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Dynamic Magnetic Susceptibility Method in Studies of Coordination Compounds

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Abstract—The measurement of the dynamic magnetic susceptibility is a universal method, which is used for the evaluation of magnetic properties of single molecule magnets by scientists all over the world. An information in the Russian scientific literature that can be useful for practical mastering of this method is presently insufficient. To fill this gap, in this work we present a detailed procedure of a magnetochemical experiment for observing slow magnetic relaxation in coordination compounds of 3*d*- and 4*f*-element ions and the complete characterization of the dynamics of the magnetic behavior. Special attention is given to usually omitted but important details related to all stages of studying the magnetic relaxation dynamics. The main variants of sample preparation are described, the logics of the construction of a measuring sequence and the procedure of experimental data processing are discussed, and advantages and drawbacks of some programs of the calculation of magnetic relaxation dynamics data are considered. The main concepts and equations used in experimental data analysis are presented, and the primary conclusions that can be made from the obtained results are proposed.

Keywords: magnetic properties, dynamic magnetic susceptibility, experimental procedures, magnetic relaxation, molecular magnetism

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INTRODUCTION

Single molecule magnets have been studied in rather detail by the world scientific society using a whole number of procedures for the characterization of substances and materials. Since the early 1990s when the first single molecule magnets have been found [1], scientists all over the world actively use measurements of the dynamic magnetic susceptibility (χ_{ac}) as the most universal, available, and objective method for the characterization of the remagnetization rate of molecules. The world scientific literature has accumulated a large body of high-class publications that provide the complete representation about this field of knowledge [2–25].

Wonderful books, manuals, and textbooks devoted to magnetochemistry [26–28], magnetic properties, magnetism, and magnetic materials [29] are available in the domestic scientific literature. However, a substantial drawback in the Russian literature should be mentioned concerning procedures of magnetochemical experiments in the field of characterization of the magnetic behavior dynamics. For instance, an excellent book *Modern Magnetochemistry* [30] by Yu.V. Rakitin and V.T. Kalinnikov was published as far as in 1994. The authors indicate in the preface to this book: "magnetochemistry as one of the trends in the chemical science underwent substantial changes in the years gone by." The changes in magnetochemistry that even could not be mentioned in this book took place within almost thirty years passed since the date of publishing the *Modern Magnetochemistry* book. One of such fields of magnetochemistry that was not mentioned in the above book is monomolecular magnetism. The review by Valentin Nikonov [31] sheds light on the most part of the main points of monomolecular magnetism for Russian-speaking researchers. Research groups dealing with cardinally different objects of the study are very significant researchers of molecular magnetism in Russia.

The decisive contribution to the foundation of molecular magnetism as a large trend of studies in Russia was made by researchers of the scientific schools guided by V.I. Ovcharenko, V.M. Novotortsev, and S.M. Aldoshin. Nowadays systematically significant studies of various aspects of molecular magnetism in our country are carried out by many research groups [32–43].

As follows from the title, the purpose of this work is to fill the gap in the area of optimum (from the viewpoint of instrument time expenses) procedures of magnetochemical experiments and in the knowledge necessary for the primary correct interpretation of obtained results.

This article becomes more topic due to the appearance of new laboratory magnetometers capable of measuring the dynamic magnetic susceptibility and because the available magnetometers in centers for collective use of many scientific institutions were reoriented to the study of molecular magnetism.

This article is primarily oriented towards experimentalists who for the first time met the measurements and interpretation of data on the dynamic magnetic susceptibility of coordination compounds of anisotropic 3*d*- and 4*f*-metal ions and who know the review by V. Novikov. In this work, we present an information concerning the theoretical aspect of this branch of knowledge only in the volume necessary for experimental data processing.

The procedures of magnetochemical experiment as applied to single molecule magnets presented in this article are composed of the experience of Rodolphe Clérac, the world-known magnetochemist working at the Paul Pascal Research Center (Centre de Recherche Paul Pascal, Bordeaux, France) [44–47], where one of the authors, N.N. Efimov, worked as a trainee in January 2015 and 2016, as well as of the personal, more than ten-years-old experience of N.N. Efimov's work in the area of molecular magnetism.

MAIN CONCEPTS

The following concepts specific for this branch of magnetochemistry are necessary for working in the area of molecular magnetism.

Single molecule magnet is a compound, whose individual molecule is capable of magnetizing and retaining magnetization for rather prolonged time in the absence of external magnetic field and is an analogue of classical ferromagnet in the scale of one molecule.

Measurements of the dynamic magnetic susceptibility (ac-magnetic susceptibility) are the main method for studying the dynamics of magnetic processes in substances and materials of different nature. The essence of the method is that the studied sample is placed in an alternating magnetic field, the direction of which varies via the harmonic law $H_{ac}(t) = H_0\cos(\omega t)$, and the magnetization of the sample is measured. The magnetization also varies via the harmonic law $M_{ac} = M_0\cos(\omega t - \varphi)$, where t is time, H_0 is the amplitude of the magnetic field modulation, ω is the cyclic frequency of magnetic field change ($\omega = 2\pi\nu$), M_0 is the magnetization of the sample, and φ is the phase delay. The dynamic magnetic susceptibility is written by the equation $\chi_{ac} = dM/dH$, i.e., is the tangent angle to the magnetization $M(H)$ at H equal to the intensity of the permanent external magnetic field H_{dc}. Reminding the equations for the cosine of the sum $\cos(\alpha + \beta) = \cos(\alpha)\cos(\beta) - \sin(\alpha)\sin(\beta)$ and cosine of the difference in angles $\cos(\alpha - \beta) = \cos(\alpha)\cos(\beta) + \sin(\alpha)\sin(\beta)$, M_{ac} can be rewritten in the form of Eq. (1).

$$\begin{aligned} M_{ac} &= M_0 = M_0\cos(\omega t)\cos(\varphi) \\ &+ M_0\sin(\omega t)\sin(\varphi) = (M_0/H_0)\sin(\varphi)H_0\sin(\omega t) \\ &= \chi' H_0\cos(\omega t) + \chi'' H_0\sin(\omega t), \qquad (1) \\ \text{where} \quad \chi' &= (M_0/H_0)\cos(\varphi); \\ \chi'' &= (M_0/H_0)\sin(\varphi). \end{aligned}$$

Slow magnetic relaxation is a relatively slow (characterized by the relaxation time τ) change in the direction of magnetization of the system with respect to the frequency ν of the applied alternating magnetic field H_{ac}. If the change in the magnetization of the sample is synphase (no phase delay, Fig. 1a) to the change in the alternating magnetic field, then the relaxation is considered to be fast. If the experimentally measured magnetization of the sample has the phase delay by some angle φ from the change in the alternating magnetic field, the magnetization relaxation is considered to be slow (Fig. 1b).

