Nonlinear spin-wave phenomena in the $[Mn\{(R/S)\text{-}pn\}_2]_2[Mn\{(R/S)\text{-}pn\}_2H_2O][Cr(CN)_6]$ molecular ferrimagnet

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We report an observation of the instability of the ferromagnetic resonance spectrum in $[Mn\{(R/S)\text{-}pn\}_2]_2[Mn\{(R/S)\text{-}pn\}_2H_2O][Cr(CN)_6]$ single crystals initiated by the microwave irradiation. The value of the threshold microwave power leading to the instability, $P_{th}=0.2-0.9$ mW, depends on the relative orientation of the easy magnetization axis of the crystal and magnetic field. It was found that in the region of the high microwave power, $P>P_{th}$, the spin-wave bistability develops.

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I. INTRODUCTION

Molecular metal-organic magnets provide an inimitable possibility of relatively straightforward tailoring of their electronic and magnetic structure by chemical methods and, thus, open vast prospects for research and management of spin-wave processes in crystals. In particular, development of new magnetochiral molecular crystals allows detection of collective spin phenomena and nonlinear magnetic effects. This boosts the fundamental understanding of such classic effects as, for example, spin waves and their interactions in solids[1,2] as well as allows detection of novel collective spin phenomena in metal-organic magnets.

Appearance of nonlinear spin excitations (spin solitons) under microwave irradiation of a low power ($\sim 10^{-2}-10^{-3}$ mW) was theoretically predicted and experimentally demonstrated in chiral molecular ferrimagnets $[Mn\{(R/S)\text{-}pn\}_2]_2[Mn\{(R/S)\text{-}pn\}_2H_2O][Cr(CN)_6]$ (yellow needle, YN) both in static magnetic fields[3] and in ferromagnetic resonance (FMR) conditions.[4] The existence of a threshold microwave power (~ 1 mW), above which the dramatic change in FMR parameters occurred in YN crystals, was reported in Ref. 5. It was also shown[5] that a significant change in the spectrum was generally caused by development of a Suhl's instability.[6] The present work aims to establish the main rules causing a transition between high and low microwave power regions as well as to study FMR spectra above the power threshold in YN single crystals.

II. EXPERIMENTAL SETUP

Synthesis and the crystallographic structure of dielectric, optically transparent YN crystals are described in detail in Ref. 7. Static and high-frequency magnetic properties of YN crystals were extensively studied in Refs. 3, 4, and 7. In particular, the anisotropy field had been identified and it was shown that the shape anisotropy of the sample had little or no impact on the angular dependence of the ferromagnetic resonance and the magnitude of the resonant field. The crystals studied here are of $0.5\times 0.1\times 0.05$ mm^3 size and have a nearly rectangular shape with rounded edges preventing the emergence of magnetoacoustic resonant modes (Fig. 1). To study spin dynamics, we have used an electron spin resonance (ESR) spectrometer (Bruker ESR 500) with a rectangular X-band resonator (the microwave field frequency ~ 9.5 GHz) with the quality factor $Q=2000-3000$ at $T=4$ K equipped with ESR 910 cryostat (Oxford Instruments), which allows measurements in the temperature range 3–300 K with a relative precision of 0.05 K. The microwave power P was varied in the range $10^{-6}-2\times 10^{-1}$ W. The measured signal intensity dI/dH was directly proportional to the first field derivative of the imaginary part of the magnetic susceptibility of crystals, $d\chi''/dH$. The modulation frequency was 100 kHz in all the experiments. Special precautions were undertaken to control the microwave frequency of the spectrometer, which was stabilized with the precision 10^{-5}. Overall, the frequency deviations in the ferromagnetic resonance conditions were insignificant. A similar behavior was also observed for a control paramagnetic sample. Stability of the spectrometer at high microwave fields was provided by a small mass of ferromagnetic samples, where the excitation of a ferromagnetic resonance essentially did not change the quality of the resonator.

III. EXPERIMENTAL RESULTS

Typical spectra of the magnetic resonance at low microwave power are shown in Fig. 2. In the case when the dc magnetic field is oriented along the c axis of the crystal, $\phi=0$, the FMR spectrum contains a sequence of resonant lines at $H_{res}\sim 2$ kOe. The amplitude of the lines decreases with magnetic field ("right-hand" sequence). As it was shown in Ref. 4, this sequence corresponds to a spin-soliton resonance. As the angle ϕ increases, individual lines overlap, and the whole series shifts toward larger magnetic fields. When the dc magnetic field is oriented perpendicular to the c axis, $\phi=90°$, the position of the resonant lines is further shifted to $H_{res}\sim 4$ kOe. Conversely, at this orientation the amplitude of the lines increases with magnetic field ("left-hand" sequence). This type of the spectrum corresponds to a spin-wave resonance.[4] The observed spectra are independent of the direction of the magnetic field sweep (Fig. 2).

