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## Effect of contact with a metal surface on magnetic relaxation in monomolecular magnets in zero magnetic field

© E.I. Kunitsyna<sup>1</sup>, R.B. Morgunov<sup>1,2,3,¶</sup>, R.A. Valeev<sup>3</sup>, V.P. Piskorskii<sup>3</sup>, M.V. Burkanov<sup>3</sup>

<sup>1</sup>Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS, Chernogolovka, Russia

<sup>2</sup>Tambov State Technical University, Tambov, Russia

<sup>3</sup>All-Russian Scientific Research Institute of Aviation Materials of the Research Center „Kurchatov Institute“, Moscow, Russia

¶ E-mail: spintronics2022@yandex.ru

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The appearance of relaxation maxima on the frequency dependence of magnetic susceptibility was discovered when ferromagnetic demagnetized microparticles of the PrDyFeCoB metal alloy were mixed with an erbium-based molecular magnet complex. At 2 K, ferromagnetic metal microparticles, as well as molecular complexes, did not exhibit magnetic relaxation in the frequency range of 0.1–1400 Hz, accessible to the SQUID magnetometer. In a pressed mixture of a composite material made from these components, the magnetic relaxation signal has a maximum at  $\sim 1$  kHz. X-ray photoelectron spectroscopy (XPS) of the composite material and comparison of the XPS spectra with the spectra of the initial components of the composite showed that the 10-coordinated complex is oxidized to 8-coordinated as a result of contact with the surface of demagnetized metal microspheres.

**Keywords:** molecular magnets, hybridization of molecular orbitals, magnetic relaxation, composite materials.

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### 1. Introduction

Molecular magnets (MM) are metal-organic complexes, wherein a metal ion is surrounded by atoms which create certain symmetry of the crystal field and thereby specify splitting of energy electron levels in the metal ion. As a rule, there is strategy of chemical modification of such complexes during preparation thereof as a result of the multi-stage chemical reactions. It can adjust the ligand field inside the complexes and control magnetic relaxation of the metal ions therein. In the crystal lattice, the complexes are bonded by Van der Waals forces, so the magnetic interactions therebetween are quite small. It ensures isolation of separate complexes and enables discussing a unit complex, such as a nanomagnet that can be switched by an external magnetic field into various states of its magnetization. The modern physics of molecular magnetism is diverse and required both for creating q-bits and quantum registers on separate molecular magnets and for other single-molecule devices (see, for example, reviews [1,2]).

One of the strategies for controlling the MM electron state is its modification by a metal surface [3–6]. The literature mentions several possible mechanisms of influence of the metal surface on the electron processes in the complexes located thereon: 1) hybridization of molecular orbitals of the complex, 2) orientation of the molecular complex axis by the surface, 3) ionization of the complex in a transition of the electron between it and the metal surface, 4) influence of the magnetic field of scattering of the ferromagnetic

metal on spin transitions inside the complex, 5) a chemical reaction of oxidation of the complex by oxygen available on the metal surface. The initial experiments in this field have shown that diamagnetic metals (platinum, gold) can significantly affect the molecular magnets by hybridization of the molecular orbitals of the complexes [3,6,7]. Recently, considerable interest is paid to the experiments which select a superconductive [7–9] or ferromagnetic metal [4–6] for creating a contact with the molecular magnet. In both the cases, modification of the electron states and the processes of spin relaxation of the complexes is additionally controlled by Zeeman interaction resulting from a scattering field of the superconductor or the ferromagnetic. Thus, for example, when creating the MM composites with the ferromagnetic material, the latter can keep an internal residual magnetic field, which is a regulator of the rate of magnetic relaxation in the molecular magnet. In some cases, it brings significant improvements as the magnetic field inhibits magnetic relaxation blocking its Raman and Orbach parts [4–6]. As a result, even those molecular magnets that have too fast relaxation without the magnetic field and thus are unsuitable for quantum logic operations can be functionalized by introducing them into the superconducting or ferromagnetic matrix. Even without the external magnetic field, the residual magnetic field in such a medium sustains retarded spin relaxation providing for conditions for q-bit decoherence. At the same time, it is often unclear whether contact factors which are observed for diamagnetic metals act together with Zeeman interaction. In particular, in

the studies [4–6] which have considered the ferromagnetic scattering field for interpretation of the obtained results, a role of other above-listed channels of impact of the surface on the complexes is still unclear. In particular, they provide no data specifying what is relaxation in the composite with demagnetized ferromagnetic particles.