The magnetization relaxation time (τ, s) is the time interval within which the magnetization decreases by e times (e is the base of the natural logarithm). The magnetization relaxation time is the key characteristic of single molecule magnets and provides an idea about a possible time of information storage in the material.

The measurements of the magnetization in an alternating magnetic field provide two values: the magnetization amplitude and phase shift of the measured signal with respect to the alternating magnetic field φ. These data allow one to calculate the real χ' (dispersion, synphase, real, in-phase) and imaginary χ'' (corresponding to absorption, antiphase, nonsynphase, antiphase, dissipative, out-of-phase) components of the magnetic susceptibility. In this case, the magnetic susceptibility is a complex value, whose components, χ' and χ'', depend on the applied magnetic field frequency. The imaginary component of the susceptibility describes energy dissipation processes. If the frequency is low ($\omega\tau \ll 1$), the magnetization rather rapidly reacts to changes in the external field and, hence, the low-frequency limit will correspond to the isothermal susceptibility χ'_0 (another variant of designation is χ_T). The system insufficiently rapidly reacts to a field change with an increase in the frequency, and the opposite limit would correspond to the adiabatic susceptibility χ'_∞ (another variant of designation is χ_S).

SAMPLE PREPARATION

Measurements should be carried out for the samples in which the orientational rotation of individual crystallites under the external magnetic field was prevented by this or other method. These methods can be the following: pelleting of polycrystalline samples

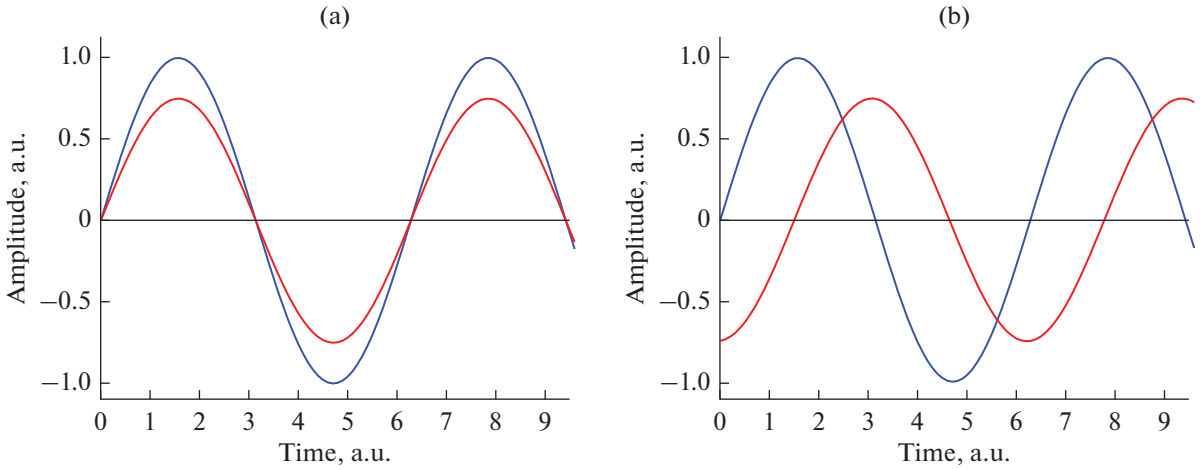


Fig. 1. Change in the magnetization of the sample (red line) vs. change in the alternating magnetic field amplitude (blue line). (a) Fast magnetic relaxation (change in the sample magnetization is synphase to the change in the external magnetic field intensity), and (b) slow magnetic relaxation (phase delay of the measured signal from the applied alternating magnetic field).

(drawbacks: this procedure requires a fairly large amount of the substance, solvate molecules can evaporate during pelleting, and amorphization of the sample is possible) and immobilization in eicosane (drawbacks: eicosane should be heated above its melting point, which can result in the loss of solvate molecules), Nujol, or mineral oil (drawbacks: the liquid state at relatively high temperatures imposes restraints on the magnetic field intensity at these temperatures). In the case of coordination compounds, hermetic packing of the studied sample wetted with the fluorinated (minimally prone to the negative effect of the environment and maximally inert toward the samples) mineral oil should be preferred. When the magnetic properties are measured, the sample is placed in a chamber in which a rarefied helium atmosphere is formed (pressure ~1–10 mmHg) and, therefore, hermetic packing is preferred for compounds containing solvate solvent molecules. At the same time, it should be kept in mind that more reliable methods for sample fixation should be used when studying ferromagnetic substances and materials (attracted to a magnet at room temperature).

After measurements, the contribution of the components used in sample preparation should be taken into account subtracting their magnetic contribution from the total values of magnetization of the sample and sample preparation components obtained by the measurements. A packing material (polyethylene) and a wetting agent (mineral oil, eicosane, Nujol, and others) usually contain no signals in an alternating magnetic field, and their contribution can be ignored. However, every new batch of components used in sample preparation should be checked to the absence of signals in an alternating field at temperatures of planned experiments in order to take them into account, but it is better to reject the use of similar components and replace them by “pure” analogues.

