Electron Paramagnetic Resonance Studies of $GdMnO_3$ Single Crystal and Thin Film Deposited onto a $LaAlO_3$ Substrate

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Electronic paramagnetic resonance (EPR) spectra of a $GdMnO_3$ single crystal and $GdMnO_3/LaAlO_3$ thin film have been measured at *X*- and *Q*-band frequencies in the temperature range from 4.2 to 300 K. It is found that the EPR spectrum of a $GdMnO_3$ single crystal consists of only one broad exchange-narrowed line. Unusual magnetism is observed at the interface between the $GdMnO_3$ thin film and $LaAlO_3$ substrate, where it is possible to see the fine structure of the EPR spectrum for a Gd^{3+} ion. The parameters characterizing the fine structure related to the Gd^{3+} ion in the $GdMnO_3$ film deposited onto the $LaAlO_3$ substrate are determined.

Currently, we see the growing interest in multiferroics, that is, in materials with coexisting magnetic and ferroelectric orderings, where magnetic and electrical degrees of freedom are coupled to each other. The interest is stimulated not only by the novel physical properties of such materials but also by the possibility of controlling their state by an applied magnetic or electric field, which is promising for the development of new functional materials.

The properties of a material in the form of a single crystal and thin film may be different. An interface of two substances can exhibit physical properties unusual for these compounds. For example, at the interface between two insulators, $LaAlO_3/SrTiO_3$, it is possible to observe the transition to the superconducting state at 0.1 K [1]. The results of the studies concerning different multiferroics, both of single crystals and thin films, are summarized in [2], where one can find the comparison of their magnetic and transport characteristics.

The main task of this work is to study the magnetic properties of $GdMnO_3$ deposited onto the $LaAlO_3$ substrate using the electron paramagnetic resonance technique and the comparison of the obtained results with the specific features observed in the EPR spectra of $GdMnO_3$ single crystals and of Gd^{3+} dopant ion in $LaAlO_3$.

The epitaxial thin films of gadolinium manganite $GdMnO_3$ deposited onto the single-crystalline lanthanum aluminate (001) $LaAlO_3$ were produced by radio-frequency magnetron sputtering. A $LaAlO_3$ (001) single crystal is characterized by a slightly distorted perovskite structure with $a = 3.780$ Å [3]. At room temperature, the angle between the edges of the rhombic unit cell is equal to 60.13°. At 500 K, it decreases down to 60.0°. Aluminum ions are surrounded by oxygen ions forming an octahedron with small trigonal distortions along the [111] axis [4]. The choice of $LaAlO_3$ as the substrate material is related to the results of [4] concerning the studies of the transverse cut of a $La_{0.67}Ca_{0.33}MnO_3/LaAlO_3$ film through the use of electron spectroscopy, which demonstrate the absence of secondary phases and misfit dislocations at the film–substrate interface. They also demonstrate that the film grows in a quasicoherent manner at the substrate surface. The analysis of the samples under study through the use of Rutherford backscattering shows that the thickness of the prepared films is about 100 nm and the chemical composition corresponds to the declared stoichiometry. The X-ray analysis of the structure and phase composition of the prepared films confirmed that we deal with single-phase samples; however, depending on the temperature maintained during the sputtering, they exhibit one or several types of orientation with respect to the substrate. The temperature dependence of magnetic susceptibility exhib-

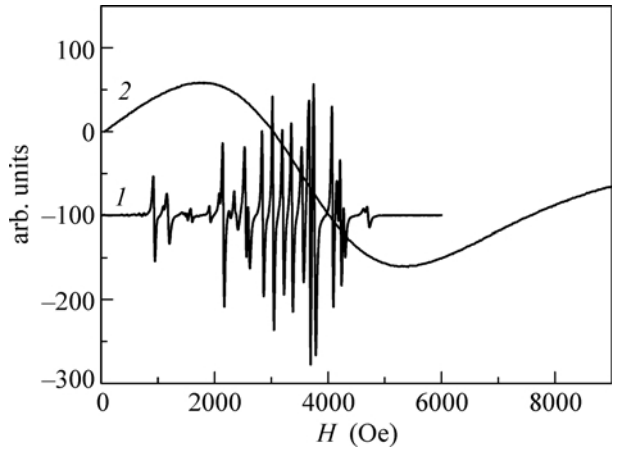

Fig. 1. Electron-paramagnetic-resonance spectrum in the *X* band for the (*1*) $GdMnO_3$ thin film and (*2*) single crystal at $T = 300$ K.

its features [5] suggesting the existence of magnetic phase transitions in $GdMnO_3$, which were observed earlier in bulk single-crystal samples [6].