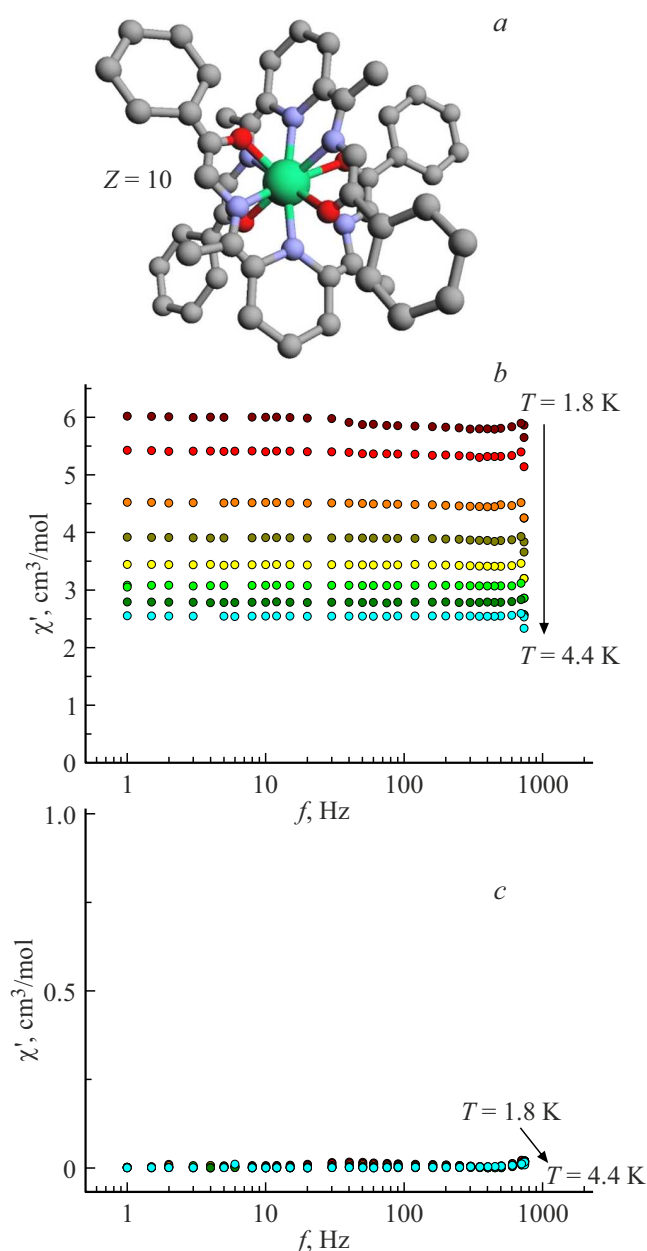
The present study is aimed at creating conditions for establishing the role of the MM contact with the surface of the demagnetized ferromagnetic in magnetic relaxation of the complexes  $\text{Er}^{3+}$  under conditions with no Zeeman interaction of the molecular magnetic with its magnetic field as well as with no external magnetic field.

## 2. Procedure and samples

The molecular complexes  $[\text{Er}(\text{HL})(\text{L})] \cdot 4\text{CHCl}_3 \cdot \text{H}_2\text{O}$ , where  $\text{L} = \text{DAPBH} = 2,6\text{-bis(phenylhydrazone)pyridine}$  contain the Kramers ion  $\text{Er}^{3+}$  in the ground state  $^4I_{15/2}$  with a high angular moment  $J = 15/2$ . The complexes were synthesized in the study [10], which specified its atomic structure (Figure 1, *a*). The crystal lattice of the molecular microcrystals corresponds to the space group  $P2_12_12_1$  [10]. In these complexes, in the zero magnetic field no magnetic relaxation is observed at the frequencies of 0.1–1400 Hz, i.e. the real  $\chi'$  and the imaginary  $\chi''$  parts of the magnetic susceptibility were constant (Figure 1, *b* and *c*). However, application of the magnetic field 1.5 kOe causes appearance of the maximums of the real and the imaginary parts of magnetic susceptibility in the frequency range, thereby corresponding to magnetic relaxation in the study [10]. The magnetic field removes the barrier  $U_{\text{eff}} = 87\text{ K}$ , which results from spin-orbit interaction that blocks spin relaxation [10].