EXPERIMENTAL

In the study of the magnetic behavior dynamics aimed at obtaining a complete information about the presence of slow magnetic relaxation in the studied complex, one should primarily measure the frequency dependences of the dynamic magnetic susceptibility (real $\chi'(\nu)$ and imaginary $\chi''(\nu)$ components) in the zero magnetic field and in magnetic fields of different intensities at a minimum possible experimental temperature. The most characteristic magnetic field intensities H_{dc} at which χ_{ac} is measured are 0, 500, 1000, 1500, 2000, 2500, and 5000 Oe. The minimum rather stable experimental temperature on the Quantum Design equipment is 2 K (temperatures below the boiling point of liquid helium (4.2 K) are reached by pumping out helium vapors). At the first stage, in order to optimize the experimental time, the measurements are carried out at the magnetic field intensities multiple of 1000 Oe. The experiment is ceased in the case of χ'' different from zero. It should be kept in mind that the criterion of χ'' different from zero values should be considered to be $\chi'' \geq \chi'/10$ in the same units of measurements; i.e., the values of χ'' that were no more than 10 times lower than χ' at the same frequency, temperature, modulation amplitude, and external magnetic field intensity (for example, see the further figures with χ' and χ'').

In the case of finding nonzero $\chi''(\nu)$, the measurements should be continued at intermediate magnetic field intensities (intensity multiple of 500 Oe: 500, 1500, and 2500 Oe). The purpose of these measurements is the search for an optimum intensity of the external magnetic field that most efficiently sup-

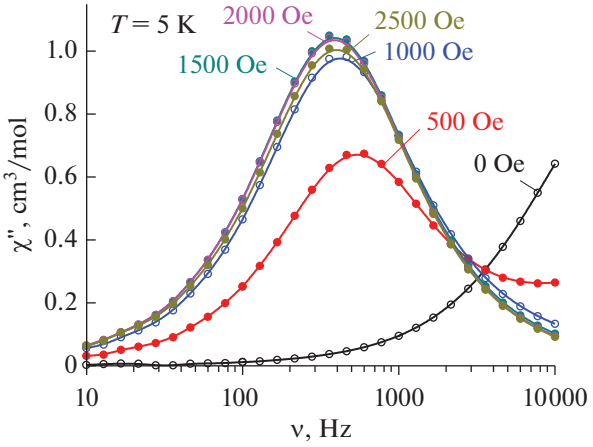


Fig. 2. Search for the optimum magnetic field intensity. The $\chi''(\nu)$ dependence for complex $[Dy(H_2O)_4(Terpy)Cl]Cl_2 \cdot 3H_2O$ at 5 K in magnetic fields of different intensities (plotted with the changes according to those in [48]).

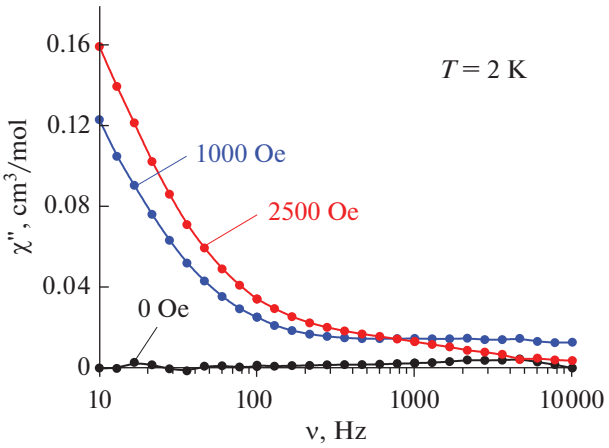


Fig. 3. Going the maximum on the $\chi''(\nu)$ dependence beyond the low-frequency range. The $\chi''(\nu)$ dependence for complex $[Yb(H_2O)_4(Terpy)Cl]Cl_2 \cdot 3H_2O$ at 2 K in magnetic fields of different intensities (plotted with the changes according to those in [48]).

presses the effect of quantum tunneling of magnetization (QTM). The criterion of the optimum intensity of the external magnetic field H_{dc} is the value at which the maximum on the $\chi''(\nu)$ dependence is observed at the minimum frequency, which corresponds to the maximum relaxation time of the system (Fig. 2). In other words, the magnetic field that most strongly retards the magnetization relaxation is optimal. In the case of a sufficient instrument time, the measurements can be conducted with a shorter increment over the magnetic field, which is especially urgent when the direct relaxation mechanism is involved and the relaxation time dependence on the magnetic field intensity must be approximated for the search for parameters of the direct relaxation mechanism and QTM (see section Data Processing and Interpretation). If the lowest relaxation rate was detected for a magnetic field intensity of 500 Oe, the search for the optimum magnetic field strength should be continued in the range of lower fields and, analogously, if the optimum magnetic field is 5000 Oe, magnetic fields of a higher intensity should be checked.

An example of the search for the optimum intensity of the external magnetic field for complex $[Dy(H_2O)_4(Terpy)Cl]Cl_2 \cdot 3H_2O$ [48] is shown in Fig. 2. It is seen that the maxima on the $\chi''(\nu)$ dependences are observed at the minimum frequency (~390 Hz) for the magnetic fields with intensities of 1500 and 2000 Oe. A lower value should be chosen as the optimum H_{dc} in the case of the exact (within inaccuracy) coincidence of the frequency at which the maximum on $\chi''(\nu)$ is observed. In this example, 1500 Oe were chosen as the optimum H_{dc}.

When the maximum is achieved on the $\chi''(\nu)$ dependence at the variation of the magnetic field intensity below the low-frequency limit (Fig. 3) accessible on the used equipment (for instance, 10 Hz in the case of the PPMS-9 equipment (Quantum Design), and 0.1 Hz for the MPMS-XL equipment), the optimum H_{dc} should be searched for at a higher temperature (e.g., 5 K, Fig. 2) at which the maxima on the $\chi''(\nu)$ plot can be observed in the working frequency range of the used equipment (10–10000 Hz for PPMS-9, and 0.1–1500 Hz for MPMS-XL).

