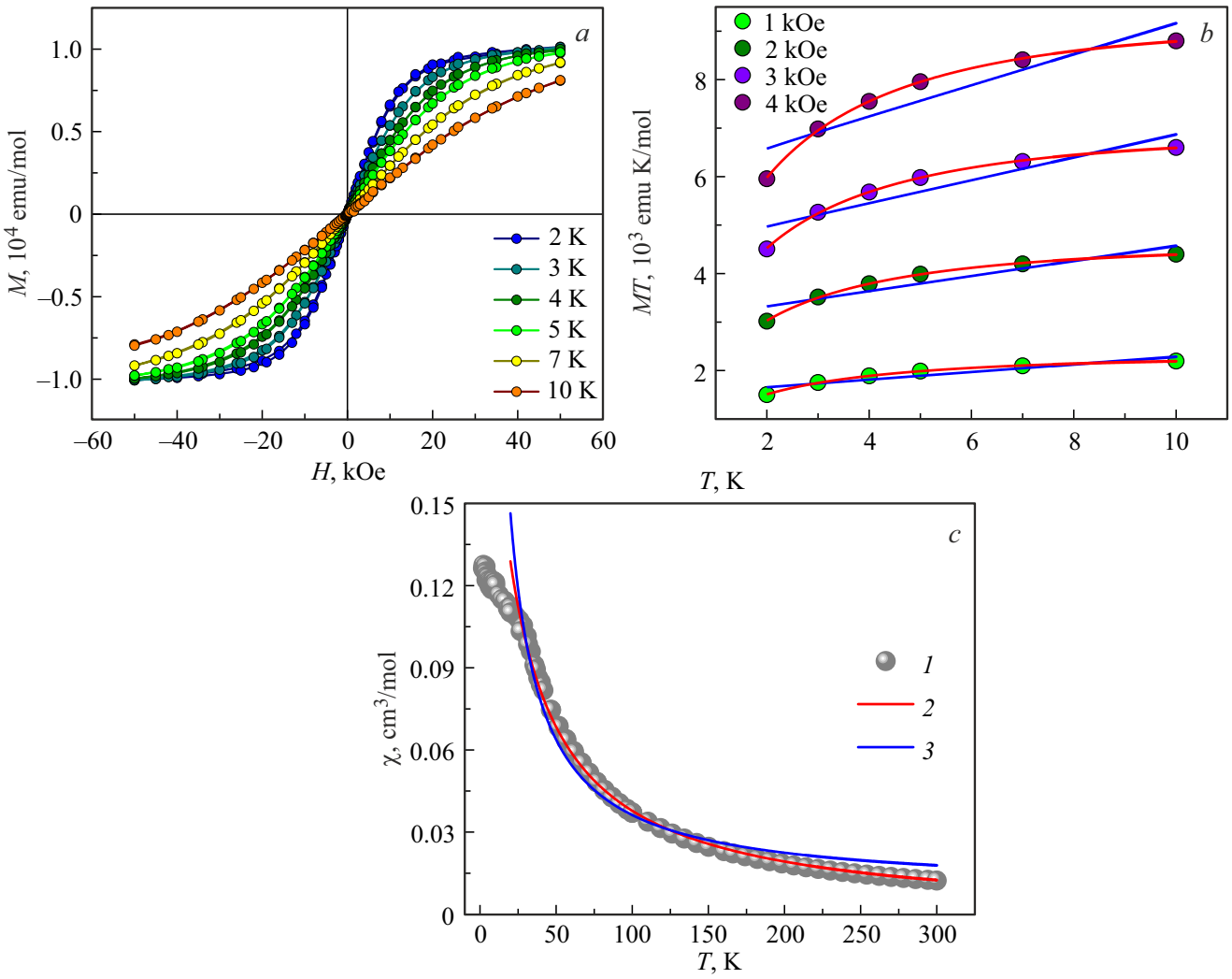

Figure 3. (*a*) Dependence of the magnetization M on the field H at temperatures 2–10 K for a single-ion magnet Co(II). (*b*) The temperature dependence of the magnetic moment M multiplied by the temperature T in the external fields $H = 0$–4 kOe for a single-ion magnet Co(II). The dependencies $MT(T)$ are approximated by the Brillouin function at a constant field: the blue curves correspond to the approximation with the parameter $T_0 = 0$, the red curves correspond to the parameter $T_0 = 1.5$ K. (*c*) The temperature dependence of the magnetic susceptibility $\chi = M/H$ for Co(II) (gray symbols *1*) approximated by the Brillouin function divided by H: the blue curve *3* corresponds to the approximation with the parameter $T_0 = 0$, the red curve *2* correspond to the parameter $T_0 = 1.5$ K.

