

Anisotropy of exchange interactions and spin reversal in the compensated ferrimagnet $\text{Ni}_4\text{Nb}_2\text{O}_9$

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Spin reversal and magnetization hysteresis loop were studied in the mean-field approximation for the anisotropic model of the compensated ferrimagnet $\text{Ni}_4\text{Nb}_2\text{O}_9$. A rigorous analysis was applied to determine the energy of exchange anisotropy in the ab plane. Based on the experimental data on the single crystal [Phys. Rev. B **111**, 014420 (2025)], the values of the main parameters of microscopic interactions were obtained. This made it possible to calculate the temperature dependence of magnetization, showing spin reversal, as well as the magnetization hysteresis loop, demonstrating the exchange bias. A good qualitative agreement between the experiment and theory was obtained. The effect of single-ion anisotropy on the magnetism of nickel niobate was analyzed and the importance of the contribution of antiferromagnetic exchange interactions with the second nearest neighbors to the stable ferrimagnetic state of the crystal is presented.

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I. INTRODUCTION

Transition metal niobates, as perspective magnetoelectric materials, have attracted the attention of researchers for a long time. One of the most prominent representatives of this family is the compensated ferrimagnet $\text{Ni}_4\text{Nb}_2\text{O}_9$, the Ising nature of magnetism of which was studied in detail in Ref. [1]. The subsequent structural and magnetic measurements [2–9] reflect a wide variety of the magnetic characteristics, which are closely related to the rather complex crystal structure of this compound. In particular, the neutron diffraction data [3] showed that at low temperature $T \sim 1.5$ K the crystal exhibits $Pb'cn'$ magnetic structure, whereas at higher T the structure $Pbc'n'$ with ferrimagnetic moment along the crystal a axis is realized [8,9]. Note that the difficulties in determining the magnetic structure of the ground state are connected with a weak anisotropy of the exchange interactions of Ni^{2+} ions and are caused by a small difference between its g factors in neighboring ab planes.

One of the most interesting questions is the presence of a weak ferrimagnetism in $\text{Ni}_4\text{Nb}_2\text{O}_9$ single crystal, since according to the experimental data all exchange interactions between the nearest nickel ions are antiferromagnetic (AFM), which causes a staggered order for magnetic moments with a zero magnetization. Apparently, the interactions with the next nearest neighbors have a significant effect on magnetic order.

The effects of negative magnetization [5], spin reversal induced in weak magnetic fields at certain temperatures [9], as well as the exchange bias effect [8,9] are characteristic properties of compensated ferrimagnets (FIM) [10]. Therefore,

along with traditional ferromagnets (FM), these systems give rise to a new trend in the development of modern components for spintronics [11].

The rather complex crystal structure of $\text{Ni}_4\text{Nb}_2\text{O}_9$ with various octahedral oxygen complexes around nickel ions, which form chains and planes, causes certain difficulties in describing its magnetic properties. In particular, the values of g factors, exchange interaction parameters, and magnetic moment are still the subject of discussions in the literature [1,3–10]. On the other hand, a combination of neutron diffraction data and *ab initio* methods for calculating the electronic structure allows a deeper understanding of the nature of nickel niobate ferrimagnetism. Thus, a significant difference between the experimental and calculated magnetization values near the critical phase transition temperature is apparently due to the hybridization of electron states in one coordination complex of the nickel ion and a change in its spin [12]. However, the exchange interaction parameters calculated within the framework of this method do not allow them to be reconciled with the observed Neel temperature or the paramagnetic Curie-Weiss temperature.

In the case of $\text{Ni}_4\text{Nb}_2\text{O}_9$, an abrupt change of magnetization in weak magnetic field is due to the weak anisotropy of exchange interactions in the ab planes. Therefore, overcoming a potential barrier between two equivalent directions of the AFM axis with spontaneous order does not require strong magnetic field. One of the problems to be solved in this work is related to determining the pointed anisotropy and critical magnetic field of spin reversal. Another type of anisotropy discussed is due to the spin-orbit interaction for the nickel ion in a distorted octahedral complex of oxygen ions. Note that in this case the quantum effects in the ground state play an important role at spin ordering. The unidirectional anisotropy is assumed to be determined by the honeycomb structure of NiO_6 octahedra or by the domain walls, when an additional surface anisotropy with nonequivalent directions along and

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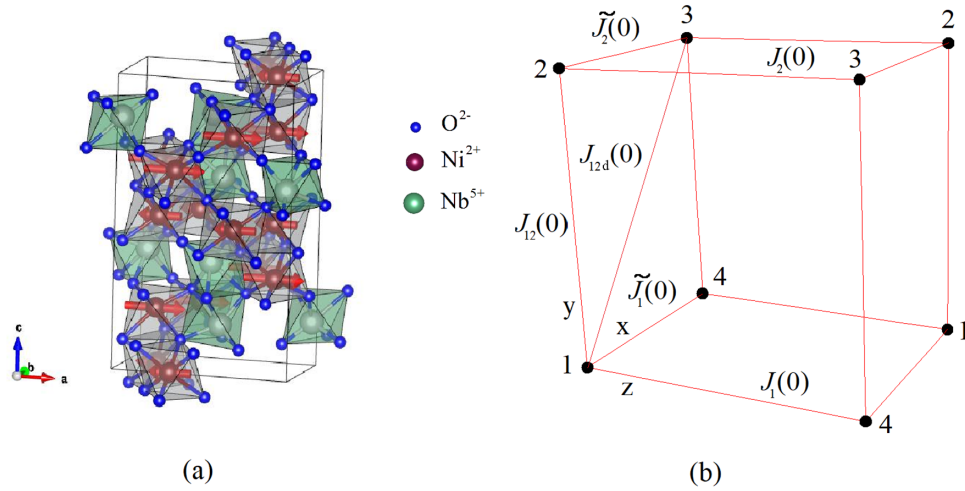


FIG. 1. (a) High-temperature magnetic structure of $\text{Ni}_4\text{Nb}_2\text{O}_9$ and (b) corresponding schematic representation of the exchange interactions of nickel ions along the x , y , and z axes (crystal b , c , and a axes, respectively). The figure indicates the sublattice numbers, used to account for exchange interactions of nickel ions with their next-to-nearest neighbors.

opposite to magnetic field occurs at their boundaries, as was considered in Refs. [13,14]. The different microscopic mechanisms of unidirectional anisotropy presented in the work [15] for perovskite systems, with generalization to other materials, can also take place for nickel niobate. For example, indirect exchange interaction of spins between neighboring FM planes is realized through oxygen ions. Due to hybridization of cation-ion states and ferroelectric polarization, an additional uniform exchange field of the KS^z type can be formed on oxygen ions. In this case, the constant K appears as a result of compensation of two staggered effects: alternating superexchange coupling at the interface, and alternating spin orientation of the FM plane along the c axis.