Then the $\chi''(\nu)$ isotherms are measured in the magnetic field of an optimum intensity at higher temperatures ($T > 2$ K, Fig. 4) up to the temperatures at which the maximum on the $\chi''(\nu)$ dependence goes beyond the high-frequency limit ν (10000 Hz for PPMS-9, and 1500 Hz for MPMS-XL) with an increment of 1 K. If the maximum on $\chi''(\nu)$ went beyond the high-frequency limit of the used equipment already in the first (at 3 K) or second (4 K) step of changing temperature, the measurements should be performed with a shorter increment (by dividing in half: 0.5, 0.25, or 0.1 K) in the temperature range where the maximum on $\chi''(\nu)$ lies yet in the accessible frequency range. The criterion of choosing the temperature increment is the presence of at least three to four isotherms of the frequency dependences with a pronounced maximum on $\chi''(\nu)$, which is necessary for the construction of the temperature dependence of the relaxation time and its further processing (see section Data Processing and Interpretation). For the cases where the maximum on $\chi''(\nu)$ does not go beyond the accessible frequency range at temperature above 10 K, the temperature change increment can be increased to 2 K and more.

Since the position of the maximum on the $\chi''(\nu)$ dependence is very sensitive to a slightest temperature change, an additional holding at the measurement temperature from one to three minutes should be performed every time after the temperature change and

stabilization in order to neutralize the influence of the heat capacity of the sample and packing materials on the shape of the studied dependences. Therefore, a very precise temperature stabilization is needed for both sample holding and measurements.

A fairly great number of 3*d*-, 4*f*-, and 5*f*-element complexes can demonstrate slow magnetization relaxation at low temperature and external magnetic field application. These substances are named magnetic field-induced single molecule magnets. However, the uniqueness of the true single molecule magnets is that their slow magnetization relaxation can be observed without magnetic field application. The procedure described above for measuring the dynamic magnetic susceptibility was developed, first, for the characterization of the magnetic behavior of true single molecule magnets and continues to be the most convenient procedure for obtaining data on the magnetic relaxation of similar compounds.

The $\chi''(\nu)$ dependences are measured at the modulation amplitudes H_{ac} equal to 5, 3, and 1 Oe in frequency ranges of 10–100, 100–1000, and 1000–10000 Hz, respectively. This choice of H_{ac} favors the best signal/noise ratio in the low-frequency range and prevents a possible heating of the sample at high frequencies of an alternating magnetic field.

For the qualitative visualization of specific features of the $\chi'(\nu)$ and $\chi''(\nu)$ dependences and their subsequent approximation by the generalized Debye model, 10 measurements uniformly distributed over the logarithmic scale are needed per each frequency range of 10–100, 100–1000, and 1000–10000 Hz (as in Figs. 2–4). The tentative time of measuring one isotherm of the $\chi'(\nu)/\chi''(\nu)$ dependence for these number and position of points on the frequency axis using PPMS-9 is ~1 h.

DATA PROCESSING AND INTERPRETATION

It should be kept in mind that for the Quantum Design instruments the values in the output file are given in the real M' and imaginary M'' magnetization components. To determine the values of dynamic magnetic susceptibility components, the corresponding dynamic magnetization should be divided into the modulation amplitude: $\chi'(\nu) = M'(\nu)/H_{ac}$ or $\chi''(\nu) = M''(\nu)/H_{ac}$.

If the signal amplitude $\chi''(\nu)$ increases with increasing temperature (Fig. 5), this fact is worth mentioning. This effect is related to the collective behavior due to weak dipole–dipole or exchange interactions between paramagnetic ions [48–52].

When analyzing experimental data of measurements of the dynamic magnetic susceptibility, it is necessary to determine the relaxation times of the system at different temperatures, which can be performed by determining the frequency at which the isotherm of the $\chi'(\nu)$ dependence has an inflection or the $\chi''(\nu)$ dependence has a maximum. An analogous information can be obtained from an analysis of the temperature dependences $\chi'(T)$ and $\chi''(T)$ measured at constant frequencies (Fig. 6). Since the position of the maximum on the $\chi''(\nu)$ dependence can be determined with a sufficient accuracy without using a special mathematical apparatus, the relaxation time at this temperature is determined from the frequency at which the maximum is observed (ν_{max}). The relaxation time of the system at constant temperature is calculated by the following equation: $\tau = 1/\nu_{max}$. When the relaxation time of the system is estimated from the $\chi''(T)$ temperature dependences, the position of the maximum on this dependence is determined at fixed frequencies, which corresponds to the temperature at which the relaxation time is equal to the inverse measurement frequency $\tau = 1/\nu_{meas}$.

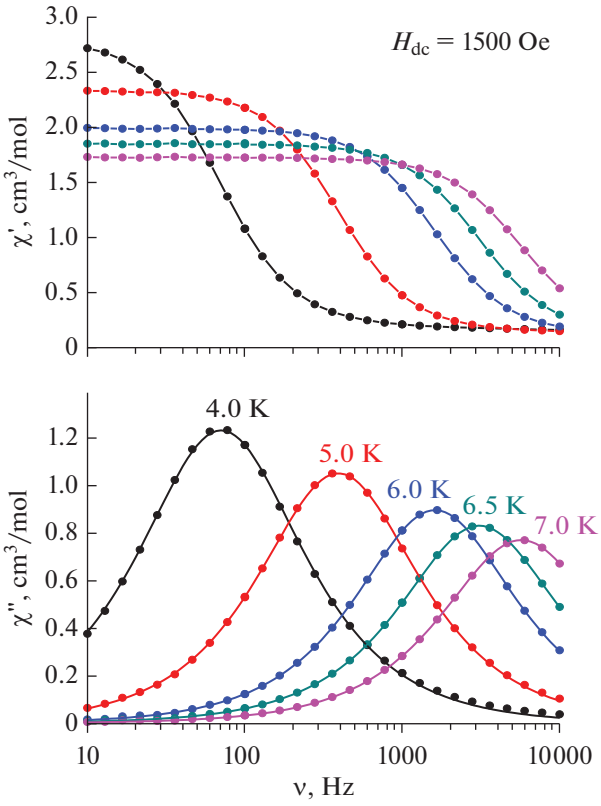


Fig. 4. Frequency dependences of the real $\chi'(\nu)$ and imaginary $\chi''(\nu)$ components of the dynamic magnetic susceptibility for complex $[Dy(H_2O)_4(Terpy)Cl]Cl_2 \cdot 3H_2O$ in the magnetic field with an optimum intensity of 1500 Oe (plotted with the changes according to those in [48]).