ond harmonic $\chi^{(2)}_{\mathrm{Re}}(f)$ and $\chi^{(2)}_{\mathrm{Im}}(f)$ demonstrate maxima near 1 Hz at temperature 2 K in a constant magnetic field $H_{\mathrm{DC}} = 1$ kOe (Fig. 4, *c*, *d*). In the same magnetizing field near 1 Hz, the maxima of the third harmonic $\chi^{(3)}_{\mathrm{Re}}(f)$ and $\chi^{(3)}_{\mathrm{Im}}(f)$ are observed (fig. 4, *e*, *f*). For all harmonics, there is a slight rise in the frequency range 100–1000 Hz, i.e. at the same frequencies where the maximum of the imaginary part of the first harmonic is observed.

With increasing temperature, the amplitude of the maxima of the second and third harmonics decrease rapidly and approach zero already at 5 K (Fig. 5).

In the field $H_{\mathrm{DC}} = 3200$ Oe the first harmonic demonstrates a step for the real part of the magnetic susceptibility $\chi^{(1)}_{\mathrm{Re}}(f)$ and a maximum for the imaginary part $\chi^{(1)}_{\mathrm{Im}}(f)$ at the same frequencies as the components of the total magnetic susceptibility in operation [15] (Fig. 6, *a*, *b*). The contributions of the second and third harmonics in this field at 1 Hz are even smaller in amplitude and are detected only at the lowest available temperature 2 K (Fig. 6, *c*–*f*). These data directly indicate the occurrence of nonlinearity and the presence of interaction between the magnetic moments of ions at low temperatures 2–3 K.

4. Discussion

First, we will discuss the deviations of the temperature dependence of the magnetic moment of the sample from the predictions of the theory for a paramagnet. In a constant

