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Influence of proton irradiation on the magnetic properties of two-dimensional Ni(II) molecular magnet

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The influence of 1.9 MeV proton irradiation on structural and magnetic properties has been explored in the two-dimensional (2D) NiSO₄(1,3-phenylenediamine)₂ coordination ferrimagnet. The X-ray powder diffraction and IR spectroscopy revealed that the octahedrons with Ni ion in the center remain unchanged regardless of the fluence a sample received. In contrast, proton irradiation greatly influences the hydrogen bonds in the flexible parts in which the 1,3-phenylenediamine is involved. Dc magnetic measurements revealed that several magnetic properties were modified with proton irradiation. The isothermal magnetization measured at $T=2.0$ K varied with the proton dose, achieving a 50% increase in magnetization in the highest measured field $\mu_0 H_{dc}=7$ T or a 25% decrease in remanence. The most significant change was observed for the coercive field, which was reduced by 90% compared to the non-irradiated sample. The observed results are accounted for the increased freedom of magnetic moments rotation and the modification of intralayer exchange couplings.

The recent intensive investigations in the field of multifunctional molecular materials are integrally related to their possible application in modern technology, such as high-density data storage and processing^{1–4}, magnetic refrigeration^{5–8}, or optically active sensors and switches^{9,10}. The broad capability of molecular magnetism emerges from the variety of available structures^{11,12} and the possibility of changing their properties with external stimuli, including temperature¹³, pressure¹³, and light irradiation¹⁴. Proton irradiation is another approach for tuning material properties by external factors. It is currently widely employed in the studies of carbon allotropes^{15,16}, semiconductors¹⁷, films¹⁸, superconductors¹⁹, and alloys²⁰ to engineer material features in a controllable manner^{21–24}. Solids irradiated with energetic particles are exposed to extremely high-density local energy deposition that causes nonlinear and threshold effects²⁵. As a result, new materials with novel properties can be obtained.

In particular, ion irradiation is used to modify magnetic properties. The induced defects may give rise to paramagnetic response in non-magnetic materials when the defect concentration exceeds a specific threshold value^{26–28} or alter the magnetic properties of paramagnets and systems with long-range magnetic order (LRMO), especially when strong magnetostructural correlations are present. The irradiation can increase Curie temperature^{29–31} and impact such properties as the coercive field, magnetization saturation, g-factor, and shape of the magnetic hysteresis loop^{32–34}. Proton irradiation can generate changes at the atomic level over the selected area and depth by adjusting protons energy, which makes this approach perspective for the controlled engineering of magnetic materials²⁹.

Currently, there are no systematic studies on the response of molecular magnetic materials to ion irradiation. To fill this gap, we examined the effects of 1.9 MeV proton irradiation on the magnetic properties of the NiSO₄(1,3-phenylenediamine)₂ coordination polymer, hereafter abbreviated as Ni(MPD)₂SO₄. This molecular magnet reveals a considerable size of the coercive field and long-range magnetic ordering below $T_C=24$ K. X-ray powder diffraction, infrared spectroscopy, and magnetic measurements were performed to investigate the influence of proton fluence $\phi = 5 \times 10^{13} - 2.2 \times 10^{15}$ cm⁻² on structural and magnetic properties. Although structural changes were observed only within the polymer part related to the C–H and N–H bonds, the proton

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irradiation has induced significant modifications of magnetic properties, especially the coercive field, degree of irreversibility, and maximum magnetization.

Results

X-ray powder diffraction (XRPD). The $\text{Ni}(\text{MPD})_2\text{SO}_4$ (Fig. 1) crystallizes in a monoclinic crystal system (Cc space group). The nickel (II) ions are bridged by tetrahedral SO_4^{2-} anions forming 2D layers parallel to the bc plane, and each layer is separated from one another by the 1,3-phenylenediamine (MPD) ligand. The nickel atom occupies the center of a distorted octahedron formed by two nitrogen atoms from the diamine molecules (MPD) and four oxygen atoms from three SO_4^{2-} anions. Each Ni^{2+} possesses six Ni^{2+} nearest neighbors and is separated from them by a distance of 4.914 Å, 4.931 Å, or 6.546 Å (two of each). The interlayer Ni–Ni distance is equal to 14.559 Å. More details regarding $\text{Ni}(\text{MPD})_2\text{SO}_4$ structure were described in³⁵. The XRPD measurements of all samples have not shown meaningful changes in the diffraction patterns pointing to the conservation of the $\text{Ni}(\text{MPD})_2\text{SO}_4$ core structure after proton irradiation (see Supplementary Information Figure S1 online). However, greater half-widths of the diffraction peaks after proton irradiation may indicate the increase in crystal lattice microstrains or crystallites size reduction.