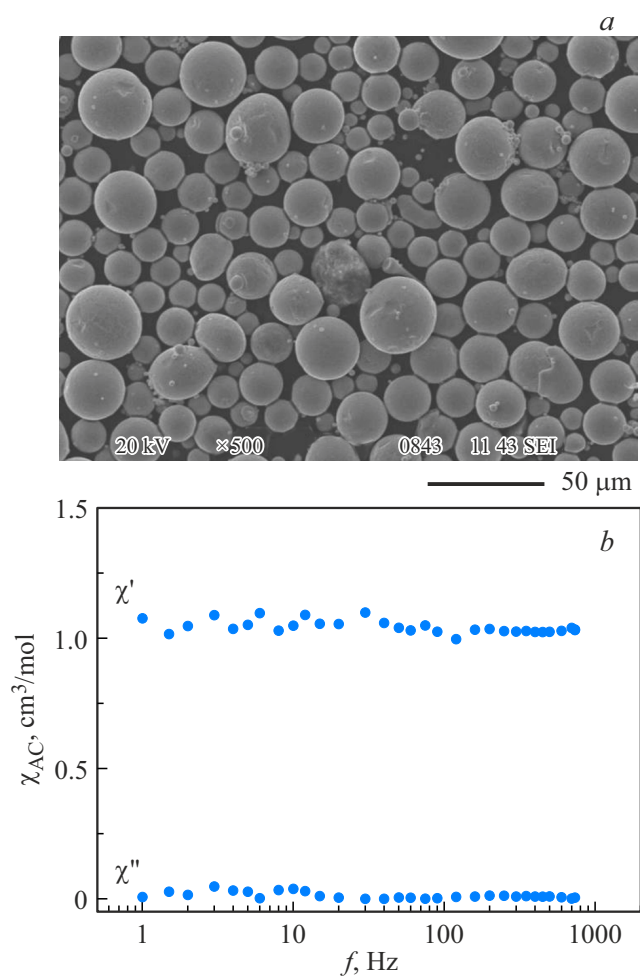
Another composite component consisted of the PrDyFeCoB microparticles with the average diameter of  $10\ \mu\text{m}$ , which have a high coercive force of 20 kOe at 2 K and are usually used for creating baked magnets (Figure 2, *a*). The detailed information about manufacturing of these particles and properties thereof are given in the study [11]. These particles were demagnetized in the variable magnetic field, so the residual magnetic field possibly created in the composite by them, did not exceed 10 Oe. It has almost no difference from the zero field, as it does not result in appearance of magnetic relaxation in the frequency range available for the SQUID magnetometer. The real  $\chi'$  and the imaginary  $\chi''$  parts of magnetic susceptibility of the microparticles have not exhibited maximums on the frequency dependence at a temperature at which magnetic relaxation of the erbium complexes in the composite was studied (Figure 2, *b*).

Composited plates of the diameter of 5 and the thickness of 1 mm were pressed by a mechanic press from a mixture of the 85 vol.% microparticles and the 15 vol.% complex. X-ray photoelectron spectroscopy (XPS) was used to obtain the spectra that characterize a degree of oxidation of the elements at the depth of  $\sim 1\text{ nm}$ . The XPS spectrometer



**Figure 1.** *a* — the atomic structure of the complex  $[\text{Er}(\text{HL})(\text{L})] \cdot 4\text{CHCl}_3 \cdot \text{H}_2\text{O}$  (the green ball — the Er atom, the violet balls — the N atoms, the red ones — the O atoms, and the grey ones — the C atoms); *b, c* — the dependences of the real  $\chi'$  and the imaginary  $\chi''$  parts of magnetic susceptibility on the frequency for a powder of the complex  $[\text{Er}(\text{HL})(\text{L})] \cdot 4\text{CHCl}_3 \cdot \text{H}_2\text{O}$  without microparticles in the zero DC-field within the temperature range  $T = 1.8\text{--}4.4\text{ K}$ .

was Specs PHOIBOS 150 MCD-9 designed with an X-ray cathode with Mg  $K\alpha$  radiation of the energy of 1253.6 eV and with the electron gun SPECS FG20. The complete spectrum was recorded with a step of 1 eV, so were the spectra of separate lines with a step of 0.1 eV. During XPS, the composite sample was placed on a surface of a conducting carbon tape in ultra-high vacuum  $3 \cdot 10^{-8}\text{ Pa}$ .