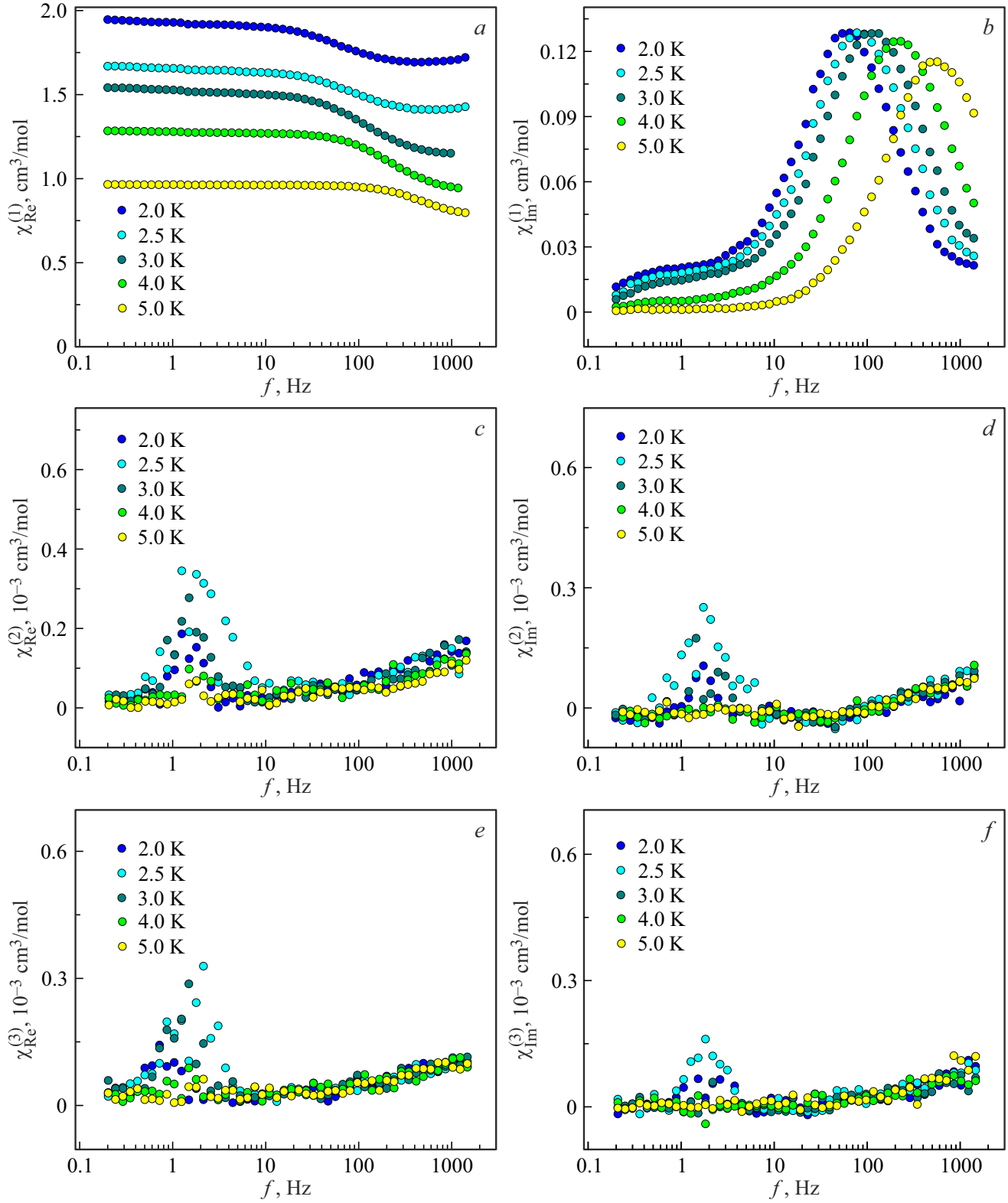

Figure 4. Frequency dependencies of real $\chi^{(1)}_{Re}$ (*a*), $\chi^{(2)}_{Re}$ (*c*), $\chi^{(3)}_{Re}$ (*e*) and imaginary $\chi^{(1)}_{Im}$ (*b*), $\chi^{(2)}_{Im}$ (*d*), $\chi^{(3)}_{Im}$ (*f*) parts of the magnetic susceptibility of the sample in a constant field 1000 Oe for harmonics $n = 1, 2, 3$ at a temperature in the range 2–5 K.

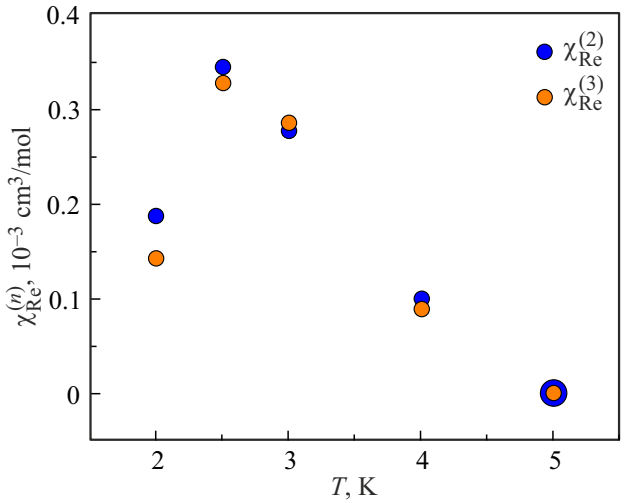

Figure 5. The amplitudes of the maxima of the real parts of the second $\chi^{(2)}_{Re}$ and the third $\chi^{(3)}_{Re}$ harmonics of the magnetic susceptibility of the sample in a constant field 1 kOe.

magnetic field, the paramagnet must follow the Brillouin function [24]:

$$B_S(x) = \frac{2S+1}{2S}\,\mathrm{cth}\left[\frac{2S+1}{2S}\,x\right] - \frac{1}{2S}\,\mathrm{cth}\left[\frac{1}{2S}\,x\right]. \qquad (3)$$

$$x = \frac{g\mu_B B}{k(T+T_0)}\,S, \qquad (4)$$

x — the argument of the Brillouin function, which determines the ratio between the Zeeman energy and thermal energy, $B = \mu_0 H$ — magnetic field induction; J — angular momentum of the metal ion; $g = 2$ — g-factor; $\mu_B = 927.4 \cdot 10^{-23}$ erg/G — Boron magneton; $\mu_0 = 1$ — absolute magnetic permeability; $k = 1.38 \cdot 10^{-16}$ erg/K — Boltzmann constant; T — temperature; T_0 — parameter characterizing the energy of interactions between ions leading to a deviation from the Brillouin function [24].