The structure of the paper is as follows. The Hamiltonian of FIM system in a mean-field approximation with weak anisotropic exchange interactions of nickel ions in crystal ab planes is considered in Sec. II. A rigorous analysis allowed us to establish the anisotropy energy and to determine the critical fields of spin reversals. A general expression for the compensation temperature is presented. Section III uses the experimental data of Ref. [9] and the obtained formulas are applied to determine the main parameters of microscopic interactions. Spin reversal temperature is calculated and magnetic hysteresis loops are built, and are in good agreement with experiment. The contribution of single-ion anisotropy (SIA) is analyzed in Sec. IV. A generalization of the well-known Moriya criterion for an existence of magnetically ordered state is carried out, taking into account the intrasublattice exchange interactions. The conditions for realization of the FIM structure observed for $\text{Ni}_4\text{Nb}_2\text{O}_9$ are considered using the generalized mean-field theory.

II. QUANTUM MODEL OF ANISOTROPIC EXCHANGE INTERACTIONS IN $\text{Ni}_4\text{Nb}_2\text{O}_9$: MEAN-FIELD APPROXIMATION

The orthorhombic compensated FIM $\text{Ni}_4\text{Nb}_2\text{O}_9$ exhibits a rather complex crystallographic structure with the space group $Pbcn$ [2,3]. Figure 1(a) shows the corresponding

high-temperature magnetic structure $Pbc'n'$ with Ni^{2+} ion magnetic moments along the a axis [16]. As a rule, a simplified model of the exchange interactions of nickel ion spins, shown by the dots in Fig. 1(b), is used. A strong isotropic intersublattice exchange $J_{12}(0)$ for spins in the neighboring ab planes along the c axis (y axis) with intrasublattice exchanges $J_1(0)$ and $J_2(0)$ in the pointed planes for the nearest neighbors along the a axis (z axis) is supposed [1,17]. The presence of exchange anisotropy in the ab planes is also assumed to be with additional exchange parameters $\tilde{J}_1(0)$ and $\tilde{J}_2(0)$ along the b axis (x axis).

Let us write the Hamiltonian in a mean-field approximation for a given system with spin $S = 1$ and parameters in $2J_{12}(0)$ units in the following form:

$$\begin{aligned} \hat{H}_{MF} = & \sum_i^N \left((\langle S_2^z \rangle + \nu_1 \langle S_1^z \rangle + K - g_1 H \sin \psi) S_{1i}^z \right. \\ & + (\langle S_2^x \rangle + \tilde{\nu}_1 \langle S_1^x \rangle - g_1 H \cos \psi) S_{1i}^x \\ & + (\langle S_1^z \rangle + \nu_2 \langle S_2^z \rangle + K - g_2 H \sin \psi) S_{2i}^z \\ & \left. + (\langle S_1^x \rangle + \tilde{\nu}_2 \langle S_2^x \rangle - g_2 H \cos \psi) S_{2i}^x \right) + H_{\text{const}}. \end{aligned} \quad (1)$$

Here, the non-operator part H_{const} of the Hamiltonian has the form

$$\begin{aligned} \frac{H_{\text{const}}}{N} = & -\frac{1}{2} \nu_1 \langle S_1^z \rangle^2 - \frac{1}{2} \tilde{\nu}_1 \langle S_1^x \rangle^2 - \frac{1}{2} \nu_2 \langle S_2^z \rangle^2 - \frac{1}{2} \tilde{\nu}_2 \langle S_2^x \rangle^2 \\ & - \langle S_{1z} \rangle \langle S_{2x} \rangle - \langle S_{1x} \rangle \langle S_{2z} \rangle, \end{aligned} \quad (2)$$

where $\langle S_i^{x,z} \rangle$ is mean spin of Ni^{2+} for i -th sublattice along x or z directions, respectively, and N is the number of sites. The dimensionless parameters are defined as follows: $\nu_1 = J_1(0)/J_{12}(0)$, $\nu_2 = J_2(0)/J_{12}(0)$, $\tilde{\nu}_1 = \tilde{J}_1(0)/J_{12}(0)$, and $\tilde{\nu}_2 = \tilde{J}_2(0)/J_{12}(0)$. The unidirectional anisotropy with parameter K is taken into account in Hamiltonian (1). For convenience, it is assumed that the Bohr magneton $\mu_B = 1$, and the interaction of spins with an applied magnetic field H in the ab plane, directed at angle ψ to the

z axis, is described by g factors, g_1 and g_2 for the first and second ab planes, respectively

From Hamiltonian (1), using a unitary transformation for i th sublattice, one can obtain the diagonalized one (see procedure and Eq. (S5) in the Supplemental Material [18]). In the simplest case, when $H = K = 0$, $v_1 \sim \tilde{v}_1$, $v_2 \sim \tilde{v}_2$, and $v_1 > 0$, $v_2 > 0$, we have collinear FIM with the angles $\theta_i = 0, \pi$, and $\pm\pi/2$ for local quantum axis directions of the i th sublattice relative to the z axis. Let us consider the effect of a weak magnetic field and unidirectional anisotropy on the magnetic characteristics of $\text{Ni}_4\text{Nb}_2\text{O}_9$. Obviously, in the linear approximation, these interactions provide the linear corrections to angles θ_i . It follows from Hamiltonian (S5) in the Supplemental Material [18] that these corrections to energy levels are of a higher order. Therefore, we can further consider the states with $\theta_1 = 0$ and $\theta_2 = \pi$ (state A) and $\theta_1 = \pi/2$ and $\theta_2 = -\pi/2$ (state B). In the linear approximation over field H and K , the following order parameters describe state A at temperature $T = 1/\beta$:

$$\begin{aligned}\sigma_1 &= \sigma_1^0 + (g_1 H \sin \psi - K) \chi_{1z}, \\ \sigma_2 &= \sigma_2^0 - (g_2 H \sin \psi - K) \chi_{2z},\end{aligned}\quad (3)$$

where the susceptibility $\chi_{iz} = \beta \{ \langle (\tilde{S}_i^z)^2 \rangle - (\sigma_i^0)^2 \}$. The order parameters with $K = 0$ in a zeroth magnetic field are expressed as

$$\begin{aligned}\sigma_1^0 &= \frac{e^{\beta(\sigma_2^0 - v_1 \sigma_1^0)} - e^{-\beta(\sigma_2^0 - v_1 \sigma_1^0)}}{1 + e^{\beta(\sigma_2^0 - v_1 \sigma_1^0)} + e^{-\beta(\sigma_2^0 - v_1 \sigma_1^0)}}, \\ \sigma_2^0 &= \frac{e^{\beta(\sigma_1^0 - v_2 \sigma_2^0)} - e^{-\beta(\sigma_1^0 - v_2 \sigma_2^0)}}{1 + e^{\beta(\sigma_1^0 - v_2 \sigma_2^0)} + e^{-\beta(\sigma_1^0 - v_2 \sigma_2^0)}}.\end{aligned}\quad (4)$$