The EPR spectra were measured at *X*- and *Q*-band frequencies using a Bruker EleXsys E500 spectrometer equipped with a continuous flow helium cryostat as well as a Varian spectrometer within the temperature range from 4 to 300 K.

In the thin $GdMnO_3/LaAlO_3$ film, we observed a set of lines with a pronounced angular anisotropy. The form of the EPR spectrum for $GdMnO_3/LaAlO_3$ in the *X* band at room temperature is illustrated in Fig. 1 (curve *1*). The angular dependence of the positions for the EPR spectral lines in $GdMnO_3/LaAlO_3$ at room temperature in the applied magnetic field directed along the normal to the [001] axis of the thin film measured in the *X* and *Q* bands is shown in Fig. 2. We suppose that the observed set of lines stems from the paramagnetic Gd^{3+} centers.

The paramagnetic gadolinium ion has the electron configuration $4f^7$ and belongs to the $^8S_{7/2}$ state. The combined effect of the spin–orbit interaction, crystal field, and magnetic dipole–dipole interaction between $4f$ electrons leads to the splitting of the ^8S state, which is described by the spin Hamiltonian [8]

$$H_{\rm cr} = \frac{1}{3}\sum_m (b_2^m O_2^m + c_2^m \Omega_2^m)$$

$$+ \frac{1}{60}\sum_m (b_4^m O_4^m + c_4^m \Omega_4^m) \qquad (1)$$

$$+ \frac{1}{1260}\sum_m (b_6^m O_6^m + c_6^m \Omega_6^m),$$

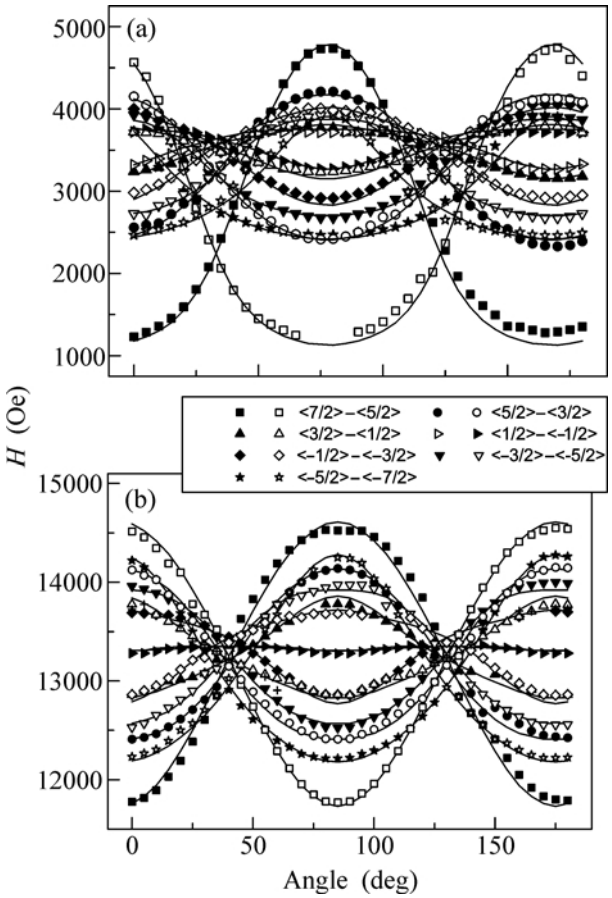

Fig. 2. Angular dependence of the positions for the EPR spectral lines in the $GdMnO_3/LaAlO_3$ thin film in the (a) *X* and (b) *Q* bands. The closed and open symbols denote the measured values of resonance magnetic fields for the first and second paramagnetic centers, respectively; the solid lines correspond to the calculations (allowed transitions). In the inset, the symbols denote the transitions between the sublevels of the fine structure; the closed and open symbols correspond to the first and second paramagnetic centers, respectively.

where b_n^m and c_n^m are the parameters characterizing the fine structure and O_n^m and Ω_n^m are the spin Stevens operators.