The dependences of $MT(T)$ in Fig. 3, *a* are approximated by the Brillouin function at a constant field 1 cfu. The blue solid lines correspond to an approximation with the parameter $T_0 = 0$ K, which does not match the experiment. The red solid lines correspond to the parameter $T_0 = 1.5$ K, the introduction of which leads to a satisfactory agreement with the experiment. Parameter $T_0 = 1.5$ K is at least an order of magnitude greater than the interspin dipole-dipole interaction ~ 0.1 K. It could be explained by the splitting of the energy levels of a single ion in a crystal field, as it is convincingly shown in [15]. However, the presence of 2nd and 3rd nonlinear harmonics of magnetic susceptibility (Fig. 3) strongly indicates interionic exchange interactions. Therefore, the most probable reason for the deviation of the field dependences of magnetization from the Brillouin function at low temperatures — is the occurrence of spin correlations, which does not lead to a long-range order up to the lowest temperature 2 K used in our experiments. However, at the same time, spin correlations known from the literature arise in the sample regions, leading to the state of spin glass at temperatures higher than the temperature of magnetic ordering. Since at $T < 5$ K the magnetization lies below the Brillouin function, and the Weiss temperature defined in [15] is negative, it can be assumed that at $T < 2$ K there should be a transition to the antiferromagnetic state and the Neel point $T_N < 2$ K. The presence of nonlinear harmonics of magnetic susceptibility suggests that at 2 K the system is not far from the point of magnetic transition to the antiferromagnetic state, and there are magnetic correlations in it. These conditions, as is known from experimental [25,26] and theoretical [27,28] studies, are sufficient for the formation of a spin glass state.

There are two models of spin glasses: Ising and Heisenberg. These models differ in the restrictions imposed on the orientation of the spins: the Ising model is due to the near magnetic order, describes the spin rotations up or down, while the value of the random magnetic anisotropy is $D \gg J$ (J — exchange interaction), and in the Heisenberg model ($D \ll J$) spin rotation can take different directions, because it is caused by the long-range magnetic order [29].

The typical properties of spin glass include: the presence of a sharp fracture in the dependence of magnetic susceptibility χ on temperature T in small magnetic fields (~ 1 Oe) and at low frequencies (~ 100 Hz). The fracture usually turns into a smoothed maximum when the field increases to ~ 100 Oe, which is observed in our work. There is a strong dependence of χ on the magnitude of the magnetic field H, but the dependence on the magnetic background of the sample [7] is not obvious and requires additional research. The presence in the spin glass of a large number of degenerate or metastable states separated by energy barriers, which at sufficiently low temperatures are almost infinitely high, causes a similar behavior of magnetization and magnetic susceptibility and macroscopically long relaxation times [7].

Similar situations are known from the literature. In the paramagnetic state $YbFeTi_2O_7$, the fracture on the temperature dependence of the magnetic moment and the dependence of magnetization on the magnetic prehistory of the sample with a decrease in temperature indicates a transition from the paramagnetic state to the spin-glass magnetic state with predominantly antiferromagnetic exchange interaction in the spin system [30]. In [31], the analysis of the temperature dependence of magnetic susceptibility allowed us to establish that at low temperatures in polycrystals of $HoFeTi_2O_7$ spin glass states with competing exchange interactions between the nearest neighbors, as well as frustration of exchange interactions in the absence of a long-range magnetic order, are observed.