The averages $\langle (\tilde{S}_i^z)^2 \rangle$ are determined from Eq. (4) by replacing a minus sign between the exponents in the numerator with a plus sign. Thus, it is easy to write down in a linear approximation the expression for free energy F_1 per site in the state A with the parameters H and K :

$$F_1 = \frac{1}{2} F_{10} - MH \sin \psi + \frac{1}{2} K (\sigma_1^0 - \sigma_2^0), \quad (5)$$

where the entropy contribution is expressed as

$$\begin{aligned}F_{10} &= -T \ln (1 + e^{\beta(\sigma_2^0 - v_1 \sigma_1^0)} + e^{-\beta(\sigma_2^0 - v_1 \sigma_1^0)}) \\ &\quad - T \ln (1 + e^{\beta(\sigma_1^0 - v_2 \sigma_2^0)} + e^{-\beta(\sigma_1^0 - v_2 \sigma_2^0)})\end{aligned}\quad (6)$$

and a site magnetic moment M is given by

$$M = g_1 \sigma_1^0 - g_2 \sigma_2^0. \quad (7)$$

Similarly, one can write down the formulas for both order parameters $\tilde{\sigma}_1^0$, $\tilde{\sigma}_2^0$ and entropy contribution F_{20} to the free energy F_2 in state B, which are obtained from Eqs. (4) and (6) by replacing the parameters $v_1 \rightarrow \tilde{v}_1$ and $v_2 \rightarrow \tilde{v}_2$. Then, the free energy F_2 in state B is expressed as follows:

$$F_2 = \frac{1}{2} F_{20} - MH \cos \psi, \quad (8)$$

where M has the same form (7), since it enters in the product with a small value of H . Therefore, the main corrections to the free energy in state B are connected with the entropy contribution F_{20} , containing the order parameters $\tilde{\sigma}_1^0$ and $\tilde{\sigma}_2^0$, a difference of which from the corresponding σ_1^0 and σ_2^0 is

due to a weak exchange anisotropy in the ab planes. Taking into account the experimental data, one can assume that $\Delta v_1 = v_1 - \tilde{v}_1 \ll 1$ and $\Delta v_2 = v_2 - \tilde{v}_2 \ll 1$, and the difference in the energies of states A and B is proportional to Δv_1 and Δv_2 . Then the order parameters $\tilde{\sigma}_1^0$ and $\tilde{\sigma}_2^0$ in the linear approximation over Δv_1 and Δv_2 are represented as

$$\begin{aligned}\tilde{\sigma}_1^0 &= \sigma_1^0 (1 - \Delta v_1 \chi_{1z}), \\ \tilde{\sigma}_2^0 &= \sigma_2^0 (1 - \Delta v_2 \chi_{2z}),\end{aligned}\quad (9)$$

where the susceptibilities χ_{iz} are determined from Eq. (3). Substituting the expressions (9) for $\tilde{\sigma}_1^0$ and $\tilde{\sigma}_2^0$ in the formula for F_{20} , free energy F_2 in state B expressed as follows:

$$\begin{aligned}F_2 &= \frac{1}{2} F_{10} - MH \cos \psi - \frac{1}{4} \Delta v_1 (\sigma_1^0)^2 - \frac{1}{4} \Delta v_2 (\sigma_2^0)^2 \\ &\quad + \frac{1}{2} \Delta v_1 \sigma_1^0 \chi_{1z} (v_1 \sigma_1^0 - \sigma_2^0) \\ &\quad + \frac{1}{2} \Delta v_2 \sigma_2^0 \chi_{2z} (v_2 \sigma_2^0 - \sigma_1^0)\end{aligned}\quad (10)$$

is obtained.

From a comparison of formulas (5) and (10) for the equilibrium free energies in states A and B, one can conclude that spin reorientations are determined by the Zeeman energy E_Z and the anisotropy energy $E_A = E_{A1} - E_{A2}$, where $E_{A1} = \frac{1}{2} K (\sigma_1^0 - \sigma_2^0)$ and $E_{A2} = -\frac{1}{4} \Delta v_1 (\sigma_1^0)^2 - \frac{1}{4} \Delta v_2 (\sigma_2^0)^2 + \frac{1}{2} \Delta v_1 \sigma_1^0 \chi_{1z} (v_1 \sigma_1^0 - \sigma_2^0) + \frac{1}{2} \Delta v_2 \sigma_2^0 \chi_{2z} (v_2 \sigma_2^0 - \sigma_1^0)$ are the energies of unidirectional and exchange anisotropies, respectively. Due to the smallness of the parameters Δv_1 and Δv_2 , as well as $\sigma_2^0 \sim \sigma_1^0 = \sigma_0$ and $\chi_{2z} \sim \chi_{1z} = \chi_z$, the expression for E_A is simplified and takes the form

$$E_A = \frac{1}{2} K (\sigma_1^0 - \sigma_2^0) + P, \quad (11)$$

where $P = \frac{1}{2} (\Delta v_1 + \Delta v_2) \sigma_0^2 [\chi_z (v_1 - 1) - \frac{1}{2}]$ is the energy of the potential barrier between the states of magnetic moment along and opposite to the a axis. Actually, unidirectional anisotropy has Ising origin since it depends on the z projection of spin. As one can see later on from Eqs. (13) and (14), coercivity does not depend on parameter K . Since $v_1 < 1$ and $\Delta v_1 + \Delta v_2 < 0$, then $P \geq 0$. From Eq. (11) it is seen that the energy of the exchange anisotropy is determined by the sum of the anisotropy energies in two adjacent ab planes. Thus, there is only one unknown parameter $\Delta v = \Delta v_1 + \Delta v_2$ characterizing the specified exchange anisotropy.

The obtained expressions for free energies correspond to the equilibrium states A and B. To describe the spin reversals in a magnetic field, it is necessary to write the nonequilibrium thermodynamic potential G , which includes the states with an inclination of the AFM axis from the z direction by an angle α . Neglecting the constant contributions, it can be assumed that the corrections to G caused by the energies of anisotropic barrier P and Zeeman and unidirectional anisotropy will be proportional to the projections of the order parameter onto the directions, which are perpendicular and parallel to the AFM axis, respectively. Thus, thermodynamic potential G can be written as

$$G = P \sin^2 \alpha - \{ MH - \frac{1}{2} K (\sigma_1^0 - \sigma_2^0) \} \cos \alpha. \quad (12)$$

Minimization of G over angle α gives two solutions: $\alpha = 0$ and π (see Eq. (S9) in the Supplemental Material [18]). For $T > T_{\text{comp}}$, i.e., $M > 0$, from the inequality (S9) it follows the

expression for first and second critical magnetic fields H_{cr1} and H_{cr2} below and above of which the spin reversal occurs, respectively:

$$H \geq H_{\text{cr1}} = \frac{0.5K(\sigma_1^0 - \sigma_2^0) - 2P}{M} < 0, \quad (13)$$

$$H \leq H_{\text{cr2}} = \frac{0.5K(\sigma_1^0 - \sigma_2^0) + 2P}{M} > 0. \quad (14)$$