At $\phi=0$ the change in the microwave power in the range 0.002–0.2 mW (or the microwave magnetic field in the range 0.005–0.5 Oe) neither modifies the shape of the spectrum nor affects the main parameters of the resonance. However, as

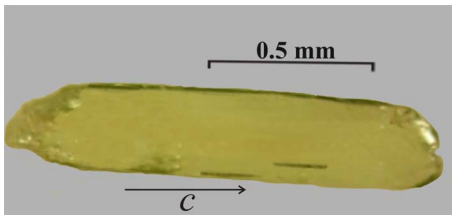

FIG. 1. (Color online) Photograph of an YN single crystal.

the microwave magnetic field increases further and reaches the threshold value, $h_{th}=1.8$ Oe, corresponding to the microwave power, $P_{th}=0.2$ mW, a sharp modification of the resonant spectrum reflected in a significant change in the shape of the resonant line and position of the resonant field is observed. A few narrow lines merge together forming a broad resonant line of an irregular shape (Fig. 3). Initial increase in the microwave power in the range 0.2–40 mW leads to the sharp increase in the resonant field up to 3.4 kOe. However, further increase in the power from 40 to 200 mW corresponds only to an insignificant rise of the resonant field up to ~3.5 kOe (Fig. 3). Thus, we demonstrate that a small change in the microwave power leads to a critical transformation of the magnetic resonance spectrum in YN crystals. It is noteworthy, that the spectrum of the calibration sample remained unchanged in the same experimental conditions. Similar modifications of FMR spectrum were observed at different values of the angle ϕ. At the same time, we found a strong orientation dependence of the threshold value of the microwave power P_{th} (Fig. 4): as ϕ increases from 0° to 45°, P_{th} raises from 0.2 to 1 mW. Further increase in the angle ϕ up to 90° does not affect the magnitude of P_{th}.

At high microwave power ($P > P_{th}$) we observe a dramatic change in the spectrum shape. Generally, there are a number of characteristics that differ in FMR spectra obtained at high and low values of the microwave power, namely:

(1) the shape of the line. At high power, the series of lines were not any longer observed. Instead, we have measured a broad spectrum with a sharp drop at the high dc field, H_0 (Fig. 3).

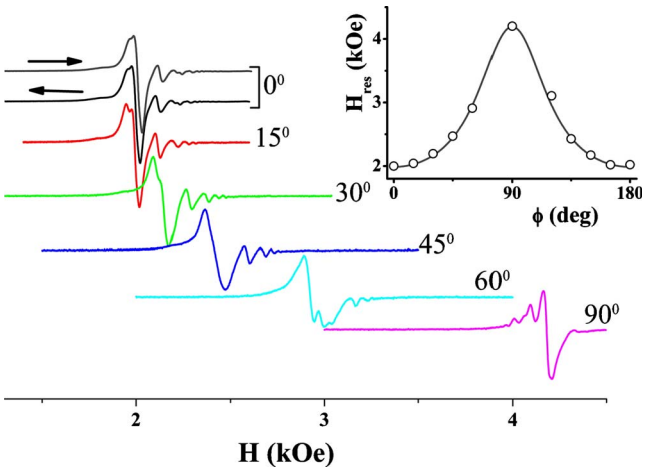

FIG. 2. (Color online) FMR spectra of YN crystals at $T=4$ K and $P=60$ dB, dc magnetic field applied at the angle ϕ to the c axis of the crystal. Arrows show the direction of the dc magnetic field sweep. Inset shows angular dependences of the resonant field H_{res}, of the most intensive line, solid line is approximation by Eq. (7).

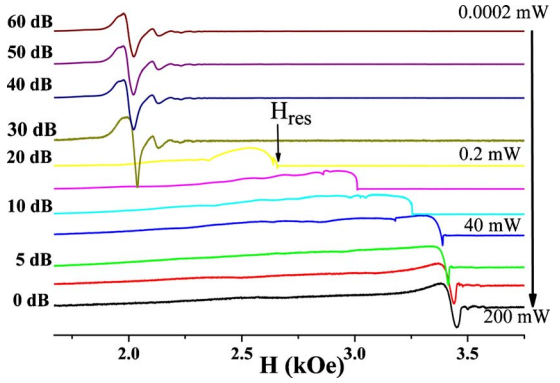

FIG. 3. (Color online) FMR spectra of YN crystals at different levels of the microwave power, $\phi=0$.