Infrared spectroscopy (IR). In the mid-infrared range, the absorption spectra observed for $\text{Ni}(\text{MPD})_2\text{SO}_4$, for samples irradiated with various fluences, have complex character (see Fig. 2). In the range of the deformation vibrations ($\nu < 2000 \text{ cm}^{-1}$), a series of $\delta_{\text{C-H}}$ bands (in a ring), overlapping with those originating from SO_4 ions,

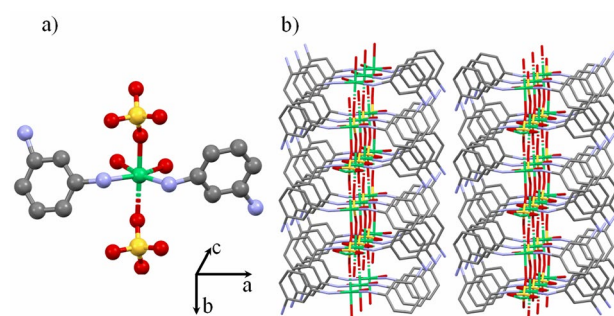


Figure 1. The crystal structure of $\text{Ni}(\text{MPD})_2\text{SO}_4$: (a) representative molecular fragment (b) packing. Colors: Ni (green), S (yellow), O (red), C (black), N (light blue). Hydrogen atoms are omitted for clarity.

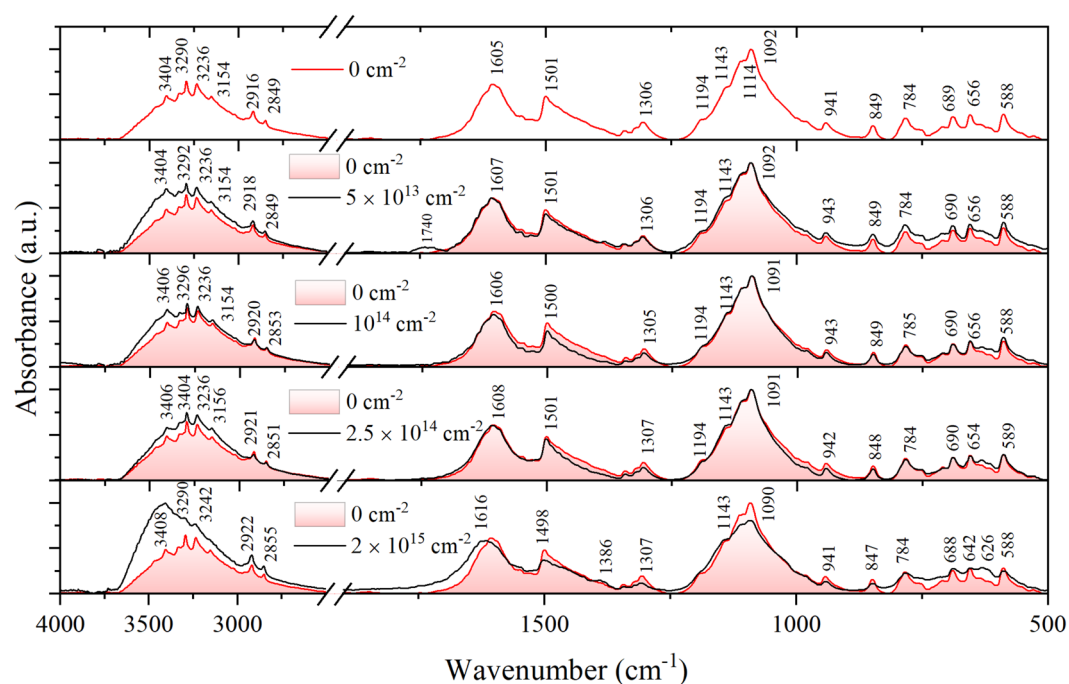


Figure 2. Fourier-transform infrared spectroscopy (FTIR) patterns of the $\text{Ni}(\text{MPD})_2\text{SO}_4$ samples irradiated with various fluences.