As can be seen from Eqs. (S10) and (S11), the equality $H_{\text{cr1}} = -H_{\text{cr2}}$ is fulfilled for $K = 0$. Thus, nonzero values of the parameter K determine the shift of the hysteresis loops relative to the origin, i.e., the phenomenon of exchange bias. On the other hand, if a nonequilibrium state is realized in a magnetic field for the FC or FW (cooling or warming) protocols, then the positive sign of the Zeeman energy is determined by the signs of M and H . In particular, at $T < T_{\text{comp}}$ the value $M < 0$, which yields a metastable state for an arbitrarily small positive magnetic field. The critical fields H_{cr1} and H_{cr2} also determine the temperatures of spin reversals for the FC or FW protocols. It is obvious that for $T < T_{\text{comp}}$ the change of the signs of H_{cr1} and H_{cr2} is opposite. For H_{cr1} and H_{cr2} determined as $H_{\text{cr1}} < 0$ and $H_{\text{cr2}} > 0$, the replacement $H_{\text{cr1}} \leftrightarrow H_{\text{cr2}}$ occurs below T_{comp} .

Let us consider the temperature dependence of the magnetization (site magnetic moment) M in the FC process. At temperatures $T > T_{\text{comp}}$, the system in a weak field is in a stable state ($M > 0$ and the Zeeman energy is negative). Upon crossing the compensation temperature, the magnetization becomes negative due to the fact that $g_2 > g_1$. In this case, the positive sign of the Zeeman energy indicates the metastability of the whole system, being in such a state as long as $H < H_{\text{cr1}}$, defined by Eq. (S10). If this inequality is violated below the compensation, a spin reversal occurs with an appearance of the positive magnetization, i.e., the whole system goes into the stable state. Since H_{cr1} increases with increasing temperature for $T < T_{\text{comp}}$, then with an increase of applied field the spin reversal temperature approaches compensation temperature.

The main known formulas for the Neel temperature T_N , susceptibility, and Curie paramagnetic temperature θ [1,17], obtained with Eq. (4), are given in the Supplemental Material [18].

The compensation temperature T_{comp} is found from Eq. (7) at $M = 0$. It is easy to show that T_{comp} , expressed through the order parameter σ_1 at $T = T_{\text{comp}}$, is the solution of the self-consistent equation

$$\left[\frac{\sigma_1 + \sqrt{4 - 3\sigma_1^2}}{2(1 - \sigma_1)} \right]^d = \frac{\sqrt{4g_2^2 - 3g_1^2\sigma_1^2} - g_1\sigma_1}{2(g_1\sigma_1 + g_2)}, \quad (15)$$

where $d = \frac{v_2g_1 - g_2}{g_1 - v_1g_2}$. The compensation temperature is the next function of σ_1 :

$$T_{\text{comp}} = \frac{\sigma_1(g_1 - v_1g_2)}{g_2 \ln \left(\frac{\sigma_1 + \sqrt{4 - 3\sigma_1^2}}{2(1 - \sigma_1)} \right)}. \quad (16)$$

III. MICROSCOPIC PARAMETERS OF INTERACTIONS: EXPERIMENT AND THEORY

To compare theoretical predictions with experimental data, it is necessary to determine the g factors, g_1 and g_2 , for magnetic ions in the ab planes, as well as the parameters of the exchange interactions $J_{12}(0)$, v_1 , v_2 , and exchange anisotropy $\Delta\nu$. The experimental value of magnetization $M_{\text{exp}} = -0.42$ emu/g at $T = 6.2$ K in magnetic field of 100 Oe [9] and the value of the Curie constant $C_{\text{exp}} = 6.22$ emu K/mol Oe [4]. There is a system of equations for determining the g factors, neglecting the temperature and field contributions:

$$g_1 - g_2 = M, \quad g_1^2 + g_2^2 = t, \quad (17)$$

where $M(T = 6.2 \text{ K}) = M_{\text{exp}}\mu/(4\mu_B N_A) = -0.011$, $t = 3k_B C_{\text{exp}}/(4\mu_B^2 N_A) = 12.43$, and $\mu = 564.6$ g/mol is molar mass. The solution of Eq. (17) gives the values $g_1 \approx 2.48$ and $g_2 \approx 2.50$. Note that the values of g factors given in Ref. [1] normalized to $\sqrt{2}$ are 2.49 and 2.51, respectively.

To find the parameters v_1 and v_2 , the experimental data for the Neel temperature $T_N^{\text{exp}} = 76.5$ K, Curie paramagnetic temperature $\theta_{\text{exp}} = -195$ K, and compensation temperature $T_{\text{comp}}^{\text{exp}} = 33$ K [1,4] were used. Taking the ratios $p_1 = \theta_{\text{exp}} T_N^{\text{exp}}$ and $p_2 = T_N^{\text{exp}}/T_{\text{comp}}^{\text{exp}}$ and using formulas (S12) and (S16) in the Supplemental Material [18], and (16) with account for known values g_1 and g_2 , we obtain $v_1 = 0.412$, $v_2 = 0.461$. For the pointed parameters of exchange interactions, according to formulas (15) and (16), the values $\sigma_1 = 0.968$ and $T_{\text{comp}} = 0.162$ give the value $J_{12}(0) = 101.8$ K for interplane exchange at $T_{\text{comp}}^{\text{exp}} = 33$ K.

To determine the exchange anisotropy parameters K (unidirectional magnetic anisotropy) and $\Delta\nu$, Eqs. (13) and (14) and experimental data for the coercive field $H_C = (H_{\text{cr2}} - H_{\text{cr1}})/2$ and the exchange bias field $H_{\text{EB}} = (H_{\text{cr1}} + H_{\text{cr2}})/2$ from work [9] were used. It is easy to find that $K = 2MH_{\text{EB}}/(\sigma_1^0 - \sigma_2^0)$ and the anisotropy energy $P = 0.5|M|H_C$. Taking into account the analytical expression (11) for P as a function of $\Delta\nu$, the anisotropy parameter in the form

$$\Delta\nu = \frac{2P}{\sigma_0^2(\chi_z(v_1 - 1) - \frac{1}{2})} \quad (18)$$

was obtained. Indeed, $\Delta\nu < 0$, since $P > 0$, but $v_1 < 1$ and $\chi_z > 0$.

Since H_{EB} is proportional to parameter K , one can make the linear fitting of H_{EB} to corresponding experimental values that gives $K = -6.8 \times 10^{-5}$. Unfortunately, for a such fitting for $\Delta\nu$ an essential discrepancy between experiment and theory for the temperature dependence of critical fields far from T_{comp} was obtained. Apparently, it points out a weak temperature dependence of $\Delta\nu$ below T_{comp} . Since we are interested in the temperature region near the compensation temperature, the constant values of $\Delta\nu = \Delta\nu_L = -5.5 \times 10^{-6}$ and $\Delta\nu = \Delta\nu_R = -3.3 \times 10^{-6}$ at $T < T_{\text{comp}}$ and $T > T_{\text{comp}}$, respectively, were taken. Thus, the main parameters of microscopic interactions, given in Table 1 of the Supplemental Material [18], were determined.