The fine structure parameters for the paramagnetic center with the triclinic symmetry corresponding to the gadolinium ion, which are determined by the analysis of the angular dependence for the resonance values of the applied magnetic field for the EPR spectra measured at room temperature in the *X* and *Q* bands, coincide with each other and have the following values (in units of 10^{-4} cm^{-1}): $b_2^0 = 192 \pm 1$, $b_2^2 = 62 \pm 1$, $c_2^2 = -179 \pm 1$, $b_4^0 = -4 \pm 1$, $b_4^2 = -4 \pm 1$, $b_4^4 = 8 \pm 1$, $b_6^0 = 5.6 \pm 0.5$, $b_6^6 = 7 \pm 0.5$, $g_y = 1.995$, and $g_z = 1.965$. The angular dependences of the positions of the magnetic

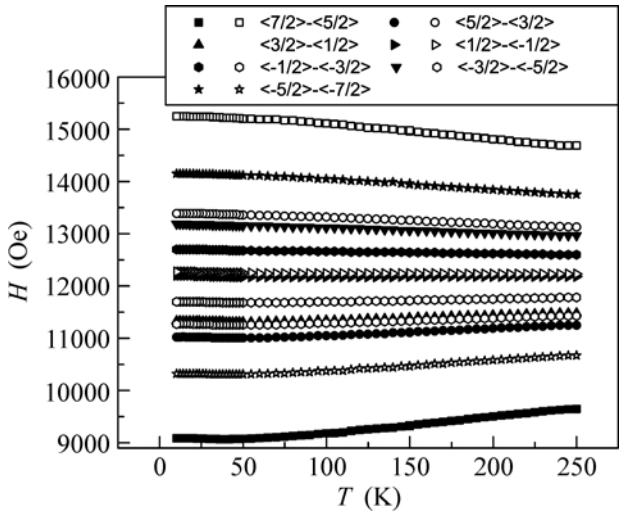

Fig. 3. Temperature dependence of the positions of EPR lines for the $GdMnO_3/LaAlO_3$ thin film in the Q band. The notation is the same as in Fig. 2.

resonance lines in the EPR spectrum for Gd^{3+} calculated using these parameters are shown by solid lines in Fig. 2. We took into account that there exist two types of paramagnetic centers with the axes directed at an angle of 90° with respect to each other and a third paramagnetic center with the axis rotated about that of the first center by an angle of 85°. To avoid a strong overlapping of the lines and experimental points corresponding to the angular dependences on the X and Q bands, we omit the results of calculations and experimental values corresponding to the center of the third type. We attribute the existence of three types of paramagnetic centers manifesting themselves in the EPR spectrum for the $GdMnO_3$ thin film deposited onto the $LaAlO_3$ substrate to the possible twinning in the substrate, which was also observed in [9]. We were not able to estimate the number of spins of gadolinium ions contributing to the EPR spectrum, since the observed behavior of the line intensities as a function of the microwave power was nonmonotonic.

The parameters of the spin Hamiltonian which we obtained for the gadolinium ion in $GdMnO_3/LaAlO_3$ coincide in order of magnitude with the values determined by the analysis of the angular dependence for the resonance values of the applied magnetic field for the EPR spectra of a gadolinium dopant ion in the $LaAlO_3$ single crystal [10]. In the latter case, the parameters of the spin Hamiltonian for the paramagnetic center with the trigonal symmetry at $= 293$ K are $g_{\|} = 1.9908$, $g_{\perp} = 1.986$, $b_2^0 = 371.2 \times 10^{-4}$ cm^{-1}, $b_4^0 = 6.17 \times 10^{-4}$ cm^{-1}, $b_6^0 = 1.0 \times 10^{-4}$ cm^{-1}, and $b_6^6 = 7.6 \times 10^{-4}$ cm^{-1}.

In the EPR spectrum for $GdMnO_3/LaAlO_3$, we can also observe the lines attributed to the forbidden transitions. The observation of the forbidden lines in the EPR spectrum is possible in the case of a low symmetry of a paramagnetic center [11]. Just this situation takes place for the gadolinium ion in the $GdMnO_3$ thin film, since in the description of the angular dependence of the positions of the magnetic resonance lines, we used the spin Hamiltonian for a paramagnetic center with the triclinic symmetry corresponding to the local symmetry of the gadolinium ion in $GdMnO_3$.