(2) Existence of hysteresis (Fig. 5 right inset). If the spectrum is measured while the dc magnetic field is ascending, we observe a broad resonance line with a sharp drop of intensity at H_{down}. However, if the magnetic field is descending, a delay in the appearance of the resonance line is observed, followed by a series of sharp narrow peaks. Then, at H_{up} the resonant signal returns to its original value recorded during the initial sweep. Thus, we observed two levels of the microwave power absorption corresponding to a single value of the dc magnetic field. Hence, the high microwave power range is characterized by an absorption bistability. It is noteworthy that such bistability has never been observed at $P < P_{th}$.

(3) Shift of the resonance field, H_{res} (Fig. 5). It should be noted that for lines of an irregular shape the resonant field was defined as a position of the drop line.

IV. DISCUSSION

Previously it has been shown[5] that the value of the threshold power could be satisfactorily described by Suhl's relation,[6] according to which the resonance instability develops at a minimum value of the pumping microwave field h_{th},

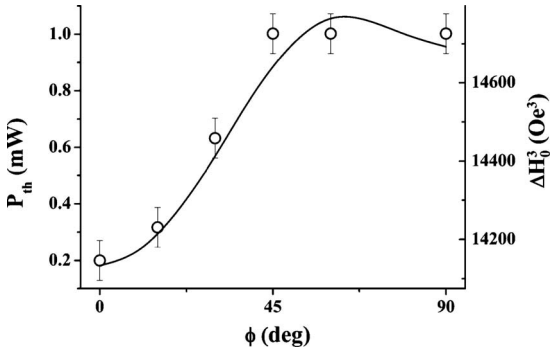

FIG. 4. Experimental dependence of the threshold microwave power P_{th} (symbols) and calculated dependence of ΔH_0^3 (solid line) on the angle ϕ between the c axis of the YN crystal and magnetic field H_0.

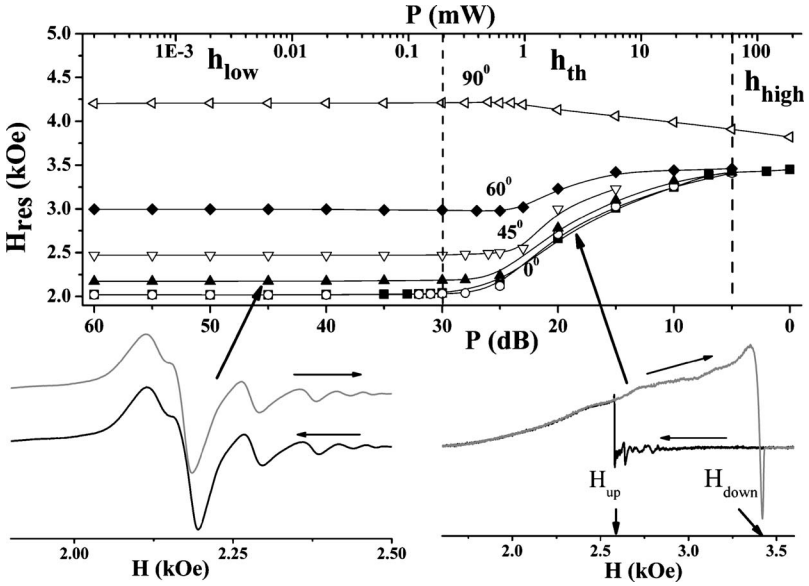

FIG. 5. Dependence of the resonant field on the microwave power for different orientations of the YN crystal and magnetic field $\mathbf{H_0}$. Bottom panels show FMR spectra obtained at different directions of the magnetic field sweep. The spectra are obtained at $P<P_{\rm th}$ (left) and $P>P_{\rm th}$ (right) at $T=4$ K.

$$P_{\rm th} \sim h_{\rm th}^2 > 2(\Delta H_0)^3/4\pi M, \tag{1}$$

where ΔH_0 is the width of the resonance line ~24 Oe, M is the sample magnetization, which can be derived from the magnetization of the primary cell, $2\ \mu_B = 1.8 \times 10^{-20}$ erg Oe^{-1}, and equals to 5.6 emu/cm^3 at 4 K and at $B>1$ kOe.[7] Thus, we can estimate that the threshold microwave power P required for the development of the resonant instability in YN crystals should be above 1 mW, which is still 30 times lower than the power required for the resonance saturation. In our experiments in the case of the dc magnetic field H_0 oriented along the easy crystallographic axis c ($\phi=0$), the notable alteration of the spectrum has been observed at the microwave pumping power above 0.2 mW. Thus, the experimental value $P_{\rm th}$ is in a good agreement with the theoretical estimation.