are visible. The IR spectra show NiSO₄ sharp peaks of the characteristic S–O stretch [$\nu_{\text{S-O}}(\text{SO}_4)$ 900–1500 cm⁻¹] and deformation [$\delta_{\text{S-O}}(\text{SO}_4)$ 400–700 cm⁻¹] vibrations. On the other hand, a band corresponding to the stretching vibration from the Ni=O group is visible at about 600 cm⁻¹. Broad bands, corresponding to S–O vibrations in the SO₄ atomic group, were observed at about: ~525 cm⁻¹ as $\delta_{\text{S-O}}$ deformation vibrations, and ~1100 cm⁻¹ and ~1600 cm⁻¹ as $\nu_{\text{S-O}}$ stretching vibrations³⁶.

Vibration bands of the lighter atoms, i.e., C–H and N–H in MPD ligand, both deforming, i.e., in the range of 500–2000 cm⁻¹, and the range of stretching vibrations, i.e., above 2000 cm⁻¹, strongly overlap with the vibrations of the groups containing heavy atoms. They are visible in the form of low-intensity bands emerging from wide bands corresponding to the vibrations of the group, e.g., SO₄. Bands at about (~700, ~1551) cm⁻¹ are assigned to the vibrations of the CN group³⁷.

The range of stretching vibrations deserves special attention. The broad band in this range (ν_{CH} , ν_{NH}) becomes asymmetric with the increase of the irradiation dose. The band is shifted towards a higher wavenumber (blue shift) which means that the strengths of the C–H and N–H are weakened³⁸. The C–H and N–H bonds are involved well in forming hydrogen bonds, and the molecule's structure (shown in Fig. 1) perfectly enables it. A substantial change in the shape of the band with increasing irradiation dose proves the considerable influence of the hydrogen bonds on the ordering of the structure in its flexible parts in which MPD is involved.

Moreover, the visible asymmetry of the band indicates that there are different types of hydrogen bonds in which the nitrogen atom is involved. The nitrogen atom from the molecule's core (close to the nickel atom) is very stable (rigid) due to its involvement in covalent bonds. In contrast, the steric conditions for the "free" nitrogen atom favor the rapid formation/breaking of intermolecular bonds. Therefore, these weak interactions only affect the elastic part of the molecules, while the core of the molecule does not feel their presence. The assignments of major vibrational bands in the FTIR spectra of the Ni(MPD)₂SO₄ samples irradiated with various fluences are in Table 1.

Magnetic properties. The general magnetic properties of Ni(MPD)₂SO₄ were investigated in the recent work by González Guillén et al.³⁵. Three magnetic couplings were found in the system: two competing intralayer superexchange pathways, antiferromagnetic and ferromagnetic, that lead to non-collinear ordering within a layer and a dipole–dipole coupling between layers. The low anisotropy of Ni(II) ions does not promote 2D long-range magnetic ordering (LRMO). Therefore, the LRMO occurs below the Curie temperature $T_C = 24$ K when all three interactions (where the dipolar coupling is the weakest one) are strong enough to couple magnetic moments in 3D. The product of molar magnetic susceptibility and temperature χT of Ni(MPD)₂SO₄ measured

Wavenumber (cm ⁻¹)					Assignment
0 (cm ⁻²)	5 × 10 ¹³ (cm ⁻²)	10 ¹⁴ (cm ⁻²)	2.5 × 10 ¹⁴ (cm ⁻²)	2.2 × 10 ¹⁵ (cm ⁻²)	
3404	3404	3406	3406	3408	$\nu_{\text{N-H}}$ (of free amines)
			3404		
3290	3292	3296		3290	
3236	3236	3236	3236	3242	
3154	3154	3154	3156		$\nu_{\text{C-H}}$ (in ring)
2916	2918		2921	2922	$\nu_{\text{C-H}}$ (in CH ₂)
2849	2849	2853	2851	2855	$\nu_{\text{C-H}}$ (in CH ₂)
	1740				
1605	1607	1606	1608	1616	$\delta_{\text{N-H}}$ (rocking vibrations)
1501	1501	1500	1501		
				1498	ν_{CN}
				1386	$\nu_{\text{Ni-S}}$
1306	1306	1305	1307	1307	$\delta_{\text{C-H}}$
1194	1194	1194	1194		$\delta_{\text{C-C}}$
1143	1143	1143	1143	1143	$\delta_{\text{C-C}}$
1114	1114	1114	1114	1114	ν_{SO_4}
1092	1092	1091	1091	1090	ν_{SO_4}
941	943	943	942	941	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
849	849	849	848	847	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
784		785	784	784	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
689	690	690	690	688	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
656	656	656	654	642	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
				626	$\delta_{\text{S-O}} + \delta_{\text{C-H}}$
588	588	588	589	588	$\delta_{\text{S-O}} + \nu_{\text{C-N}} + \delta_{\text{C-H}}$

Table 1. Assignment of major vibrational bands in the FTIR spectra of the Ni(MPD)₂SO₄ samples irradiated with various fluences^{36–38}.