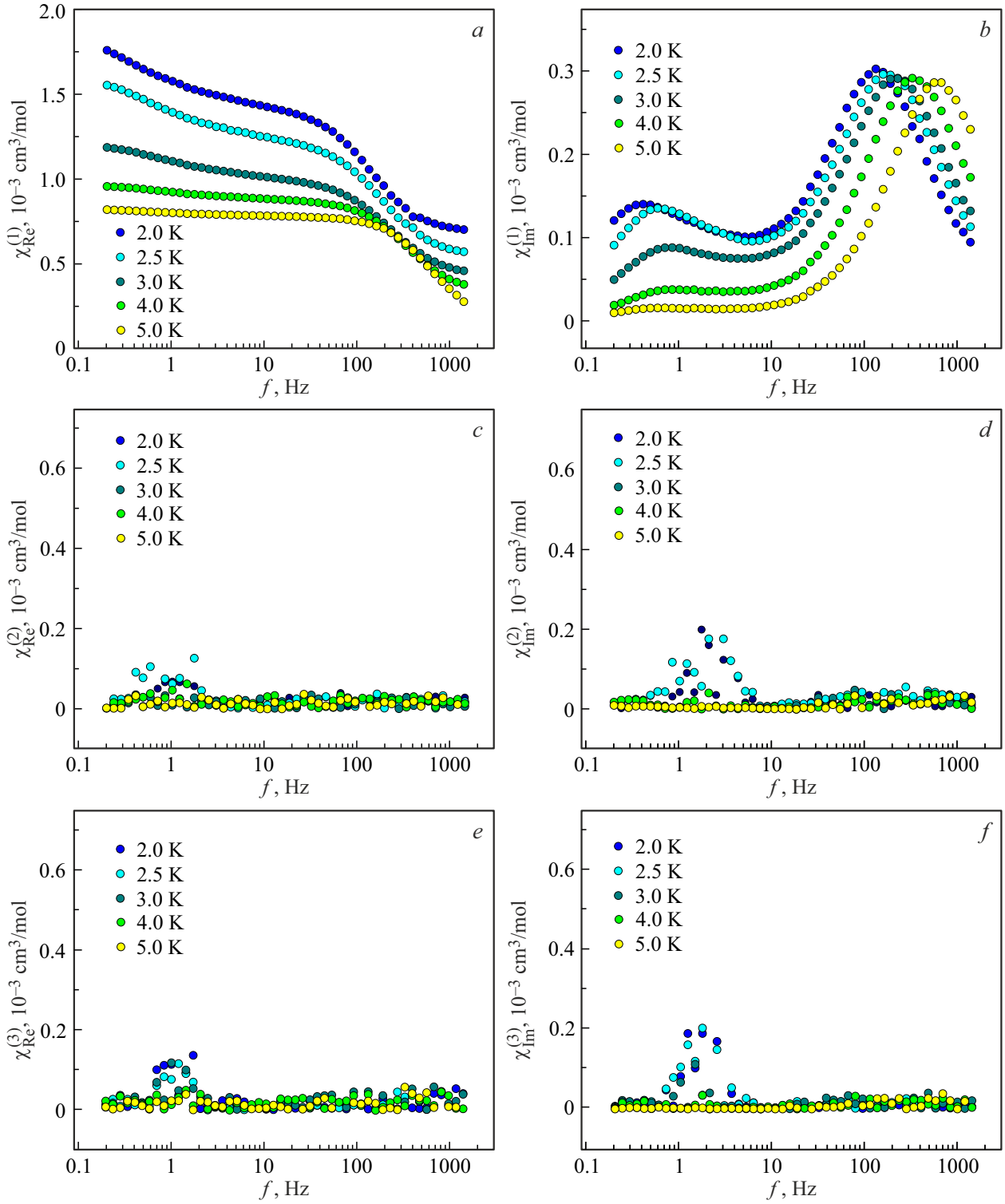

Figure 6. Frequency dependencies of the real $\chi^{(1)}_{Re}$ (a), $\chi^{(2)}_{Re}$ (c), $\chi^{(3)}_{Re}$ (e) and imaginary $\chi^{(1)}_{Im}$ (b), $\chi^{(2)}_{Im}$ (d), $\chi^{(3)}_{Im}$ (f) parts of the magnetic susceptibility of the sample in a constant field of 3200 Oe for harmonics $n = 1, 2, 3$ at a temperature in the range 2–5 K.

5. Conclusions

In the low-temperature region 2–5 K, where deviations of the temperature dependence on the predictions of the Brillouin function are observed, nonzero frequency-dependent components of the second and third harmonics of magnetic susceptibility are found. These components indicate non-linearity in the spin system when a magnetic field is applied and may be related to the inter-spin interaction.

Antiferromagnetic correlations of the spin complexes are observed in the studied temperature range, however, the Neel temperature is not reached at the lowest available temperature of 2 K. The sample is in a spin glass state, in which there are spin-matched ion clusters, but there is no long-range magnetic order.

The high energy of single-ion anisotropy of Co^{2+} ions, exceeding the exchange interaction between ions, suggests that spin glass can be described within the framework of Ising theory, in which even in the absence of an amorphous disordered state of the crystal lattice, disorder in the spin subsystem is provided by local single-ion anisotropy, unlike from the Heisenberg model.