In the parallel orientation ($\phi=0$), after passing the threshold the resonant field is gradually increasing with the microwave power from ~2.0 to 3.5 kOe (Fig. 5). However, the opposite behavior was observed when the dc magnetic field is perpendicular to the c axis ($\phi=90°$). In this case the resonant field decreases from 4.2 to 3.5 kOe with the power. Thus, regardless of the crystal orientation in the magnetic field, at $P>P_{\rm th}$ the resonant field reaches its limit $H_{\rm res}=3.5$ kOe, which is attributed to the resonance in the absence of the magnetocrystalline anisotropy (Fig. 5). This magnitude of the resonant field corresponds to g factor, $g=2$, for a given microwave frequency. Hence, that particular resonance has a purely electronic (spin) nature in the absence of the magnetocrystalline contribution. The obtained results imply that the transition to stable high-power conditions depends on the magnetocrystalline anisotropy of YN crystals. This conclusion is supported by the fact that the threshold power $P_{\rm th}$, at which the change in the spectrum occurs, is dependent on the orientation of the crystal to the dc magnetic field H_0.

The equation of a vector magnetization $\mathbf{M}$ motion in a magneto-ordered media can be described by the Landau-Lifshitz-Gilbert (LLG) equation[1,2]

$$\partial \mathbf{M}/\partial t = -\gamma \mathbf{M} \times \mathbf{H_{eff}} + (\alpha/M)\mathbf{M} \times \partial \mathbf{M}/\partial t, \tag{2}$$

where $\mathbf{H_{eff}}$ is the effective magnetic field, α is the damping constant, and γ is gyromagnetic ratio. In the case of FMR conditions and neglecting the exchange interaction, the LLG equation describes single frequency oscillations in a spin system with several degrees of freedom. For a static field $\mathbf{H}$ (along the z direction) $\mathbf{H_{eff}}=[h\cos(\omega t), h\sin(\omega t), H-M_z]$. According to transcendental equation[8] in this case of the magnetization circularly precessing along the z direction the cone angle Θ is

$$\Theta^2 = \frac{(1-\Theta^2/2)^2 h^2}{(H-M+M\Theta^2/2-\omega/\gamma)^2 + (\alpha\omega/\gamma)^2(1-\Theta^2/2)^2}, \tag{3}$$

where $\omega=2\pi\nu$ and $\nu=9.4$ GHz is the microwave frequency of the spectrometer. Neglecting the higher order $h^2\Theta^2$ and $\alpha^2\Theta^2$ terms, Eq. (3) becomes the well-known form of the cone angle in the nonlinear regime,

$$\Theta^2 = \frac{h^2}{(H-H_0+M\Theta^2/2)^2 + \Delta H_0^2}, \tag{4}$$

where $H_0=\omega/\gamma+M$ is the resonance position at $h\to 0$, ΔH_0 is FMR linewidth at $h\to 0$.

If the amplitude h of the microwave magnetic field is small, the field dependence of the precession angle $\Theta(H)$ is described by the Lorentz distribution with the center at $H=H_0$ [see a schematic $\Theta^2(H)$ dependence in Fig. 6]. As the amplitude h increases, the $\Theta(H)$ dependence becomes asymmetric and its maximum shifts toward smaller fields. When the amplitude of the microwave magnetic field reaches the threshold value, $h=h_{\rm th}$, the $\Theta(H)$ dependence can be characterized by an appearance of a sharp maximum (foldover). As the amplitude of the microwave magnetic field exceeds the threshold level, $h>h_{\rm th}$, three values of the precession angle Θ correspond to a single magnitude of the field H in the range $(H_{\rm down}, H_{\rm up})$. The field range between points b and c (Fig. 6) is unstable and the steady spin precession there is