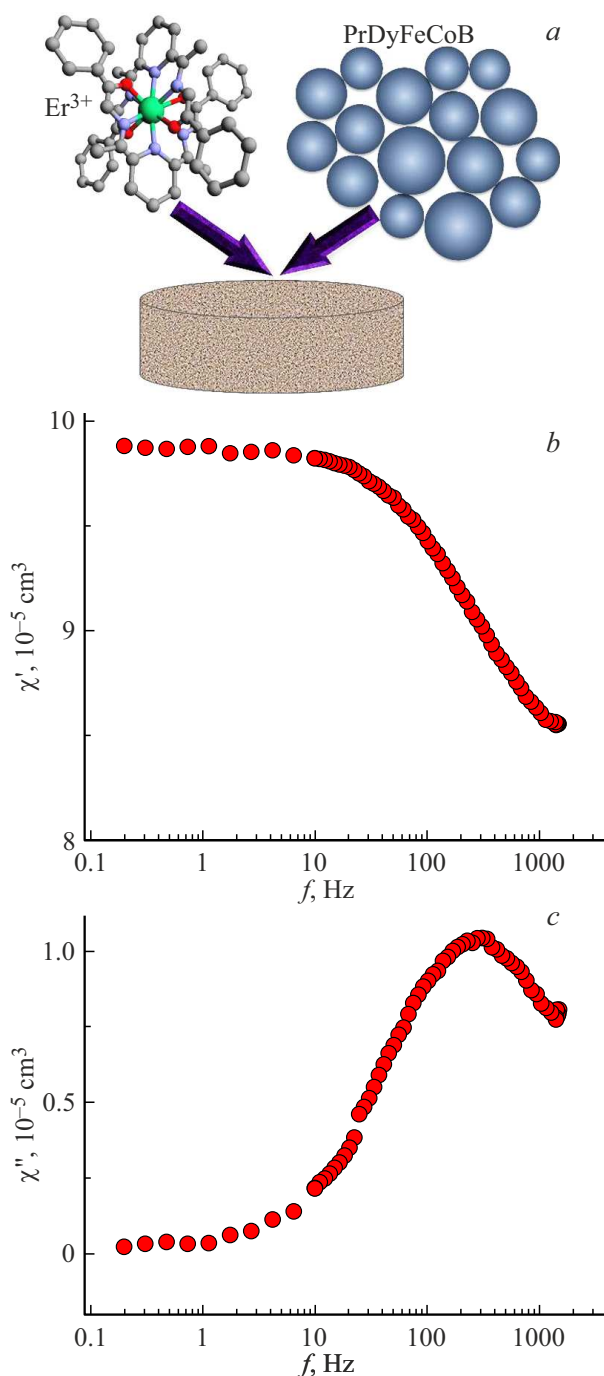
**Figure 2.** *a* — the image of the ferromagnetic microparticles in the electron microscope; *b* — the dependences of the real  $\chi'$  and the imaginary  $\chi''$  parts of magnetic susceptibility of the microparticles on the frequency of the variable magnetic field, as recorded in the constant field  $H_{DC} = 0$  Oe at the temperature of 2 K without pre-magnetization with no erbium complex.

The magnetic measurements were conducted by means of the magnetometer SQUID MPMS XL, Quantum Design. The magnetic susceptibility was measured in the variable magnetic field of the amplitude of 4 Oe at the frequencies within the range 0.1–1400 Hz in the temperature range of 1.8–5 K. The real  $\chi'$  and the imaginary  $\chi''$  parts of magnetic susceptibility were recorded.