The temperature dependence of the line positions in the EPR spectrum of the $GdMnO_3/LaAlO_3$ thin film is shown in Fig. 3. In the temperature range from 250 to 50 K, the resonance values of the applied magnetic fields change. These changes correspond to the behavior of the dopant Gd^{3+} ion in $LaAlO_3$ [10]. Here, below the temperature of the transition to the cubic phase occurring at 720 K, the changes in the parameters of the spin Hamiltonian were observed within the whole temperature range from 300 to 4.2 K. In particular, it was found that the value $b_2^0 = 67 \times 10^{-4}$ cm^{-1} at 690 K increases to 490×10^{-4} cm^{-1} on cooling down to 20 K. In the thin $GdMnO_3/LaAlO_3$ film, the evolution of the parameters characterizing the spin Hamiltonian is observed only down to 50 K. Below this temperature, the resonance values of the applied magnetic field remain unchanged. It is necessary to note that the $GdMnO_3$ single crystal undergoes the magnetic phase transition below 40 K [6]. Just this transition seems to affect the temperature dependence of Gd^{3+} ions in the thin $GdMnO_3/LaAlO_3$ film.

The form of the EPR spectrum for the $GdMnO_3$ single crystal significantly differs from that for the thin film. Within the whole temperature range, the EPR spectrum for the $GdMnO_3$ single crystal consists of only one broad exchange-narrowed line of Lorentzian shape at all orientations of the applied magnetic field with respect to crystallographic axes. The form of the EPR spectrum for the $GdMnO_3$ single crystal at $T =$ 300 K is illustrated in Fig. 1 (curve *2*). The observed Lorentzian shape is described taking into account the contribution of dispersion characterized by the parameter $|\alpha| \ll 0$. Since the EPR linewidth in this compound is of the order of the resonance field H_{res}, it is necessary to take into account the circular component of the exiting linearly polarized microwave field and hence to include the resonance corresponding to the opposite direction of the resonance field $-H_{res}$ [7]. The angular dependence of the EPR linewidth for the $GdMnO_3$ single crystal at room temperature is shown in Fig. 4a. We compared the integral intensities for the EPR signals from the $GdMnO_3$ samples and from the reference material $BaMnF_4$ at room temperature. The ratio of integral intensities of the EPR lines for these two samples coincides with the theoretical estimate based on the assumption that nearly all manganese

ions Mn^{3+} with spin $S = 2$ and gadolinium ions Gd^{3+} with spin $S = 7/2$ contribute to the EPR spectrum of $GdMnO_3$.

Figure 4a shows the angular dependence of the EPR linewidth for the (*ab*) plane of the $GdMnO_3$ single crystal at room temperature in the case where the applied magnetic field is rotated in the plane perpendicular to the *c* axis of the crystal. In the high-temperature limit, the angular dependence of the linewidth for the exchange-narrowed EPR line was fitted using the relation $\Delta H \approx \frac{\hbar}{g\mu_B}\frac{M_2}{\omega_{ex}}$, where M_2 is the second moment of the line and $\omega_{ex} \approx J/\hbar$ is the exchange frequency. The Hamiltonian describing the interactions between the spins of manganese ions has the form

$$H(\mathrm{Mn}) = \sum J_{ij}(\mathbf{S}_i\mathbf{S}_j) + \sum \mathbf{G}_{ij}[\mathbf{S}_i\mathbf{S}_j] + H_{cr}, \qquad (2)$$