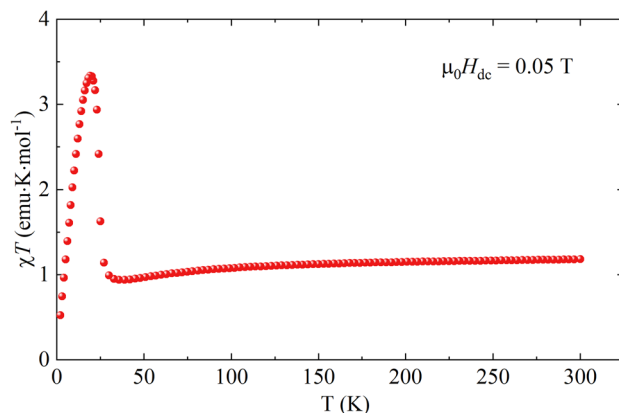


Figure 3. Temperature dependence of χT product for Ni(MPD)₂SO₄ reference sample in the static magnetic field of $\mu_0 H_{dc} = 0.05$ T.

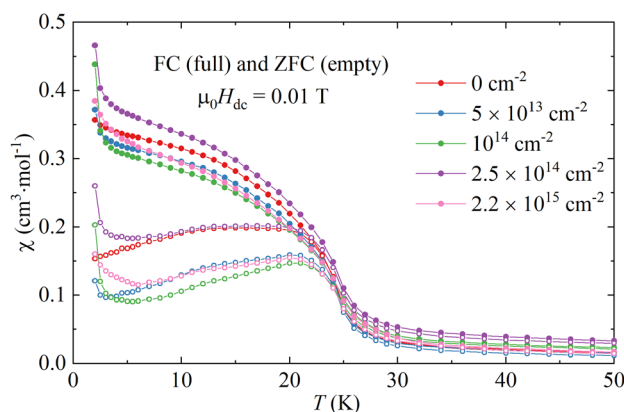


Figure 4. Field cooling (FC—full points) and zero-field cooling (ZFC—empty points) magnetic susceptibilities of Ni(MPD)₂SO₄ samples irradiated with various fluences ϕ measured in static magnetic field $\mu_0 H_{dc} = 0.01$ T at $T = 2.0$ – 50 K.

in the temperature range $T = 2.0$ – 300 K in a constant magnetic field of $\mu_0 H_{dc} = 0.05$ T is shown in Fig. 3. At $T = 300$ K, χT equals 1.18 emu·K·mol⁻¹, which can be obtained for a single isolated Ni^{II} ion with spin $S_{Ni} = 1$, assuming a spectroscopic factor $g = 2.17$. Such enhancement of g is expected for the Ni^{II} ion placed in the octahedral ligand field³⁹.

The field cooling (FC) and zero-field cooling (ZFC) magnetic susceptibilities of Ni(MPD)₂SO₄ as a function of temperature are shown in Fig. 4 for proton fluences ranging from $\phi = 0$ cm⁻² to $\phi = 2.2 \times 10^{15}$ cm⁻². The temperature of phase transition to LRMO obtained from the temperature derivatives of FC and ZFC curves was $T_C = 24$ K regardless of the sample radiation dosage. Compared to the reference sample, an additional increase in susceptibility was observed at the lowest temperatures for the samples irradiated with protons. However, the overall shapes of FC/ZFC were preserved above about $T = 5.0$ K. The obtained susceptibility magnitude varied between each sample; for the FC mode, from 90 to 130% of the reference sample's corresponding value, whereas for ZFC, it varied between 55 and 170%. The largest FC/ZFC signal was obtained for $\phi = 2.5 \times 10^{14}$ cm⁻² and the lowest for $\phi = 10^{14}$ cm⁻². The former sample was also the only one for which the FC/ZFC values above $T = 5.0$ K were greater than the values for the reference sample.