The generalized (for the case of some set of relaxation routes of the system, which is usually observed for real systems) Debye model is used for a more detailed analysis of the experimental dependences $\chi'(\nu)$ and $\chi''(\nu)$

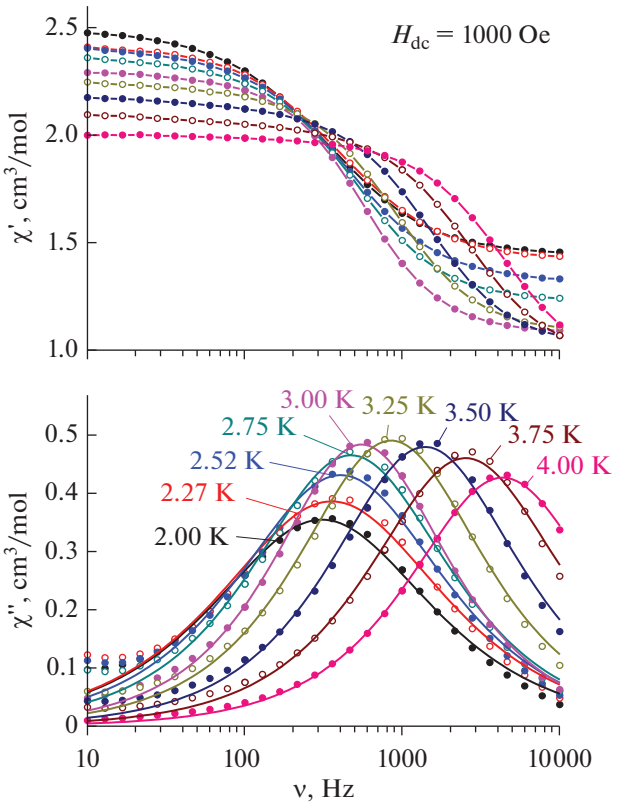


Fig. 5. Increase in the signal amplitude χ"(ν) with increasing temperature from 2 to 3 K indicates magnetic interactions between the paramagnetic centers. The frequency dependences of the real χ'(ν) and imaginary χ"(ν) components of the dynamic magnetic susceptibility for complex $[Dy(H_2O)_6Cl_2]Cl$ in the magnetic field with an optimum intensity of 1000 Oe (plotted with the changes according to those in [48]).

$$\chi' = \chi'_\infty + \frac{\left(\chi'_0 - \chi'_\infty\right)\left(1 + (2\pi\nu\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}\right)}{1 + 2(2\pi\nu\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2} + (2\pi\nu\tau)^{2(1-\alpha)}}, \quad (2)$$

$$\chi'' = \frac{\left(\chi'_0 - \chi'_\infty\right)(2\pi\nu\tau)^{1-\alpha}\cos\frac{\alpha\pi}{2}}{1 + 2(2\pi\nu\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2} + (2\pi\nu\tau)^{2(1-\alpha)}}, \quad (3)$$

where χ'_∞ is the adiabatic susceptibility at $\nu\tau \gg 1$ (high frequency), χ'_0 is the isothermal susceptibility at $\nu\tau \ll 1$ (low frequency), ν is the frequency, τ is the relaxation time, and α is the parameter of relaxation time distribution ($\alpha = 0$ for an ideally narrow distribution, and $\alpha = 1$ corresponds to an infinitely broad distribution). The examples of the experimental data approximation by the equations of the generalized Debye model are given in Figs. 4 and 5.

Both an individual analysis of the data on χ' and χ" and the simultaneous approximation of both dependences with the same values of the parameters, for instance, in the Origin program,[1] are possible [53]. If necessary, this equation can readily be transformed for the use in other programs that make it possible to perform the data approximation, for example, KaleidaGraph [54], and others.

When analyzing experimental data, the Argand diagram is constructed, which is analogous to the Cole–Cole plot: the χ"(χ') dependence of the imaginary component of the dynamic magnetic susceptibility on the real component. The example is shown in Fig. 7 [55, 56]. The construction of these dependences makes it possible to visually evaluate the presence of two routes of passing relaxation in the studied sample. Liviu F. Chibotaru and coauthor [57] consider (from the theoretical point of view) the possibility of the appearance of two peaks on the dependence of the imaginary component of the dynamic magnetic susceptibility. The model that adequately describes the appearance of two maxima on these dependences was constructed on the basis of the theoretical concepts for the system of three levels. It is shown that in the system containing *n* levels, the $n - 1$ maximum can appear on the χ"(ν) dependence. Two relaxation routes are often related to the presence of two nonequivalent paramagnetic centers with a similar coordination environment [58], and the nonequivalence can be associated with structure disordering. In turn, the disordering results in an insignificant change in the relaxation characteristics and, as a consequence, in the observation of two maxima on the frequency dependences of χ". In particular, it was reasonably assumed [59–61] that two maxima on the frequency dependence of χ" is most probably related to the disordering of one proton by the coordinated water molecule.

In the case of two maxima on the χ"(ν) dependences, the experimental data should be approximated by the sum of two Eqs. (2) and (3) (see Appendix in [62]).