where the first term corresponds to the Heisenberg-type exchange between the spins of manganese ions, the second one describes the anisotropic Dzyaloshinskii–Moriya interaction between the spins of manganese ions (G_{ij} is the Dzyaloshinskii–Moriya constant), and H_{cr} is the spin Hamiltonian related to the crystal field. The magnitudes of the isotropic exchange interaction between manganese ions in $RMnO_3$ compounds in the (*ac*) plane of single crystals and between the planes are different. The corresponding values are $J_{ac} = 0.8$ meV and $J_b = 1.25$ meV for $GdMnO_3$ [12], and $J_{ac} = 1.2$ meV and $J_b = 2.5$ meV for $LaMnO_3$. At the same time, the crystal field parameters for manganese ions are nearly equal for both compounds [13]. Assuming that $J \sim \sqrt{4J_{ac}^2 + 2J_b^2}$ and using the values of the exchange coupling constant first for lanthanum manganite and then for gadolinium manganite, we find that the averaged exchange coupling constant and hence the exchange frequency in $LaMnO_3$ are about twice as large as those in $GdMnO_3$. Thus, the contribution of anisotropic exchange interactions between the spins of manganese ions of the crystal field effects to the EPR linewidth in $GdMnO_3$ increases by about a factor of two in comparison to that in $LaMnO_3$. The calculated contributions of the crystal field and of the Dzyaloshinskii–Moriya interaction to the EPR linewidth from [14] multiplied by a factor of 2 are shown in Fig. 4a by the solid line.

In Fig 4a, the difference between the EPR linewidth multiplied by two for $La_{0.95}Sr_{0.05}MnO_3$ and its linewidth measured in the (*ab*) plane of $GdMnO_3$ is indicated by the circles. The contribution to the EPR linewidth comes also from the crystal field acting on Gd ions and from the dipole–dipole interaction between manganese and gadolinium ions. We calculated the contribution of the crystal field at gadolinium ions to the EPR linewidth using the parameters of fine structure determined for Gd^{3+} ion in the thin film.

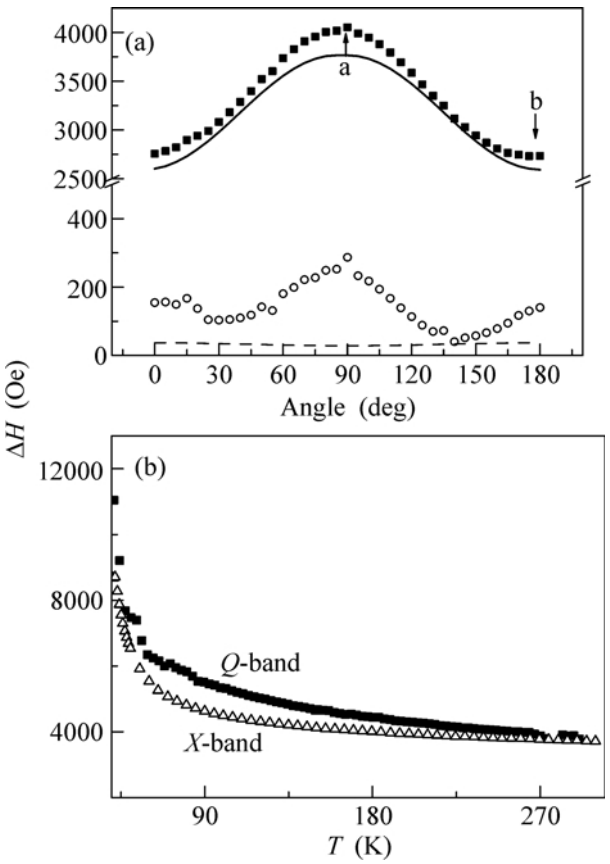

Fig. 4. (a) Squares denote the angular dependence of the EPR linewidth for $GdMnO_3$ single crystal in the (*ab*) plane at room temperature. The solid line corresponds to the doubled EPR linewidth for $La_{0.95}Sr_{0.05}MnO_3$ calculated in [14]. The circles denote the difference between the measured values of the EPR linewidth in the (*ab*) plane and the theoretical estimate for the contribution of manganese ions to the EPR linewidth. The dashed line corresponds to the contribution from the fine structure in the spectrum of gadolinium ions. (b) Temperature dependence of the linewidth in the EPR spectrum of $GdMnO_3$ single crystal in the (a) *X* and (b) *Q* bands.

This contribution appears additively in the second moment since it commutes with the terms in Hamiltonian (2) related to manganese ions. This contribution calculated using the formulas given in [13] is shown in Fig. 3 by the dashed line. An additional contribution to the linewidth in $GdMnO_3$ is related to the dipole–dipole interactions between manganese and gadolinium ions. According to the calculations, these contributions after taking into account the exchange narrowing effect are about 60 Oe; this value agrees well with the values deduced from experimental data and shown in Fig. 4a by circles. The spins of gadolinium ions are ordered at 6 K [6]. Knowing this temperature, we can estimate the magnitude of the isotropic exchange interaction between gadolinium ions using the relation $T_N/S(S+1)$. It approximately equals 0.4 K. Since gadolinium ions are in the *S* state, we

neglected for them the anisotropy of the exchange interaction.