The pair of ZFC and FC curves coincide with each other only above a certain irreversibility temperature T_{irr} ⁴⁰, which can be found by plotting the difference between FC, $\chi_{FC}(T)$, and ZFC, $\chi_{ZFC}(T)$, susceptibilities, and determining the temperature above which the difference becomes less than 5%. The degree of irreversibility $\Delta\chi_{irr}$ was estimated for each studied fluence using the following integral⁴¹:

$$\Delta\chi_{irr} = \int_{T_1}^{T_2} (\chi_{FC}(T) - \chi_{ZFC}(T)) dT, \quad (1)$$

where $T_1 = 2.0$ K and $T_2 = T_{irr}$.

The T_{irr} and $\Delta\chi_{irr}$ are summarized in Fig. 5 for each irradiation dose. The T_{irr} weakly depends on the irradiation dose revealing values between 23 and 25 K, corresponding to 105–115% of the reference sample's T_{irr} .

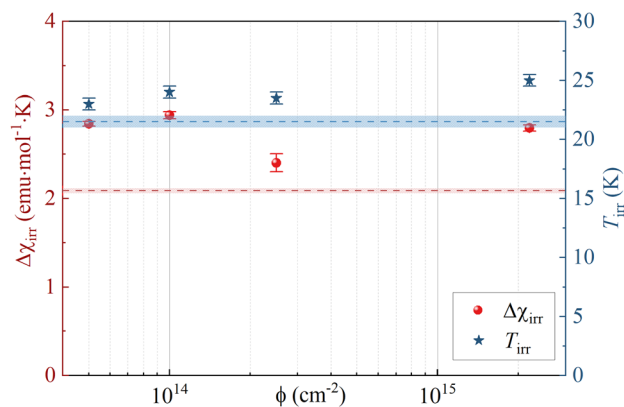


Figure 5. The degree of irreversibility $\Delta\chi_{\text{irr}}$ (1) (left axis) and irreversibility temperature T_{irr} (right axis) for Ni(MPD)₂SO₄ samples irradiated with various fluences. The dashed lines represent the values obtained for the reference sample $\phi=0\text{ cm}^{-2}$ and dotted areas their errors.

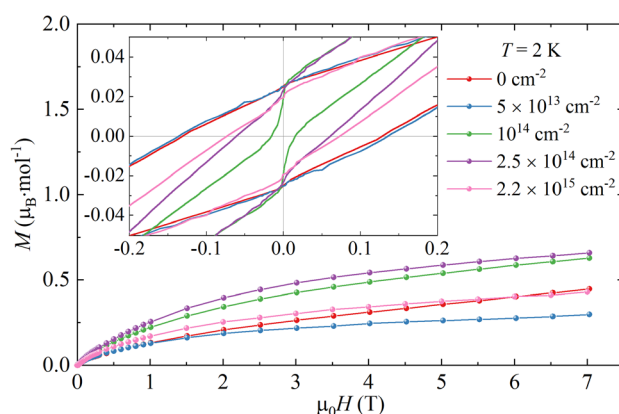


Figure 6. The isothermal magnetization of Ni(MPD)₂SO₄ samples irradiated with various fluences ϕ measured at $T=2.0\text{ K}$ and in applied magnetic fields from zero to $\mu_0H=7\text{ T}$. Inset: the picture enlarged on $\mu_0H=[-0.2, 0.2\text{ T}]$ range to show the coercivity and remanence of the samples.

However, proton irradiation has a stronger influence on the degree of irreversibility. The obtained values of $\Delta\chi_{\text{irr}}$, between $2.4\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$ and $2.95\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$, are from 115 to 140% of the reference sample's $\Delta\chi_{\text{irr}}$. The highest $T_{\text{irr}}=25\text{ K}$ was found for $\phi=2.2\times 10^{15}\text{ cm}^{-2}$, while the maximal value of $\Delta\chi_{\text{irr}}=2.95\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$ was for $\phi=10^{14}\text{ cm}^{-2}$.

The Fig. 6 shows the isothermal magnetization of Ni(MPD)₂SO₄ obtained at $T=2.0\text{ K}$ for all studied fluences ϕ . In $\mu_0H=7\text{ T}$, the lowest value of magnetization $M_{7\text{T}}=0.3\text{ }\mu_{\text{B}}\cdot\text{mol}^{-1}$ was observed for $\phi=5\times 10^{13}\text{ cm}^{-2}$ sample and the highest $M_{7\text{T}}=0.65\text{ }\mu_{\text{B}}\cdot\text{mol}^{-1}$ for $\phi=5\times 10^{14}\text{ cm}^{-2}$ sample, compared to $M_{7\text{T}}=0.45\text{ }\mu_{\text{B}}\cdot\text{mol}^{-1}$ for the reference sample (where $M_{7\text{T}}$ is the magnetization at $\mu_0H=7\text{ T}$).