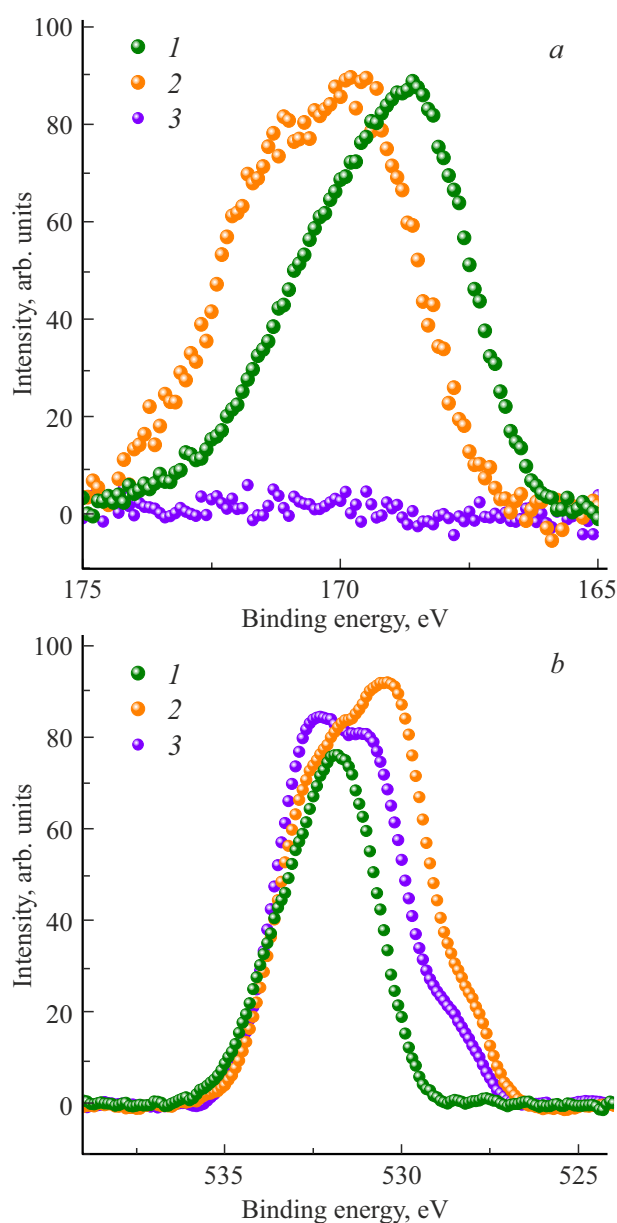
### 3. Experimental results

The pressed plate of the composite consisting of the microparticles and the erbium complex powder (Figure 3, *a*) demonstrates the frequency dependences of the real and imaginary parts of magnetic susceptibility, which are typical for magnetic relaxation (Figure 3, *b* and *c*). Since the microparticles were demagnetized and their created magnetic field 10 Oe was small, it means that only one

contact of the microparticles with the erbium complexes results in reduction of the rate of magnetic relaxation. Without contact with the metal surface in the zero field, this relaxation was certainly present, but it occurred at the high frequencies  $\sim 10$ – $100$  kHz, which are unavailable for the SQUID magnetometer. That is why pressing the mixture of the microparticles and the complexes results in reduction



**Figure 3.** *a* — the diagram of pressing the composite plate; *b, c* — the dependences of the real  $\chi'$  and the imaginary  $\chi''$  parts of magnetic susceptibility of the composite sample on the frequency at the temperature of 2 K in the zero DC-field without pre-magnetization.



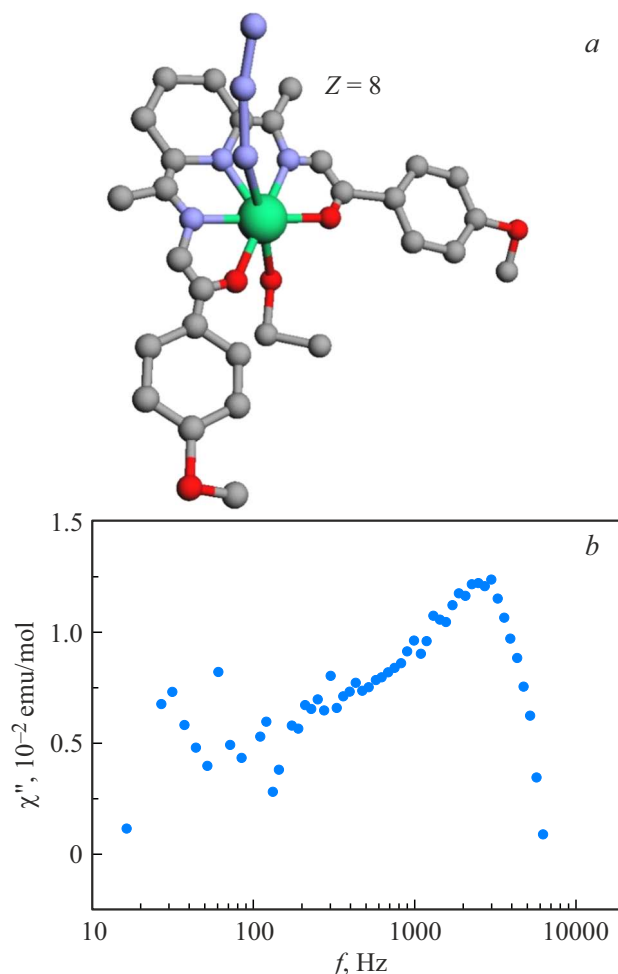
**Figure 4.** XPS spectra within the areas: *a* — Er 4*d*, *b* — O 1*s*, in the sample containing only the complexes [Er(HL)(L)] · 4CHCl<sub>3</sub> · H<sub>2</sub>O (1), in the composite sample containing the complexes and the microparticles (2), in the sample containing only the microparticles (3).