The CC-FIT2 program was developed by the research group under the leadership of Nicholas F. Chilton (The University of Manchester) [63] for the processing of experimental data, particularly, the χ"(χ') dependences [64, 65]. This program makes it possible to automatically process files of AC measurement data output from the Quantum Design instruments. Experimental data can be approximated by the Debye model, generalized Debye model, or the sum of two generalized Debye models using the CC-FIT2 program. The program gives the relaxation times τ at each temperature and their determination inaccuracy from the results of the work for the χ"(χ') dependences with maxima. The CC-FIT2 program also allows approximations to be performed using various sets of relaxation mechanisms.

The MagSuite program [66] developed by Rouzières Mathieu (research group guided by Rodolphe

[1] For writing equations in Origin 8.5, see Appendix.

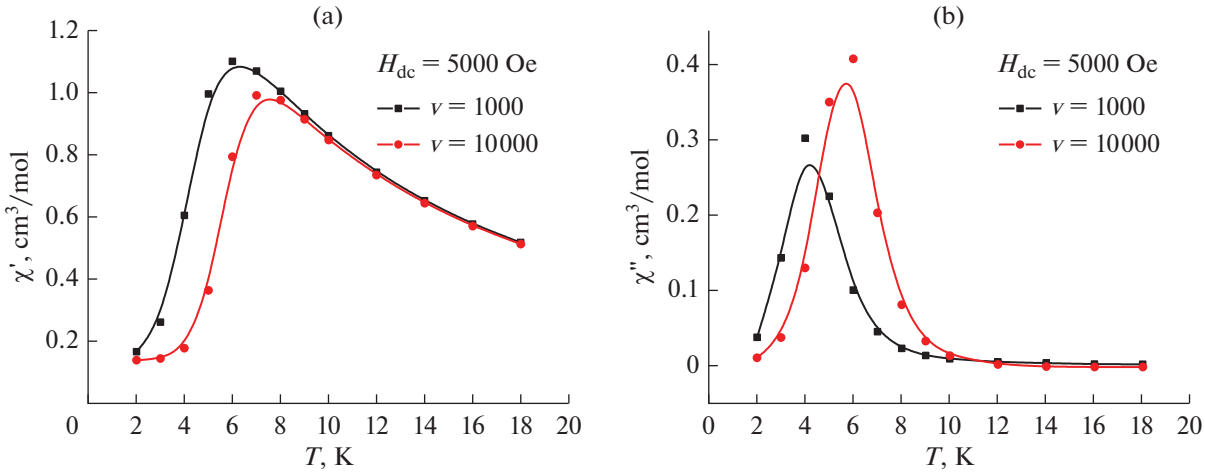


Fig. 6. Temperature dependences of (a) χ' and (b) χ" for complex $[Er(H_2O)_6Cl_2]Cl$ [48].

Clérac at the Paul Pascal Research Center (Centre de Recherche Paul Pascal, Bordeaux, France)) is another program that makes it possible to process data of AC experiments [67]. The MagSuite program has the whole functional of the CC-FIT2 program and additionally makes it possible to manipulate with the data: sorting, applying corrections, norming data, and exporting data to various formats.

Among drawbacks of the CC-FIT2 program (at the moment of writing this article) is the inconvenient interface, which can be changed by developers during further modifications of the program. A significant drawback of the MagSuite program, which can affect a wide abundance of the program, is the necessity to use the LabView shell for operation.

An undisputable advantage of the CC-FIT2 and MagSuite programs is a substantial automation of the processing leading to an increase in the velocity of experimental data processing.

RELAXATION MECHANISMS

When interpreting the results of measurements of the dynamic magnetic susceptibility, the experimental data on $\tau(T)$ are approximated by the mathematical expressions that describe different relaxation routes of the system or the sum of several possible relaxation routes. The following relaxation mechanisms are usually considered: Orbach mechanism, Raman mechanism, direct relaxation mechanism, and QTM. The simplified mathematical expressions for these relaxation mechanisms, scheme of the mechanism, and parameters with the dimensionalities used in the approximation are given in Table 1.

The temperature dependence of the relaxation time can be presented in different forms: $\tau(T)$, $\tau(1/T)$, $1/\tau(T)$, $1/\tau(1/T)$, $\log\tau(1/T)$, $\log\tau(\log T)$, and others. The $\tau(1/T)$ form using the logarithmic scale along the relaxation time axis is accepted to be priority. This construction of the dependence makes it possible to reveal the Orbach relaxation mechanism, which is the most interesting for researchers and represents a straight line in this system of coordinates. A similar shape is characteristic of the dependence in the $\log\tau(1/T)$ form, but an advantage of the construction of the dependence in the $\tau(1/T)$ form in the semilogarithmic system of coordinates is a possibility of determining the τ_0 parameter by the conceptual lengthening of the linear region of the dependence to the intersection with the relaxation time axis (infinitely high temperature limit): the intersection point will correspond to the time of the fastest relaxation of the system via the Orbach mechanism, i.e., parameter τ_0. For the