Figure 2 shows the nonequilibrium thermodynamic potential G in $2J_{12}(0)$ units with potential barrier as a function of the angle α of the AFM axis inclination from the crystallographic

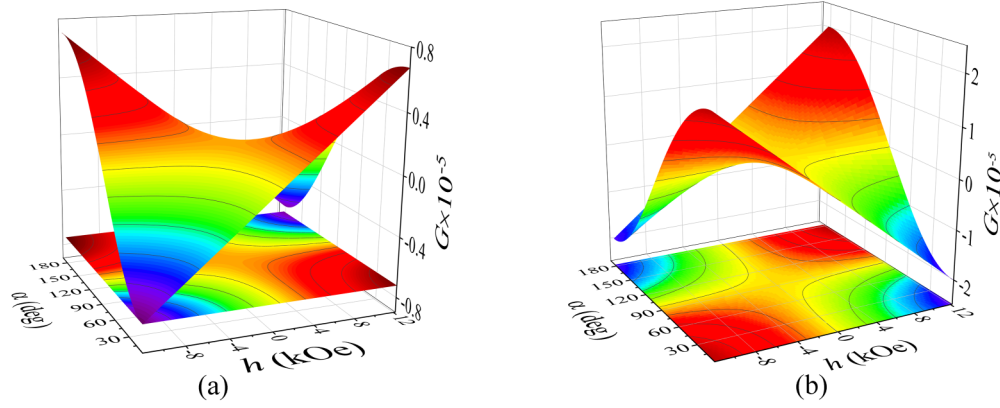


FIG. 2. Nonequilibrium thermodynamic potential G in $2J_{12}(0)$ units as a function of the angle α of AFM axis inclination from the crystallographic axis a and magnetic field h at temperatures (a) $T = 30.6$ and (b) 40.7 K for the parameters $\nu_1 = 0.412$, $\nu_2 = 0.461$, $\Delta\nu = -3.304 \times 10^{-6}$, $K = -6.8 \times 10^{-5}$, $g_1 = 2.48$, and $g_2 = 2.50$.

axis a and magnetic field h at temperatures $T = 30.6$ and 40.7 K, i.e., below and above the compensation temperature of about 33 K.

Since the sign of the site magnetic moment M changes to the opposite at the crossing of the compensation temperature, the minimal energy at $T < T_{\text{comp}}$ [see Fig. 2(a)] is realized for the AFM axis along the z direction for negative fields. The rotation of the AFM axis of 180° is possible only at a certain positive magnetic field with the Zeeman energy exceeding the height of the potential barrier. For $T > T_{\text{comp}}$, an opposite situation take place.

Figure 3(a) gives the temperature dependence of H_{cr1} , and shows the region of fields below the compensation temperature, above which the spin reversals occur. Figure 3(b) shows the critical fields H_{cr2} of spin reversal for definite temperature above the compensation point with the FW warming protocol, when the system goes from a stable state at $T < T_{\text{comp}}$ upon crossing the compensation point into a metastable state, not due to a change in the signs of the order parameters σ_1^0 and σ_2^0 but due to a change in the contributions $g_1\sigma_1^0$ and $g_2\sigma_2^0$

to the magnetization M at $g_2 > g_1$. In fields $H > H_{\text{cr2}}$, a spin reversal with a change of the sign of M is realized and the system returns to a stable state (see Fig. 3).

Figure 4 shows the temperature dependence of the anisotropy parameter $\Delta\nu$ with the experimental values of H_C substituted into Eq. (18), and taking into account the obtained exchange parameters and g factors from Table 1 of the Supplemental Material [18]. Figure 5 gives the experimental (points) and calculated (lines) temperature dependence of the critical fields H_{cr1} and H_{cr2} for the specified parameter values. At temperatures above the compensation temperature there is fairly good agreement between the experiment and theory. At $T < T_{\text{comp}}$, some difference between theory and experiment is observed, especially near the compensation temperature. Apparently, in this case, a stronger temperature dependence of the anisotropy parameter is realized, which is confirmed by data presented in Fig. 4.

Calculated temperature dependence of the energies of exchange and unidirectional anisotropies of $\text{Ni}_4\text{Nb}_2\text{O}_9$, which

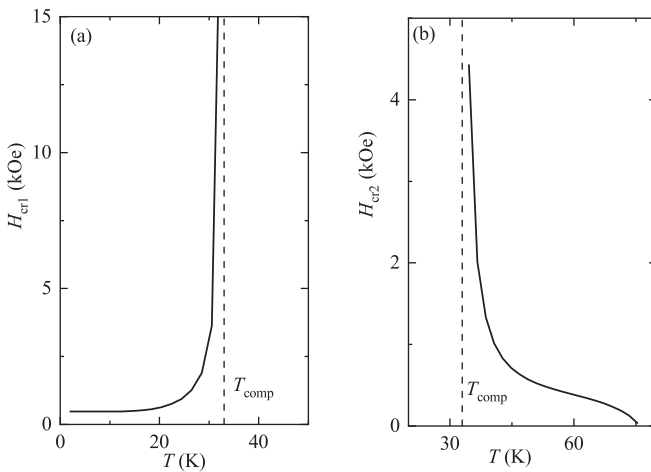


FIG. 3. Temperature dependence of the critical fields H_{cr1} (a) and H_{cr2} (b) of spin reversals for the FC and FW cooling-warming protocols at $\Delta\nu = \Delta\nu_R$, respectively. The parameters of interactions are the same as in Fig. 2.

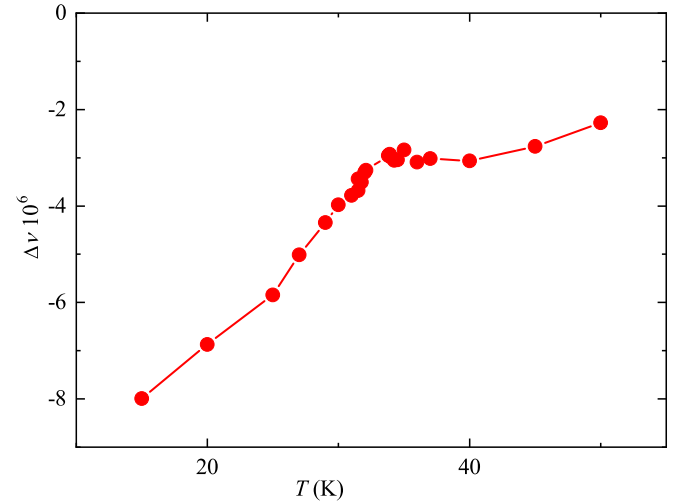


FIG. 4. Temperature dependence of the parameter of exchange anisotropy $\Delta\nu$ in the ab planes determined taking into account experimental values for the coercive field H_C .