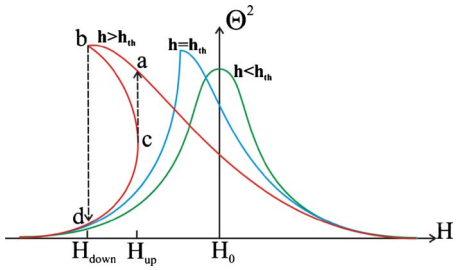

FIG. 6. (Color online) Schematic dependence of the spin precession angle Θ on the magnetic field H at various amplitudes of the microwave field, i.e., $h<h_{th}$, $h=h_{th}$, and $h>h_{th}$, where H_0 is the resonant field at $h\rightarrow 0$.

impossible. Thus, only two magnitudes of the amplitude Θ can be experimentally observed, i.e., in the intervals ab and cd, each corresponding to a single magnitude of the field H, i.e., bistability is taking place. The choice between these two values is defined by the previous history, i.e., whether the $\Theta(H)$ dependence was measured at an increasing or decreasing field H. The observed phenomenon (foldover) has been previously experimentally demonstrated in thin yttrium-iron garnet and permalloy films.[8–10]

The critical fields H_{up} and H_{down} can be quantitatively determined from the numerical solution of Eq. (4) providing $d\Theta/dH=\pm\infty$,[8]

$$H_{up}\approx H_0-a\cdot h^{2/3},\quad a=\frac{3}{2}M^{1/3}\ \text{at}\ \Theta_{up}=(h/M_0)^{1/3}, \tag{5}$$

$$H_{down}\approx H_0-b\cdot h^2,\quad b=\frac{1}{2}\frac{M}{\Delta H_0^2}\ \text{at}\ \Theta_{down}=h/\Delta H_0. \tag{6}$$

Equations (4)–(6) are usually applicable when the dc magnetic field **H** is aligned along the hard magnetocrystalline axis. The change in the sample orientation in the external magnetic field causes a consequent alteration of the magnetocrystalline anisotropy contribution to the magnetic moment precession. Change in the crystal orientation in the dc magnetic field will lead to the correspondent alteration of the resonant field H_0. Coefficients a and b in Eqs. (5) and (6) are also orientation dependent which reflects the influence of the magnetocrystalline anisotropy on the moment M. On the other hand, the power coefficients of the microwave magnetic field h are isotropic. Thus, one can expect that Eqs. (5) and (6) are applicable for any crystal orientation down to a and b coefficients. According to Eq. (5), the resonant line shift $|H_{up}-H_0|$ above the threshold should be proportional to $h^{2/2}\propto P^{1/3}$. In fact, the linear dependence $|H_{up}-H_0|$ vs $P^{1/3}$ was experimentally observed in YN crystals at any orientation of the sample in the dc magnetic field (Fig. 7). This proves applicability of the model discussed above and verifies the appropriateness of Eqs. (4)–(6) in any orientation.

Further we consider the orientation dependence of the threshold power. The transition to a bistable regime is observed when the maximum on the $\Theta(H)$ dependence is

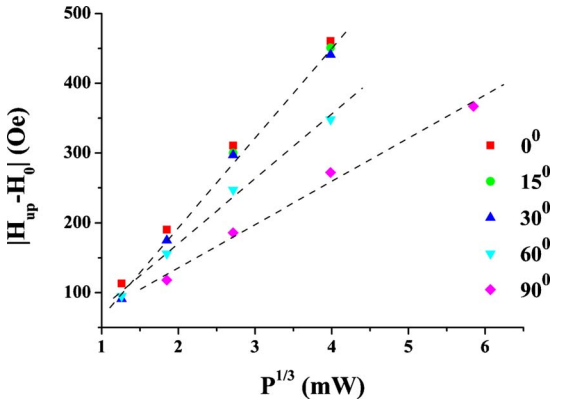

FIG. 7. (Color online) Power dependence of the resonant line shift $|H_{up}-H_0|$ at different angles ϕ between the c axis of the crystal and direction of the dc magnetic field **H**. Dashed lines are approximated by Eq. (5).

shifted by $\sqrt{3}\Delta H_0$. Thus, the threshold of the microwave power is defined only by the linewidth [Eq. (1)] and is not directly dependent on internal fields (e.g., magnetocrystalline anisotropy). Consequently, Eq. (1) is applicable for any crystal orientation. It should be noted, however, that magnetocrystalline anisotropy can indirectly affect the power threshold P_{th} through the linewidth ΔH_0. Thus, it can be implied that the angular dependence of the threshold field is predefined by the orientation dependence of ΔH_0.