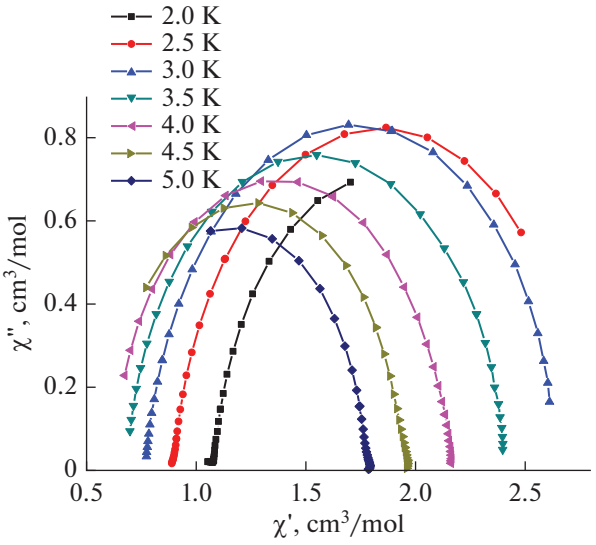
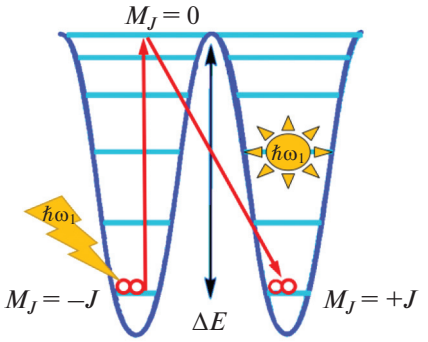
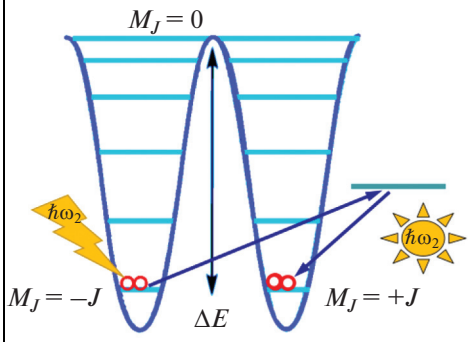
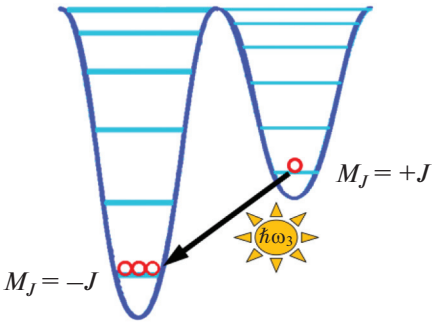
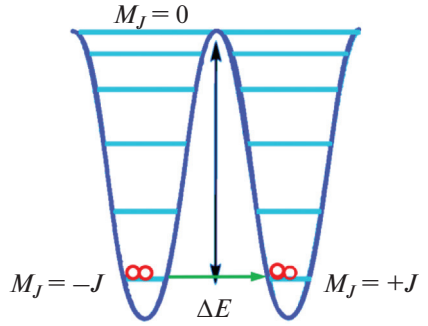


Fig. 7. Cole–Cole dependences for complex $[Er(H_2O)_6Cl_2]Cl$ in a dc magnetic field of 1000 Oe in a temperature range of 2–5 K (plotted with the changes according to those in [48]).

Table 1. Main mechanisms of the magnetization relaxation

Mathematical expression	Parameters	Schematic representation
Orbach relaxation mechanism $\tau_{Orbach}^{-1} = \tau_0^{-1}\exp\{-\Delta E/k_B T\}$ depends on temperature, independent of external magnetic field intensity	τ_0, s; $\Delta E/k_B$, K or ΔE, cm^{-1} k_B is Boltzmann constant $\tau_0 \sim 10^{-10}$–10^{-12} s 1 cm^{-1} = 1.439 K 1 K = 0.695 cm^{-1}	
Raman relaxation mechanism $\tau_{Raman}^{-1} = C_{Raman}\, T^{n\_Raman}$ depends on temperature, independent of external magnetic field intensity	C_{Raman} [K^{-n_Raman} s^{-1}] n_{Raman} [–] $C_{Raman} \sim 10^{-5}$–10^{-1} K^{-n_Raman} s^{-1} n_{Raman} = 2 (phonon bottle neck) 5 (closely arranged doublets) 7 (for non-Kramers) 9 (for Kramers)	
Direct relaxation mechanism $\tau_{direct}^{-1} = A_{direct} H^{n\_direct} T$ depends on temperature and external magnetic field intensity	A_{direct} [K^{-1} Oe^{-n_direct} s^{-1}] n_{direct} [–] n_{direct} = 2 (for non-Kramers) 4 (for Kramers)	
Quantum tunneling of magnetization $\tau_{QTM}^{-1} = B_1/(1 + B_2 H^2)$ depends on external magnetic field intensity, independent of temperature	B_1, s^{-1}; B_2, Oe^{-2}	

decisive influence of the Raman mechanism, the linear temperature dependence of the relaxation time is observed for the construction of the plot of the relaxation time on temperature with logarithmic scales along both axes. The examples of the temperature dependences of the relaxation time for the Orbach and Raman mechanisms with different sets of relaxation parameters are shown in Fig. 8 and Fig. S1. It should be mentioned that from the viewpoint of temperature dependences the direct mechanism looks as the