of the relaxation frequency, having the same-sign effect on the complexes as application of the external magnetic field [12].

The contact of the metal surface with the complexes could result in chemical modification of the complexes. In order to check this assumption, the internal surface of the composite plate, which was obtained at its section, was investigated for the XPS spectra for all the chemical elements inside the microparticles and the complexes. The changes of the spectra of the chemical elements due to pressing have been detected only for the 4*d* shell of Er<sup>3+</sup> and for the

1*s* shell of oxygen. The other elements demonstrated the identical spectra before and after pressing. Figure 4 shows comparison of the XPS spectra of erbium and oxygen in the initial pure complexes before introducing them into the composite (1), inside the composite (2) and in the microparticles outside the composite (3). Decomposition of these spectra into Gaussian components and analysis of a portion of the transformed complexes from the XPS spectra indicate that the ~20% complexes have changed their chemical state. The change of the spectra of oxygen available in the oxidized subsurface layers of the metal and the erbium complexes implies that the contact of the complexes and the surface results in oxidation of the erbium complexes.

This assumption has been checked by us by using independently synthesized eight-coordinated erbium complexes that are described in the study [13] (Figure 5, *a*). The frequency dependence of the imaginary part of magnetic susceptibility of these complexes was measured to detect



**Figure 5.** *a* — The atomic structure of the eight-coordinated complex [Er(DAPMBH)(N<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>OH]C<sub>2</sub>H<sub>5</sub>OH; *b* — the dependence of the imaginary part  $\chi''$  of magnetic susceptibility on the frequency for the eight-coordinated erbium complex at the temperature of 2 K in the zero DC-field.

a maximum at the frequency of  $\sim 3000$  Hz in the zero magnetic field (Figure 5, *b*). The frequency dependence  $\chi''(f)$  in the eight-coordinated complex does not coincide with those detected in the composite. Nevertheless, the very fact of magnetic relaxation of such complexes falling into an available frequency window indicates that contact of the complexes with the metal surface may result in oxidation thereof. The same is indicated by the fact that as a result of pressing the XPS spectra have only the signals of  $\text{Er}^{3+}$  and  $\text{O}^{-2}$  changed.

#### 4. Discussion

An surface area of one microparticle of the diameter of  $d = 10^{-5}$  m is  $\sim 10^{-9}$  m<sup>2</sup>. With the volume fraction of the microparticles 85% in the plate of the volume of  $2 \cdot 10^{-8}$  m<sup>3</sup>, the number of these particles will be  $\sim 5 \cdot 10^7$ . In assumption that the entire surface of each microparticle contacts the MM powder, the total area of contact with the complex will be 0.02 m<sup>2</sup>. Assuming that as per X-ray diffraction data the erbium compound under study has a distance between the neighbor complexes  $\sim 3$  nm, a single layer of these complexes fully covering the metal surface will have a volume of  $\sim 3 \cdot 10^{-11}$  m<sup>3</sup>. The full volume occupied by the complexes is 15% of the plate volume, i.e.  $3 \cdot 10^{-9}$  m<sup>3</sup>. It means that the portion of the complex in contact with the metal surface is  $\sim 1\%$ . This value enables involvement of many more erbium complexes in contact with the surface than achievable values in measurements of the properties of the complexes on a flat surface. That is why the strategy of investigating the complexes in the composite with the microparticles is much more effective than creating film single-layer samples. Besides, technically, is much simpler. However, the obtained evaluation of the expected fraction of the modified complexes makes it impossible to anticipate that the change in the XPS spectra will be 20–30% of the value after mixing the components in the composite. The ten-fold difference between the calculated fraction of the molecules in contact with the metal  $\sim 1\%$  and the experimentally evaluated fraction of the modified molecules  $\sim 20\%$  indicates that many more molecules were in contact with the metal during mixing and pressing of the composite. Even those complexes that are not in contact with the metal in the already pressed composite had such contact during preparation of the composite.