The low field part of magnetic hysteresis loops is depicted in the inset of Fig. 6, enlarged on the coercivity μ_0H_c and remanence M_R . The $M(H)$ loops were opened below $\mu_0H=1\text{ T}$ for all the samples. The hysteresis loop for the sample with the lowest fluence of $\phi=5\times 10^{13}\text{ cm}^{-2}$ coincided with the reference's loop in the field range $\mu_0H=[-1\text{ T}, 1\text{ T}]$. For the remaining samples, the values of μ_0H_c and M_R were reduced, and a step in the $M(H)$ loop near $\mu_0H=0\text{ T}$ appeared, which is especially visible for $\phi=10^{14}\text{ cm}^{-2}$. Figure 7. shows the hysteresis loop parameters for the irradiated samples, presented as a relative value to the reference sample's coercivity ($\mu_0H_c=0.13\text{ T}$), remanence ($M_R=0.45\text{ }\mu_{\text{B}}\cdot\text{mol}^{-1}$), and magnetization at $\mu_0H=7\text{ T}$ ($M_{7\text{T}}=0.3\text{ }\mu_{\text{B}}\cdot\text{mol}^{-1}$). $M_{7\text{T}}$ is reduced for $\phi=5\times 10^{13}\text{ cm}^{-2}$ to 65% of the reference level, but it raises with an increasing ϕ to 150% for $\phi=2.5\times 10^{14}\text{ cm}^{-2}$. The further increase in fluence reduces the value of $M_{7\text{T}}$, which becomes 95% of the reference level for the sample with the highest studied fluence of $\phi=2.2\times 10^{15}\text{ cm}^{-2}$. The samples irradiated with the fluences $\phi\geq 10^{14}\text{ cm}^{-2}$ showed the reduction of μ_0H_c to 10–55% and M_R to 75–90% of the reference level.

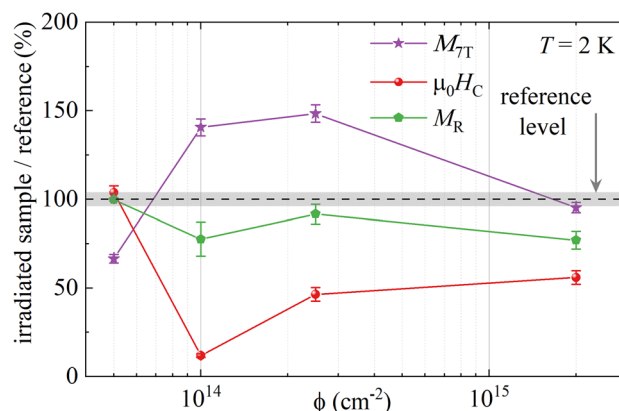


Figure 7. The relative values of magnetic hysteresis loop parameters for Ni(MPD)₂SO₄ samples irradiated with various fluences ϕ normalized to the reference sample's corresponding values. Violet stars: magnetization at $\mu_0 H = 7$ T (M_{7T}); red circles: coercive field ($\mu_0 H_c$); green pentagons: remnant magnetization (M_R). The dashed line is placed at 100% and represents the values obtained for the reference sample $\phi = 0$ cm⁻² with errors indicated by gray dotted area. The lines between points are only for an eye guide.

Φ Fluence (cm ⁻²)	T_{irr}		$\Delta\chi_{irr}$		M_{7T}		M_R		$\mu_0 H_c$	
	(K)	%	(emu·mol ⁻¹ ·K)	%	(μ_B ·mol ⁻¹)	%	(μ_B ·mol ⁻¹)	%	(Oe)	%
0 (ref.)	21.5	100	2.09	100	0.45	100	0.025	100	1310	100
5×10^{13}	23	107	2.84	136	0.3	67	0.025	99	1360	104
10^{14}	24	112	2.94	141	0.63	141	0.02	78	155	12
2.5×10^{14}	23.5	109	2.4	115	0.69	148	0.023	92	265	46
2.2×10^{15}	25	116	2.8	134	0.43	95	0.019	77	735	56

Table 2. The influence of proton irradiation on T_{irr} , $\Delta\chi_{irr}$, M_{7T} , M_R , and $\mu_0 H_c$ in Ni(MPD)₂SO₄. Absolute values and their ratio to the corresponding values for the reference sample (in percentages) are given.