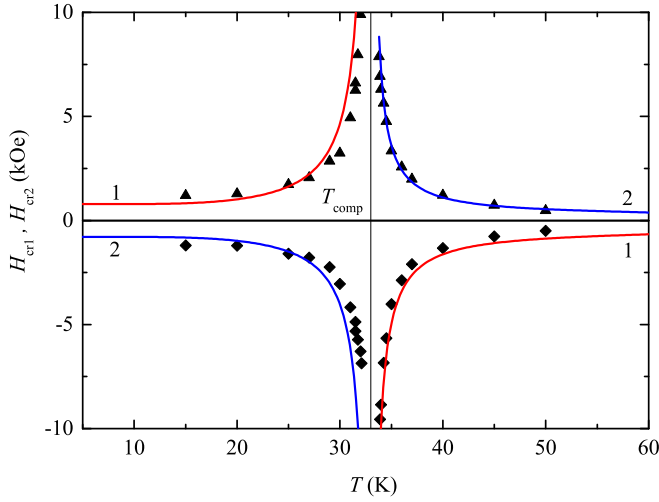


FIG. 5. Temperature dependence of the critical fields H_{cr1} (curves 1) and H_{cr2} (curves 2). Points and lines represent experiment and theory, respectively, in accordance with Eqs. (13) and (14) and parameters taken from Table 1 (see Supplemental Material [18]).

reflect a weakness of exchange and unidirectional anisotropy in the ab planes of the crystal, is presented in Fig. 6.

The theoretical temperature dependences of magnetization $M(T)$ obtained from Eq. (7) for the FW and FC warming-cooling protocols at various values of magnetic fields are presented in Fig. 7. As can be seen from the figure, a qualitative agreement between experiment [9] and theory is observed for the temperatures of the spin reversals. In the temperature region of magnetization maximum a significant quantitative difference between the data of experiment and theory is visible, as previously indicated in Ref. [1].

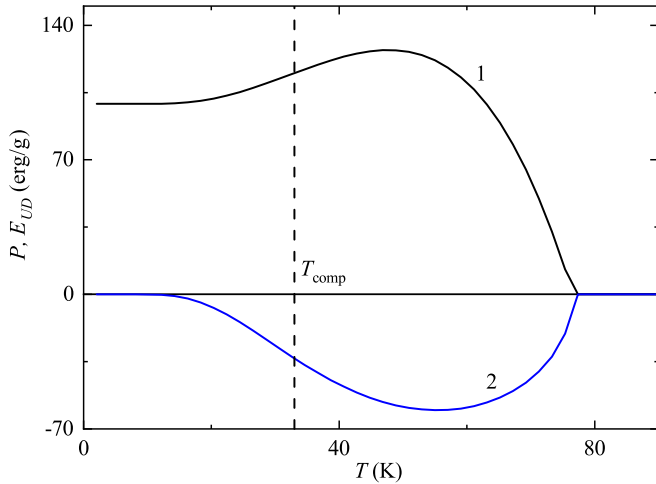


FIG. 6. Temperature dependence of the energies P and $E_{\text{UD}} = 0.5K(\sigma_1^0 - \sigma_2^0)$ exchange (curve 1) and unidirectional (curve 2) anisotropies, respectively, determined taking into account the presence of four magnetic Ni^{2+} ions in the molecule and the data from Table 1 [18]. Please note that the sign of E_{UD} is determined by the experimental value of exchange bias. The sign of $\sigma_1^0 - \sigma_2^0$ is not changed. The sign $g_1\sigma_1^0 - g_2\sigma_2^0$ is changed after crossing the compensation temperature.

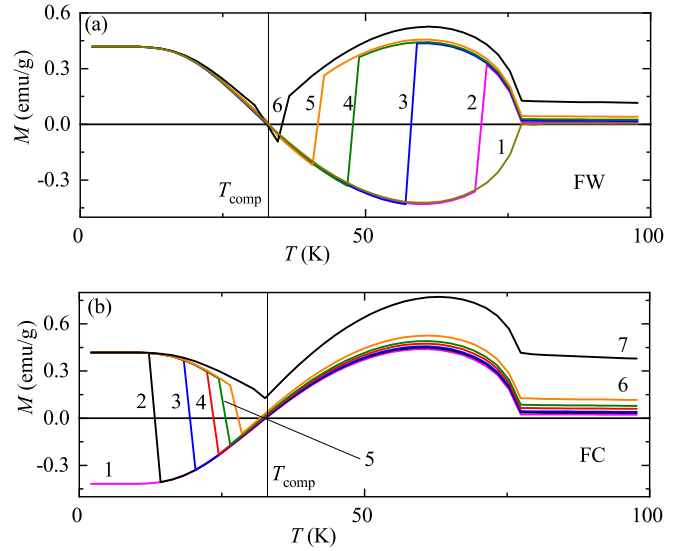


FIG. 7. Calculated temperature dependence of the $\text{Ni}_4\text{Nb}_2\text{O}_9$ magnetization for FW (a) and FC (b) warming-cooling protocols in magnetic fields: (a) 0, 0.2, 0.4, 0.6, 1.0, and 3 kOe (curves 1–6, respectively); (b) 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, and 10 kOe (curves 1–7, respectively).

Preliminary analysis shows that the magnetization value near T_N is very sensitive to changes of a few percent in g factors as well as exchange interactions. It is possible that the small structural changes occur with appearance of ferrimagnetic order, leading to changes in the relevant parameters.

Figure 8 shows the calculated magnetic hysteresis loops of $\text{Ni}_4\text{Nb}_2\text{O}_9$ at various temperatures. From the figures one can see an exchange bias, when the loops are shifted to the right at temperatures below the compensation temperature and vice versa at $T > T_{\text{comp}}$ in accordance with the sign of the constant K for unidirectional anisotropy. Good qualitative agreement between the theoretical and experimental data [9] is also observed.

IV. SINGLE-ION ANISOTROPY AND GENERALIZATION OF THE MORIYA CRITERION: FERROMAGNETISM OF THE ab PLANES

In this section, an influence of the spin-orbit interaction on the magnetic ion Ni^{2+} ground state with electron configuration $3d^8$ is considered. As can be seen from Fig. 1(a), the nickel ions are surrounded by distorted octahedra of oxygen ions. In the crystal field of the octahedral symmetry, its lower multiplet 3F is split into the orbital singlet state Γ_2 and two orbital triplets Γ_5 and Γ_4 . In this case, the energies of these levels are equal to $E_{\Gamma_2} = -12Dq$, $E_{\Gamma_5} = -2Dq$, and $E_{\Gamma_4} = 6Dq$, where Dq is the parameter of the crystal field of cubic symmetry [19]. In particular, the total splitting in the cubic field is $\Delta = 18Dq$.