The relaxation frequency  $\tau^{-1}$  of the complexes at the low temperatures can be presented as a sum of the magnetic relaxation frequencies across the four independent channels [14–19]:

$$\tau^{-1} = \tau_{\text{QTM}}(H)^{-1} + \tau_{\text{Direct}}(H; T)^{-1} + \tau_{\text{Raman}}(T)^{-1} + \tau_{\text{Orbach}}(T)^{-1}. \quad (1)$$

Here, the first two summands depend on the field. The first summand  $\tau_{\text{QTM}}^{-1}$  describes quantum tunneling of

magnetization and does not depend on the temperature. As shown earlier, it is a high value of the frequency of quantum tunneling at 2 K that results in the high frequency of magnetic relaxation outside the frequency window available in our experiments. With increase in the temperature, there is increase in three other summands in such a way that even at 10 K quantum tunneling insignificantly contributes to the total rate of magnetic relaxation.

The second summand  $\tau_{\text{Direct}}^{-1}$  describes direct magnet relaxation caused by fluctuations of the electromagnetic fields of the crystal lattice. The summand  $\tau_{\text{Raman}}^{-1}$  corresponds to the Raman relaxation process that is irrelevant of the magnetic field and occurs with involvement of excited virtual states of phonons at the temperatures below the Debye temperature. The fourth summand  $\tau_{\text{Orbach}}^{-1}$  describes thermally activated Orbach relaxation, which is a two-phonon process, wherein energy is transferred from the magnetic moment to the crystal lattice via low levels of the phonon spectrum.

Predominance of tunnel relaxation at the low temperatures makes it impossible to control magnetic relaxation by means of other relaxation channels. As our experiments have not had the magnetic field applied, it is difficult to describe in a standard way field dependences of each of the mentioned relaxation channels. It is obvious that only reduction of the first summand  $\tau_{\text{QTM}}^{-1}$  as a result of change of the atomic structure of the complex in oxidation can explain significant deceleration of the rate of quantum tunneling and the total relaxation frequency defined thereby.

In conclusion, we note advantages that are provided by the composite based on the molecular magnetic and the ferromagnetic nanoparticles: 1) the hard pressed samples are much more suitable for manufacturing of devices in comparison with the initial micropowder of the complex produced from chemical synthesis, and they can be fragmented into nano- or sub-micron samples that are separate devices with an individual frequency of magnetic relaxation, 2) application of the external field up to 1 T for suppression of magnetic relaxation and support of q-bit coherence is not required, 3) the frequency window of magnetic relaxation may be specified by a level of magnetization of the microparticles when taking into account chemical interaction of the complexes with the surface, 4) the surface of contact of the metal with the complexes in the composites is significantly higher than in the planar film samples. We also note that the trend for creating the composite materials is actively developed in the literature. In the recent studies [7,8], the MM complexes are placed on a surface of lead, which becomes superconducting at the low temperatures so that the frozen magnetic flux kept currents in it without an external field, providing for the plate scattering field. This scattering field reduced the frequency of quantum tunneling and resulted in outcomes that are similar to those described in the present study.

## 5. Conclusion

The present study proposes a new method of functionalization of the micropowders of molecular magnetics. This method lies in creating the composite, in which a significant fraction of the MM complexes is or was in contact with the metal surface during composite pressing. Even without the external magnetic field and the magnetic field created by the microparticles, the complexes in these composites are already modified just owing to contact to the metal surface. In case of the composite components selected in our study, there was evidently oxidation of the erbium complexes as a result of contact with the metal and suppression of quantum tunneling of magnetization in the complexes. It has provided for reduction of the frequency of magnetic relaxation into our frequency window that is suitable for the experiments and necessary for reduction of the level of thermal decoherence of q-bits. Generally, it can be expected that depending on a metal type and a complex type, contact of the complexes with the metal can result in other phenomena related to hybridization of the molecular orbitals, the change of the Fermi level of the metal and to polarization of the complexes and their orientation. Thus, preparation of the pressed composite with various metals is a new effective method of engineering molecular magnetics.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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