Funding

The work was carried out as part of the thematic map of the Federal Research Center for Problems of Chemical Physics and Medical Chemistry of the Russian Academy of Sciences No. AAAA19-119111390022-2. E.V. Dvoretskaya is supported by RFBR grant No. 20-33-90256.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Mito, M. Ogawa, H. Deguchi, M. Yamashita, H. Miyasaka. J. Phys. Soc. Jpn **81**, 064716 (2012).
[2] M. Mito, H. Matsui, K. Tsuruta, H. Deguchi, J. Kishine, K. Inoue, Y. Kousaka. J. Phys. Soc. Jpn **84**, 104707 (2015).
[3] K. Tsuruta, M. Mito, H. Deguchi, S. Takagi, Y. Yoshida, K. Inoue. Polyhedron **30**, 3262 (2011).
[4] K. Tsuruta, M. Mito, H. Deguchi, J. Kishine, Y. Kousaka, J. Akimitsu, K. Inoue. Phys. Rev. B **97**, 094411 (2018).
[5] E.I. Golovenchits, V.A. Sanin. FTT **41**, *8*, 1437 (1999). (in Russian)
[6] A.B. Lazuta, I.I. Larionov, V.A. Ryzhov. ZhETF **73**, *6*, 1964 (1991). (in Russian)
[7] M. Bałanda, H.-A.K. von Nidda, M. Heinrich, A. Loid. Relaxation Phenomena. Springer Berlin, Heidelberg. (2003). P. 89–135.
[8] H. Sompolinsky, A. Zippelius, Phys. Rev. B **25**, 6860 (1982).
[9] L. Onsager. Phys. Rev. **65**, 117 (1944).
[10] J.A. Mydosh. Spin glasses: an experimental introduction. Taylor & Francis, London, Washington (1993). 280 p.
[11] B. Dieny, B. Barbara. J. Phys. **46**, 293 (1985).
[12] I.V. Zolotukhin, Yu.E. Kalinin. UFN **160**, *9*, 75 (1990). (in Russian)
[13] J.R.L. de Almeida, D.J. Thouless. J. Phys. A **11**, 983 (1978).
[14] E.V. Dvoretskaya, D.V. Korolev, O.V. Koplak, R.B. Morgunov. FTT **63**, *11*, 1874 (2021) (in Russian).
[15] Y.P. Tupolova, I.N. Shcherbakov, L.D. Popov, V.E. Lebedev, V.V. Tkachev, K.V. Zakharov, A.N. Vasiliev, D.V. Korchagin, A.V. Palii, S.M. Aldoshin. Dalton Trans. **48**, 6960 (2019).
[16] Y.P. Tupolova, I.N. Shcherbakov, L.D. Popov, R.B. Morgunov, D.V. Korchagin, V.E. Lebedev, A.V. Palii, S.M. Aldoshin. Dalton Trans. **49**, 15592 (2020).
[17] O.V. Koplak, E.V. Dvoretskaya, E.I. Kunitsyna, D.V. Korolev,
[18] E. Dvoretskaya, A. Palii, O. Koplak, R. Morgunov. J. Phys. Chem. Solids **157**, 110210 (2021).
[19] S. Sanvito, Chem. Soc. Rev. **40**, 3336 (2011).
[20] G.A. Timco, T.B. Faust, F. Tuna, R.E.P. Winpenny. Chem. Soc. Rev. **40**, 3067 (2011).
[21] G. Serrano, L. Poggini, M. Briganti, A.L. Sorrentino, G. Cucinotta, L. Malavolti, B. Cortigiani, E. Otero, P. Sainctavit, S. Loth, F. Parenti, A.-L. Barra, A. Vindigni, A. Cornia, F. Totti, M. Mannini, R. Sessoli. Nature Mater. **19**, 546 (2020).
[22] F. Luis, J. Bartolome, J.F. Fernandez, J. Tejada, J.M. Hernandez, X.X. Zhang, R. Ziolo. Phys. Rev. B **55**, *17*, 11448 (1997).
[23] F. Luis, R. Lopez-Ruiz, A. Millan, J.L. Garcia-Palacios. Comptes Rendus Chimie **11**, *10*, 1213 (2008).
[24] R.B. Morgunov, R.P. Shibaeva, E.B. Yagubsky, T. Kato, Y. Tanimoto. ZHETF (IN RUSSIAN)
[25] H. Maletta, W. Felsch. Z Physik B **37**, 55 (1980).
[27] I. Morgenstern, K. Binder. Phys. Rev. B **22**, 288 (1980).
[28] I.Ya. Korenblit, E.F. Shender. UFN **157**, 267 (1989). (in Russian).
[29] K.S. Burch, D. Mandrus, J.-G. Park. Nature **563**, 47 (2018).
[30] T.V. Drokina, G.A. Petrakovsky, M.S. Molokee, D.A. Velikanov. FTT **60**, *3*, 526 (2018). (in Russian).
[31] T.V. Drokina, M.S. Molokeeva, D.A. Velikanov, G.A. Petrakovsky, O.A. Bayukova. FTT **62**, *3*, 413 (2020). (in Russian).