Discussion

The XRPD and IR spectroscopy measurements indicated that the core structure of Ni(MPD)₂SO₄ remains unchanged. Consequently, the interlayer distance and the dipolar interaction are the same regardless of the fluence a sample received. Furthermore, the Curie temperature T_C remains the same because its value is determined by the weakest magnetic coupling, the dipole–dipole one. On the other hand, irradiation significantly modifies the C–H and N–H bonds, which are involved in forming hydrogen bonds related to the MPD ligand (the flexible part of the structure). In particular, the interaction of lattice with protons may lead to the C–H and N–H bonds breakage, creating hydrogen vacancies that would not be visible in XRPD, as reported in the methylammonium lead iodide perovskites after 10 MeV proton irradiation⁴² or polymer composite of polymethyl methacrylate doped with ferric oxalate after 3 MeV proton irradiation⁴³.

The bond modification leads to changes in the crystal field, incorporation of local defects, altered intralayer exchange couplings (due to local structure modification), and increased freedom of the magnetic moments. In consequence, magnetic properties in the LRMO phase (below T_C) have been modified. Table 2. summarizes the influence of proton irradiation on the magnetic properties of Ni(MPD)₂SO₄.

The isothermal magnetization measurements (Fig. 6) confirm a strong influence of irradiation on the magnetization processes in Ni(MPD)₂SO₄. The main reason for this is the increasing number of defects with increasing fluence. Note that irradiating the samples with the selected fluences is not enough to obtain a homogenous distribution of produced defects, and the observed magnetization data may be a mixture of several defect-induced magnetic phases of Ni(MPD)₂SO₄ with well-localized clusters. Introducing defects lowers the magnetostatic energy to a minimum for the dose of $\phi = 10^{14}$ cm⁻² (the lowest value of the coercive field). However, a further increase in the number of defects leads to stronger pinning effects, which increase the coercive field for doses $\phi > 10^{14}$ cm⁻².

The mechanism of M_{7T} modification is different and related to changes in magnetic couplings in the compound. For the lowest dose of $\phi = 5 \times 10^{13}$ cm⁻², antiferromagnetic interactions are more dominant over the ferromagnetic ones, which lowers the magnetization M_{7T} down to 67% of the M_{7T} for the reference sample. For intermediate doses of $\phi = 10^{14}$ cm⁻² and $\phi = 2.5 \times 10^{14}$ cm⁻², the corresponding values are 141% and 148%, respectively, indicating the enhancement of ferromagnetic interactions, and for the maximum dose of $\phi = 2.2 \times 10^{15}$ cm⁻², the value of M_{7T} is similar to that for the reference. Note that the calculated magnetization for the parallel alignment of Ni^{II} magnetic moments ($S_{Ni} = 1$) with a spin-only Landé factor of $g = 2.17^{35,39}$ yields the magnetization saturation of $M_S = 2.17 \mu_B \cdot \text{mol}^{-1}$. Thus, the antiferromagnetic interactions are dominant in all studied samples.

Similar non-monotonic effects of proton irradiation are commonly found in the literature^{31,33,34,44–46}. In the Ni_{48.4}Mn_{28.8}Ga_{22.8} film irradiated with 120 keV protons⁴⁵, the M_S for $\phi = 10^{15}$ cm⁻² raised to 155% of the non-irradiated sample's value, but for $\phi = 2 \times 10^{16}$ cm⁻², the observed M_S was only 102%. Another case is the initially diamagnetic SiC (0001) single crystal⁴⁴ that displays ferromagnetism after 3 MeV proton irradiation treatment. For $\phi = 8 \times 10^{15}$ cm⁻², the M_S measured in-plane reached 0.17 emu·g⁻¹ but for $\phi = 1.3 \times 10^{16}$ cm⁻² it was reduced to 0.09 emu·g⁻¹.