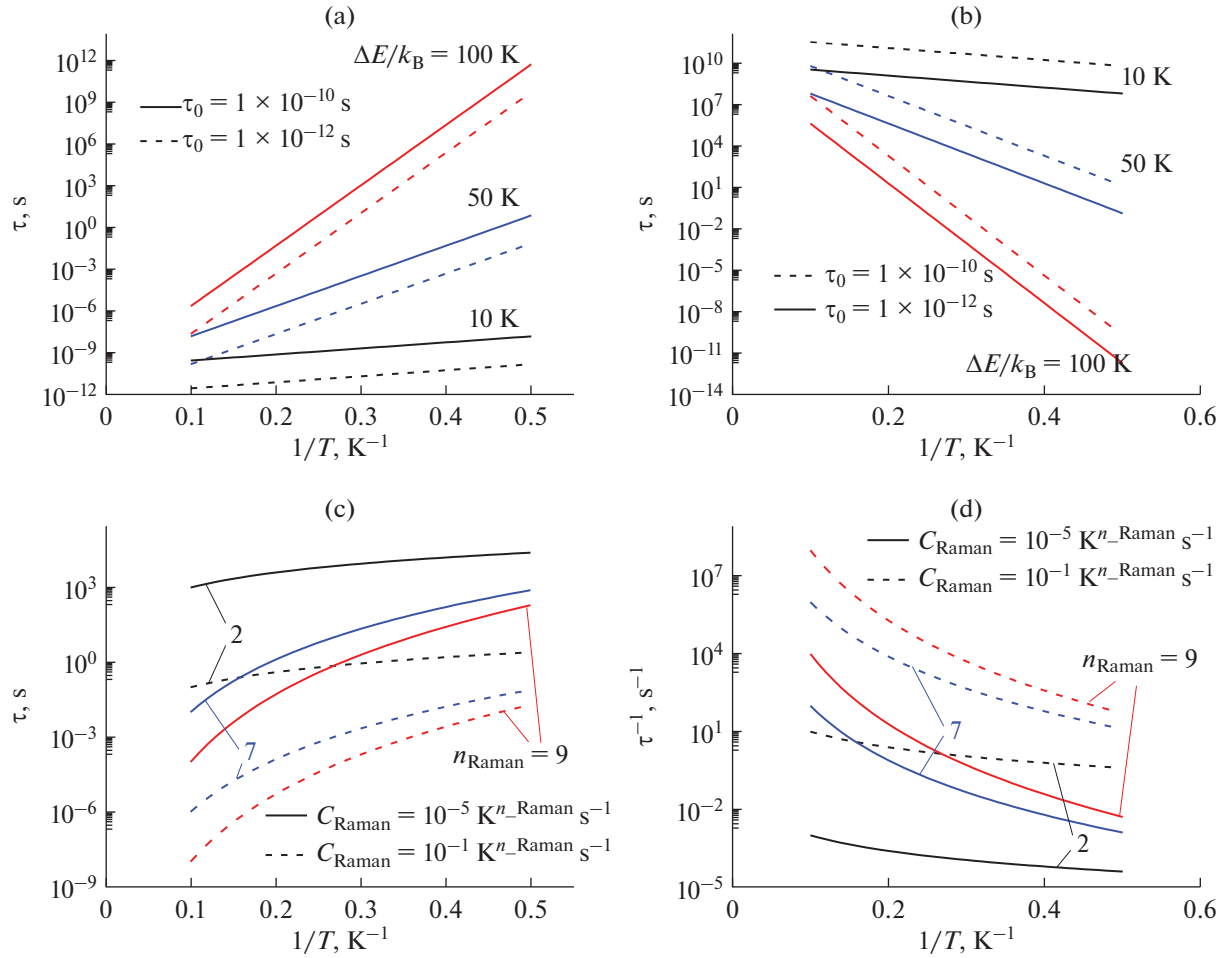


Fig. 8. Temperature dependences of the relaxation time for different constructions along the axes of coordinates for the (a, b) Orbach and (c, d) Raman mechanisms with the parameters presented on the plots.

Raman mechanism with n_{Raman}= 1 and, therefore, its temperature dependence is not presented in Fig. 8 and Fig. S1. If the QTM plays the leading role in the system, then the temperature dependence of the relaxation time is parallel to the temperature axis regardless of the form of this dependence (τ(*T*), τ(1/*T*), or others).

The Orbach relaxation, Raman relaxation, and relaxation via the direct mechanism occur due to the phonon interaction. Phonons are energy quanta of the matched vibrational motion of atoms of the solid. Two phonons are involved in the Orbach and Raman relaxations. In the first case, the magnetization relaxation proceeds through the real energy level. In the second case, the virtual level is involved. The ħω energies of the absorbed and emitted phonons coincide in the zero magnetic field. The direct relaxation mechanism is one-phonon and accompanied by the transition of the system from the higher energy level to the lower level with phonon emission. Phonons are not involved in the relaxation via the QTM mechanism.

More specific relaxation mechanisms and somewhat more complicated writing of mathematical expressions (with a greater number of parameters) of the indicated above mechanisms are sometimes used in the world scientific literature. For more details of the magnetization relaxation mechanisms, see works of Roman Boča, e.g., [47].

The parameters in the equations for some relaxation mechanisms are often found at the values characteristic of these or other systems, for instance, for Kramers (containing odd number of lone electrons) and non-Kramers (even number of electrons) ions. The most frequently used or characteristic values of the parameters are given in the column "Parameters."

When approximating the experimental temperature dependences of the relaxation time by a combination of several relaxation mechanisms, it should be kept in mind that the additive magnitude is composed of the value inverse to the relaxation time and the number of experimental points should be equal to or higher than the number of parameters of the approximating function. In the majority of cases, experimen-

tal data are satisfactorily described by the sum of at most two relaxation mechanisms.

For the relaxation mechanisms depending on the external magnetic field intensity (direct mechanism and QTM), it seems reasonable to perform simultaneously approximations of the relaxation time dependences on the temperature and intensity of the external magnetic field in order to increase the accuracy of the parameters of the model. In essence, this is equivalent to the approximation of points in the three-dimensional space "temperature–field–relaxation time."

When the experimental data are analyzed, they are approximated in fact by individual relaxation mechanisms or by their sums. For the selected mechanisms, see Appendix (Table S1).

An interesting example of considerations about the accomplishment of different relaxation mechanisms in the studied complexes is given in the supplementary materials of [68].

It should be mentioned that the results of theoretical calculations are necessary for an adequate choice of the mechanism or the sum of the relaxation mechanisms to compare the obtained experimental data, for instance, on the remagnetization barrier, with the theoretical values of the positions of the energy levels of the paramagnetic ion.

To conclude, technical details and specific features of the experiment, which are frequently omitted in both domestic and world scientific literature, sometimes prevent efficient mastering of the dynamic magnetic susceptibility method. The dynamic magnetic susceptibility method is highly sensitive and informative, but its mastering needs specific knowledge, which was enlightened in this work. As a whole, this method is rather time-consuming, but the duration of measurements can substantially be shortened due to the understanding of algorithms of setting up experiments. The data presented in this work will help both young scientist-experimentalists to understand foundations of composing measuring sequences and more experienced colleagues to use this article as a reference material on the processing and primary interpretation of the obtained experimental data.

SUPPLEMENTARY INFORMATION

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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