For nickel ions $E_{\Gamma_5} - E_{\Gamma_2} \sim 10^4 \text{ cm}^{-1}$ [20], i.e., $Dq \sim 700 \text{ cm}^{-1}$, and therefore $\Delta \sim 13000 \text{ cm}^{-1}$. It is known [19] that for Ni^{2+} the spin-orbit coupling constant $\lambda = -335 \text{ cm}^{-1}$. If an influence of only the first excited level E_{Γ_5} is considered, then, using the ion wave functions in the crystal field of octahedral symmetry, one can show that in the second

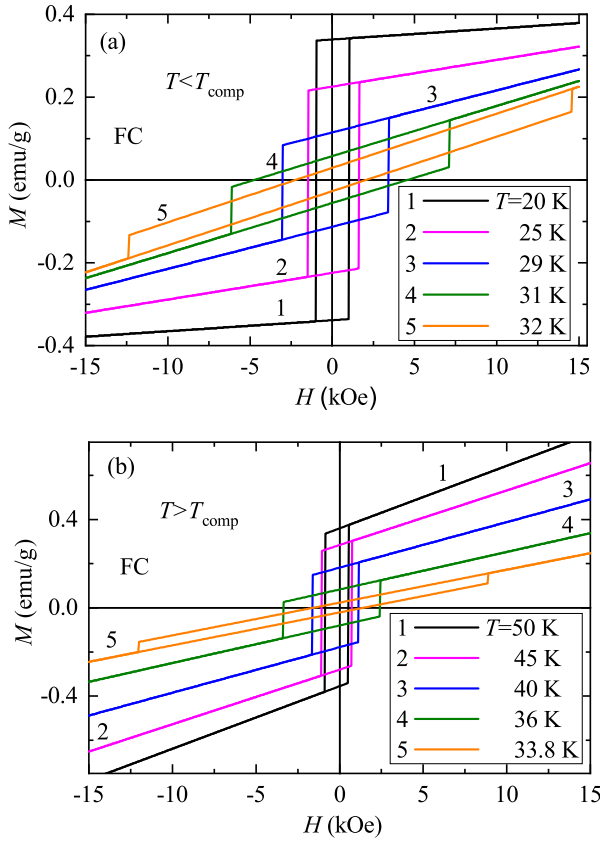


FIG. 8. Theoretical magnetic hysteresis loops of $\text{Ni}_4\text{Nb}_2\text{O}_9$ at various temperatures: (a) $T < T_{\text{comp}}$; (b) $T > T_{\text{comp}}$.

order of perturbation theory the isotropic g factor has the form

$$g = 2 - \frac{4\lambda}{5Dq}, \quad (19)$$

that gives the value $g = 2.38$, which is quite close to the values from Table 1 [18]. Unfortunately, to calculate the constant D of SIA, it is necessary to take into account the upper level E_{Γ_4} , since otherwise the contribution from the spin-orbit interaction is proportional to the square of the spin operator for the nickel ion. In addition, the sign and value of the constant D also depend on the distortions of the cubic crystal field [21]. It is possible that the somewhat smaller values of the g factors, 2.0(2) and 1.7(3) in the first and second planes at low temperatures, obtained from neutron diffraction data [3], are connected with distortions of the oxygen octahedron. Therefore, the problem of the SIA influence on the $\text{Ni}_4\text{Nb}_2\text{O}_9$ magnetic state is of further interest. In particular, one of the features of the SIA is the quantum diminution of the mean spin in the ground state, as well as the phenomenon of the long-range magnetic order disappearance at a sufficiently strong SIA, compared to the intersublattice exchange interaction. This relation between SIA and exchange is named the Moriya criterion [20]. Let us consider the indicated effects as applied to our case, i.e., taking into account the intra-sublattice exchange. In this case, one can neglect an influence of both above-considered anisotropies and applied magnetic field, i.e., write the Hamiltonian in a mean-field approximation for

two nickel ions in the form

$$\hat{H}_0 = D\{(\langle S_1^z \rangle^2 + \langle S_2^z \rangle^2) - \tilde{h}_{1x}S_1^x - \tilde{h}_{2x}S_2^x + H_{\text{const}}\}, \quad (20)$$

where the constant SIA $D > 0$ in units of $2J_{12}(0)$ corresponds to the spin-singlet ground state with ordering in the ab plane and the effective exchange fields

$$\tilde{h}_{1x} = -v_1\langle S_1^x \rangle - \langle S_2^x \rangle, \quad \tilde{h}_{2x} = -v_2\langle S_2^x \rangle - \langle S_1^x \rangle, \quad (21)$$

with the nonoperator part of the Hamiltonian:

$$H_{\text{const}} = -\frac{1}{2}v_1\langle S_1^z \rangle^2 - \frac{1}{2}v_2\langle S_2^z \rangle^2 - \langle S_1^z \rangle \langle S_2^z \rangle - \langle S_1^x \rangle \langle S_2^x \rangle. \quad (22)$$

The energy levels E_{1i} , E_{0i} , and E_{-1i} of Hamiltonian (20) for the i th ion and corresponding free energy F of a system are presented in the Supplemental Material [18]. The minimization of F over the mean spins $\langle S_1^x \rangle$ and $\langle S_2^x \rangle$ allows one to find a system of two self-consistent equations for them (see Eqs. (S18) and (S19) in the Supplemental Material [18]). In particular, at temperature $T = 0$ one can obtain the following algebraic equations for the order parameters $\langle S_1^x \rangle$ and $\langle S_2^x \rangle$ in the ground state:

$$(\sqrt{D^2 + 4\langle S_1^x \rangle^2} + 2v_1)(\sqrt{D^2 + 4\langle S_2^x \rangle^2} + 2v_2) = 4, \quad (23)$$

where $\langle S_2^x \rangle = -\frac{1}{2}\langle S_1^x \rangle(\sqrt{D^2 + 4\langle S_1^x \rangle^2} + 2v_1)$.

Assuming $v_1 = v_2 = 0$, Moriya's result [20] for the quantum diminution of the mean spin at zero temperature,

$$\langle S_1^x \rangle = -\langle S_2^x \rangle = \sqrt{1 - (D/2)^2}, \quad (24)$$

is obtained from Eq. (23). For $D = D_{\text{cr}} = 2$ the Moriya criterion is realized as well, if the long-range magnetic order disappears at a sufficiently strong SIA. In our case, it is difficult to represent analytically the generalization of the expression for the mean spin taking into account the intra-sublattice exchanges v_1 and v_2 as a solution of Eq. (23). Therefore, the limiting case of $D \ll v_1$ and v_2 , which apparently corresponds to the pointed anisotropy in $\text{Ni}_4\text{Nb}_2\text{O}_9$, is considered. In the first nonvanishing approximation with respect to the ratio $D/\tilde{h}_{ix}$ we obtain

$$\langle S_1^x \rangle = 1 - \frac{1}{2}\left(\frac{D}{2(1-v_1)}\right)^2, \quad (25a)$$

$$\langle S_2^x \rangle = -1 + \frac{1}{2}\left(\frac{D}{2(1-v_2)}\right)^2. \quad (25b)$$

From Eqs. (25a) and (25b) it follows that the inclusion of the intrasublattice exchange enhances an influence of the SIA on the diminution of the mean spin value, depending on the ab plane number.