An additional increase of the magnetization in the FC/ZFC curves observed at $T = 2–6$ K for all irradiated samples may arise from a small sample's fraction, which due to the deformation and partial destruction of a lattice, leads to the creation of localized magnetic moments due to open bonds⁴⁷ or paramagnetic amorphous zones in the lattice⁴⁴. This paramagnetic contribution may also cause the appearance of the observed step in the hysteresis loop near-zero field. The other possibility is the chemical composition modification of Ni(MPD)₂SO₄ samples by incorporating the highly energetic hydrogen atoms into the crystal lattice^{44,45}. However, no additional phases were detected in the XRPD and IR measurements. Therefore, the amount of paramagnetic phase is not significant.

Conclusions

In summary, we have investigated the impact of 1.9 MeV proton irradiation on the layered Ni(MPD)₂SO₄ molecular magnet in the function of received fluence ϕ . It was found that proton irradiation influences only the flexible part of the structure (related to the C–H and N–H bonds in the MPD ligand), while the core of the compound remains unchanged. These lead to significant changes in magnetic properties as a function of fluence: coercive field $\mu_0 H_c$ (reduction up to 90%), maximal magnetization M_{T} (between 65 and 150% of the reference sample), remanence M_R (reduction up to 25%) and degree of irreversibility $\Delta\chi_{irr}$ (increase up to 40%). Simultaneously, the Curie temperature was constant $T_C = 24$ K regardless of ϕ because the core structure, interlayer distance, and consequently, dipolar coupling of the Ni(MPD)₂SO₄ system remains the same. The observed non-monotonic magnetic properties changes are caused by the altered intralayer exchange couplings due to local structure modification, incorporation of local defects, and increased freedom of the magnetic moments.

Materials and methods

Sample preparation. The studied Ni(C₆H₈N₂)₂SO₄ compound (hereafter abbreviated as Ni(MPD)₂SO₄) was synthesized using NiSO₄·7H₂O and 1,3-phenylenediamine (MPD, C₆H₈N₂) ligand with a solvent-free synthesis approach according to the literature procedure³⁵.

The Van de Graaff accelerator was used to generate a proton beam with set conditions: energy of 1.9 MeV, particle current of 10–12 nA, and beam size of about 0.5 mm × 0.5 mm. Powder samples mounted on copper plates were used (see Supplementary Figure S2 online) with a thickness lower than the 1.9 MeV proton penetration depth (see Supplementary Figure S3 online). The obtained fluences were equal to: $\phi = 5 \times 10^{13}$ cm⁻², 10^{14} cm⁻², 2.5×10^{14} cm⁻², 2.2×10^{15} cm⁻².

Characterization methods. X-ray powder diffraction (XRPD) patterns were determined by the PANalytical X'Pert Pro instrument with a copper X-ray tube source (Cu K_{α1}, 1.541 Å), operated at 40 kV and 30 mA in the θ – 2θ geometry. Data were recorded at room temperature in the range of 5–40° 2θ . The results were adjusted by background correction and the anode's characteristic X-ray K_{α2} removal.

The infrared spectroscopy measurements were done for samples in powder form, pelleted with potassium bromide (transparent in the mid-infrared range). Fourier-transform infrared spectroscopy (FTIR) measurements were carried out in the mid-infrared range (4000–500 cm⁻¹), with a resolution of 2 cm⁻¹, on the EXCALIBUR 3000 spectrometer; 128 scans were done for the spectrum at room temperature.

The Quantum Design SQUID MPMS-XL magnetometer was used to measure the magnetic properties of all powder samples. The isothermal magnetization $M(\mu_0 H)$ was collected in the applied field of $\mu_0 H = [-7$ T, 7 T]. Static magnetic susceptibility measurements were carried out in the field cooling (FC) and zero-field cooling (ZFC) modes in the $T = 2.0–300$ K temperature range with the applied field of $\mu_0 H_{dc} = 0.01$ T. The obtained data points were processed taking the whole sample mass, i.e., assuming a homogeneous distribution of potential changes in the studied compounds after proton irradiation. The temperature-independent diamagnetic contribution of $\chi_0 = -1.84 \times 10^{-4}$ emu·mol⁻¹ estimated from Pascal's constants⁴⁸ was subtracted from the measured signals.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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D.C.: study design, magnetic properties data collection, analysis, and interpretation, manuscript preparation; P.K.: data interpretation, manuscript preparation; E.J.G.: infrared spectroscopy data collection and analysis, manuscript preparation; M.P.: powder X-ray data collection and analysis; J.L.: proton irradiation; A.B.G.G. and W.L.: sample synthesis, structure details, manuscript revision.

Competing interests

The authors declare no competing interests.

Additional information

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