The temperature dependence of the linewidth in the EPR spectrum of the $GdMnO_3$ single crystal is shown in Fig. 4b. In the temperature range above 40 K, the EPR linewidth decreases gradually on heating. Since in the *X* band the EPR linewidth is comparable to the resonance value of the magnetic field, it is rather difficult to speak about the absolute value of the linewidth for the magnetic resonance line. Therefore, we consider the EPR linewidth only in the range of paramagnetism. The EPR linewidth in the *X* band is smaller than that in the *Q* band. The difference between the EPR linewidths in the *X* and *Q* bands depends on temperature and decreases with the growth of temperature. At about 300 K, the EPR linewidth in $GdMnO_3$ is nearly independent of the frequency range under study. Probably, such a behavior is related to the dynamical effects in $GdMnO_3$, for example, to the effect of the magnetic field, the resonance value of which is 3400 Oe in the *X* band and 12300 Oe in the *Q* band. In the $GdMnO_3$ single crystal, the position of the EPR line is nearly independent of temperature in the range above 40 K. The effective *g* factor is approximately equal to 1.92.

In conclusion, we used the electron magnetic resonance method to study single-crystalline $GdMnO_3$ samples and single-crystalline $GdMnO_3$ thin films of thickness about 100 nm deposited onto the $LaAlO_3$ substrate. The measurements were performed in the *X* and *Q* frequency bands in a wide temperature range. In the EPR spectrum of the thin film, we observed a clearly distinguished fine structure characteristic of the Gd^{3+} ion, whereas in the spectrum of the single crystal, we see only one exchange-narrowed line. We performed the measurements of the angular, frequency, and temperature dependences of the resonance values of the applied magnetic field for the set of lines observed in the EPR spectrum of the thin $GdMnO_3/LaAlO_3$ film. We determined the parameters of the spin Hamiltonian corresponding to the triclinic symmetry of such a paramagnetic center as the Gd^{3+} ion in the $GdMnO_3/LaAlO_3$ film, which corresponds to the actual symmetry of the gadolinium ion in $GdMnO_3$. We suggest that the main contribution to the EPR spectra of the thin film comes from gadolinium ions located at the interface between the thin film and substrate.

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REFERENCES

1. L. Li, C. Richter, J. Mannhart, and R. C. Ashoori, Nature Phys. **7**, 762 (2011).
2. W. Prellier, M. P. Singh, and P. Murugavel, J. Phys.: Condens. Matter **17**, R803 (2005).
3. T. A. Ivanova, V. E. Petroshen', N. V. Chezhina, et al., Phys. Solid State **44**, 1468 (2002).
4. Yu. A. Boikov, T. Lil'enfors, E. Ollson, et al., Phys. Solid State **53**, 2168 (2011).
5. N. V. Andreev, T. A. Sviridova, N. Yu. Tabachkova, et al., Izv. Vyssh. Uchebn. Zaved., Mater. Elektron. Tekh. **1**, 63 (2011).
6. J. Hemberger, S. Lobina, H.-A. Krug von Nidda, et al., Phys. Rev. B **70**, 024414 (2004).
7. J. P. Joshi and S. V. Bhat, J. Magn. Reson. **168**, 284 (2004).
8. S. A. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements* (Nauka, Moscow, 1972; Halsted, New York, 1975).
9. A. Geddo Lehmann, C. Sanna, N. Lampis, et al., Eur. Phys. J. **55**, 337 (2007).
10. W. Low and Z. Zusman, Phys. Rev. **130**, 144 (1963).
11. A. D. Gorlov and A. P. Potapov, Sov. Phys. Solid State **24**, 144 (1982).
12. M. Mochizuki and N. Furukawa, Phys. Rev. B **80**, 134416 (2009).
13. I. V. Yatsyk, R. M. Eremina, M. M. Shakirzyanov, et al., JETP Lett. **87**, 447 (2008).
14. J. Deisenhofer, M. V. Eremin, D. V. Zakharov, et al., Phys. Rev. B **65**, 104440 (2002).

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