By using the values v_1 and v_2 from Table 1 [18], as well as the experimental value of the site magnetic moment $M = -0.011$ [see Eq. (17)] at low temperature, the value $D = 0.24$ is obtained from Eqs. (7) and (25a), (25b) with $\sigma_1^0 = \langle S_1^x \rangle$ and $\sigma_2^0 = \langle S_2^x \rangle$. Despite the rather large value of D , the contribution of the SIA to the quantum diminution of the mean spin is only $\sim 2\%$, i.e., $\langle S_1^x \rangle \approx \langle S_2^x \rangle \approx 0.98$. It turns out that even such diminution leads to a significant difference in magnetization at low temperatures due to the smallness of the total magnetic moment, which is reflected in Fig. 9.

It is worth paying attention to a large difference between theoretical predictions and experiment in the case of the

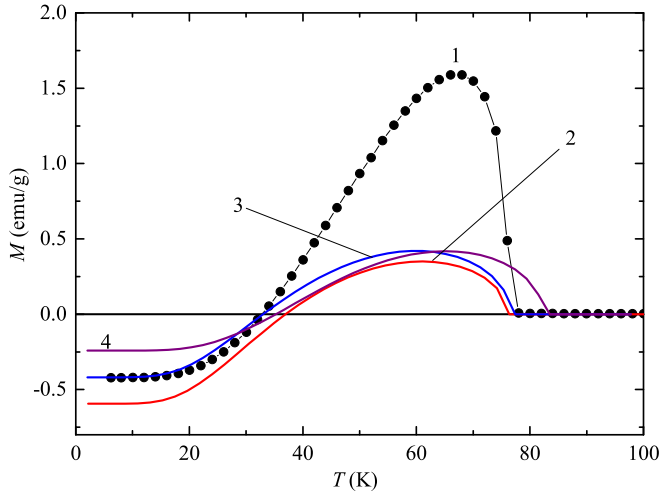


FIG. 9. Temperature dependence of magnetization of $\text{Ni}_4\text{Nb}_2\text{O}_9$: experiment [9] (points), curve 2 is built according to the data from work [1]; curves 3 and 4 are calculated at $D = 0$ and 0.24 with parameters of interaction from Table 1 (see Supplemental Material [18]), respectively.

temperature dependence of magnetization in the temperature range from 40 K to T_N in Fig. 9, which was already pointed in the work [1] and still has not been explained in the literature. Based on the data of neutron diffraction and *ab initio* methods of calculating the electronic structure [12], it was established that in a fixed temperature range, due to the effect of strong hybridization of oxygen-nickel states on one of the nickel ions, the magnetic moment decreases. This can lead to a violation of the values of the contributions to the total magnetic moment from the FM planes, predicted by the molecular field theory, where the identity of the charge states of magnetic ions is assumed.

It is not difficult to calculate the Neel temperature T_N using the high-temperature expansion of Eq. (S18) over order parameters. As a result, one obtains

$$T_N = D / \ln \left(\frac{\nu_1 + \nu_2 - \sqrt{4 + (\nu_1 - \nu_2)^2} - 2D}{\nu_1 + \nu_2 - \sqrt{4 + (\nu_1 - \nu_2)^2} + D} \right). \quad (26)$$

From the condition $T_N = 0$, the generalized Moriya criterion $D < D_{\text{cr}}$ for the existence of magnetic ordering in the *ab* plane, where

$$D_{\text{cr}} = \sqrt{4 + (\nu_1 - \nu_2)^2} - \nu_1 - \nu_2, \quad (27)$$

was obtained. For parameters from Table 1 [18] we have $D_{\text{cr}} = 1.13$.

Finally, the issue of ferromagnetism in the *ab* plane is considered, since it is not entirely clear how such a state is realized, taking into account the AFM sign of all exchange interactions in the crystal lattice. To explain this discrepancy, it is necessary to enter, along with the existing interactions, an exchange interaction with the next nearest neighbors. In our case, it will be $J_{12d}(0)$ exchange along the diagonals of the parallelepiped faces from Fig. 1(b), which in the $J_{12}(0)$ unit is denoted by ν_{12} . Obviously, then it is necessary to consider a four-sublattice structure. In this case, the sublattice numbering

[see Fig. 1(b)] is such that the nearest neighbors must be from other sublattices. Using Smart's generalized mean-field theory [22] in a zero magnetic field, one can prove that there is a nontrivial solution of a system of self-consistent equations for order parameters corresponding to ferromagnetic planes ordered antiferromagnetically (see Supplemental Material [18]). The estimation of ground state energies for both a pure staggered structure and AFM ordered ferromagnetic planes shows that the latter magnetic structure is stable, when the condition $\nu_{12} > 0.5(\nu_1 + \nu_2)$ is satisfied, i.e., the AFM exchange along the diagonals of the parallelepiped faces from Fig. 1(b) should be strong enough for the FM planes to appear.

V. CONCLUSIONS

A presented model of exchange interactions and their anisotropy qualitatively describes experimentally observed features of the magnetic behavior of the compensated ferrimagnet $\text{Ni}_4\text{Nb}_2\text{O}_9$, such as spin reversals in weak magnetic fields for various warming-cooling protocols as well as the exchange bias of the hysteresis loops. Most of the unknown parameters of the theory are determined based on the use of the given formulas by linking them to specific experimental values of the Neel temperature, paramagnetic Curie temperature and Curie constant, compensation temperature, as well as magnetization at low temperatures, when its temperature changes can be neglected. Since the coercivity and exchange bias fields are proportional to the parameters of the exchange and unidirectional anisotropies, respectively, a linear fit to the experimental data was carried out for only one parameter.

In particular, an estimation of the exchange anisotropy in the single crystal *ab* planes made it possible to determine the temperature dependence of the potential barrier height between the states of the magnetic moment along and against the direction of the magnetic field, as well as to calculate the critical fields and temperatures of spin reversal.

Based on the obtained value of this anisotropy constant, the theoretical hysteresis loops with an exchange bias are presented. The observed quantitative difference between the calculated and experimental magnetizations, also reflected in the works of other authors, is apparently due to the additional deformation of oxygen octahedra around nickel ions near the critical points of phase transitions and due to the effects of oxygen-nickel states' hybridization.

The obtained *g*-factor values correlate with approximate estimates of the spin-orbit interaction for ions in a crystal field of octahedral symmetry. A quantum diminution of the mean spin in the ground state is calculated that amounts to only several percent for this compound. However, due to a small value of magnetization M , this reduction effect at low temperatures has a significant influence on the value of M . A generalization of the Moriya criterion for an existence of magnetism in the systems with easy-plane SIA is obtained, taking into account the intrasublattice exchange interactions. It is shown that a strong AFM exchange interaction of Ni^{2+} ions with their second nearest neighbors leads to the appearance of AFM ordered FM planes, which allows us to understand the origin of ferrimagnetism in a crystal with AFM exchange interactions of the nearest neighbors.

ACKNOWLEDGMENT

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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