When the orientation of the YN crystal in the dc magnetic field was changed, we observed a mutual overlap of the resonant lines (Fig. 2) making the precise direct definition of ΔH_0 impossible. As a result, in order to retrieve the angular dependence of ΔH_0, we used a relation between the width of the resonant line ΔH_0 and parameters of the magnetocrystalline anisotropy and the resonant field H_{res} (at $h\rightarrow 0$). The resonant field is defined as[11]

$$\left(\frac{\omega}{\gamma}\right)^2=\frac{1}{M^2}\left[E_{\phi\phi}\left(\frac{E_{\phi\phi}}{\sin^2\phi}+\frac{\cos\phi}{\sin\phi}E_{\phi}\right)-\left(\frac{E_{\phi\varphi}}{\sin\phi}-\frac{\cos\phi}{\sin\varphi}\times\frac{E_{\varphi}}{\sin\phi}\right)^2\right], \tag{7}$$

where $\omega=2\pi\nu$ and $\nu=9.4$ GHz is the microwave frequency of the spectrometer, γ is the gyromagnetic ratio, M is the sample magnetization, E is the free energy density, E_{φ}, $E_{\phi\phi}$, $E_{\phi\varphi}$ are the first and second angular derivatives of the free energy density, corresponding to the angles ϕ and φ, ϕ (φ) is the angle between the c (a) axis of the crystal and the magnetization vector **M**. The density of the free energy is defined as[12]

$$E=-\mathbf{HM}-K_{2\perp}\cos^2\phi-\frac{1}{2}K_{4\perp}\cos^4\phi-\frac{1}{2}K_{4\|}\cdot\frac{1}{4}(3+\cos 4\varphi)\sin^4\phi+K_{2\|}\sin^2\phi\cos^2(\varphi-\varphi_{2\|}), \tag{8}$$

where $K_{2\perp}$, $K_{2\|}$ are the second-order and $K_{4\perp}$, $K_{4\|}$ are the

fourth-order anisotropy constants defined either perpendicular or parallel to the *ac* plane of the crystal. As in the studied experimental conditions ($H \sim 2$ kOe and at $T=4$ K) the YN crystals are in the saturated state, the magnetization vector **M** is aligned with the dc magnetic field **H**. Thus, ϕ and φ correspond to the angles between the dc magnetic field and the *c* and *a* axes of the crystal. Therefore, in an assumption of the Lorentzian line shape the homogeneous part of the linewidth can be calculated according to Ref. 1,

$$\Delta H_0 = \frac{2}{\sqrt{3}} \cdot \frac{1}{|\partial\omega/\partial H|} \times \frac{\alpha\gamma}{M}\left(E_{\phi\phi} + \frac{E_{\varphi\varphi}}{\sin^2\phi}\right). \quad (9)$$

Magnetocrystalline anisotropy coefficients were defined from the fitting of the angular dependence of the resonant field by Eq. (7): $K_{2\perp}=35$ kerg/cm^3, $K_{2\parallel}=5$ kerg/cm^3, $K_{4\perp}=2$ kerg/cm^3, and $K_{4\parallel}=0$. Using the obtained parameters we calculate the angular dependence of the homogeneous part of the linewidth, ΔH_0 vs ϕ, down to damping constant α, which generally does not affect the orientation dependence. The $\Delta H_0(\phi)$ dependence was calculated using the isotropic damping constant, $\alpha=0.0153$. At this value of α, the calculated linewidth coincides with its experimental value, $\Delta H_0=24$ Oe, used for estimation of the threshold power at $\phi=0°$ (Ref. 5). It was shown that ΔH_0^3 increases with the angle ϕ in the range $0°-45°$, however, the further increase in ϕ up to 90° leads only to an insignificant change in ΔH_0^3 (Fig. 4, solid line). Thus, orientation dependences of the threshold field P_{th} and linewidth ΔH_0^3 are qualitatively very similar. This observation implies that the dependence of the threshold power on the crystal orientation in the magnetic field is generally determined by the anisotropy of the linewidth ΔH_0.

V. CONCLUSION

Thus, in the chiral molecular ferrimagnet $[Mn\{(R/S)\text{-pn}\}_2]_2[Mn\{(R/S)\text{-pn}\}_2H_2O][Cr(CN)_6]$ we observe a sharp transformation of the line shape and change in the ferromagnetic resonance field as the microwave power reaches the threshold value. The threshold value depends on the mutual orientation of the YN crystal and dc magnetic field. The obtained results are explained by development of Suhl's spin-wave instability and transition into the bistable regime. Modification of the FMR spectrum and transition into the bistable regime are defined by the magnetocrystalline anisotropy of the sample, whereas the threshold effect of the microwave field is related to existence of stable spin precession states determined by the anisotropy field.

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