Researchers discover ferromagnetism induced by defects in correlated 2D materials

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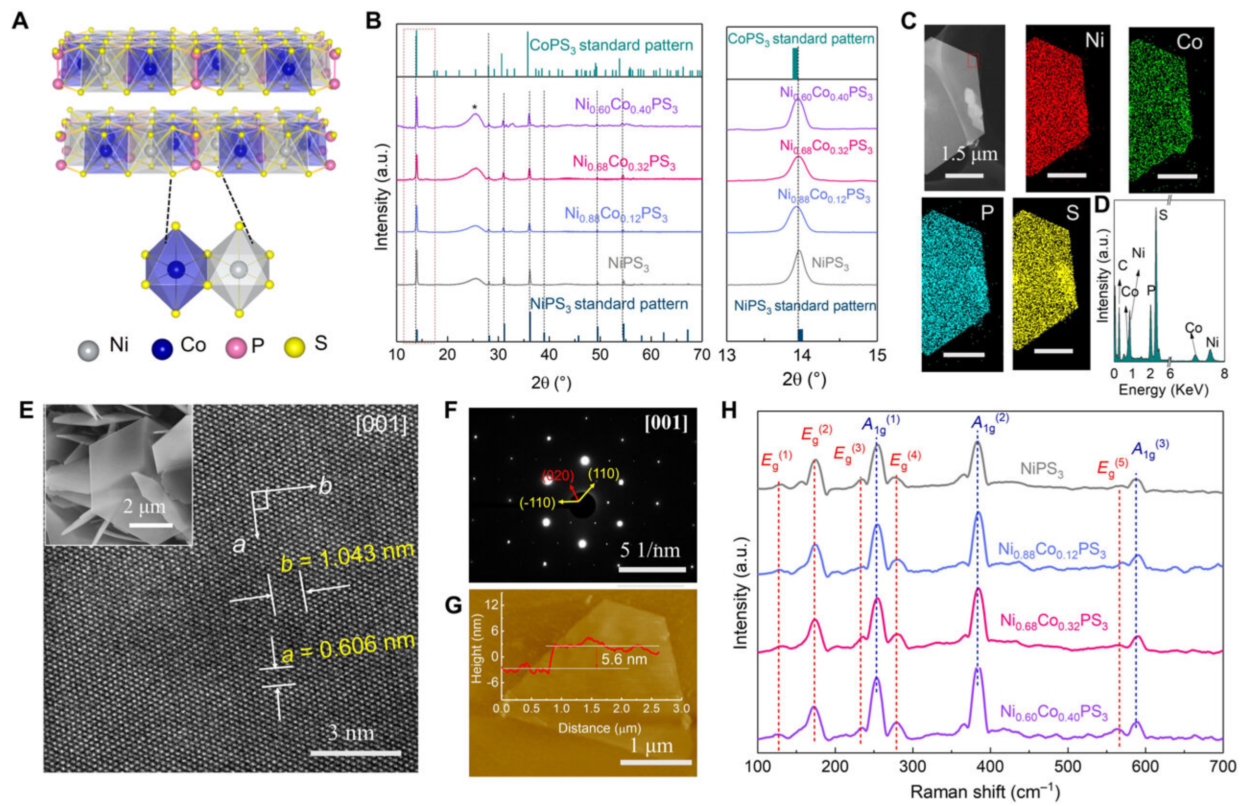

Fig. 1. Structural characterization of $Ni_{1-x}Co_xPS_3$ (0 ≤ x $_{1-x}Co_xPS_3$ with one pair of neighboring octahedral coordination units (bottom). (B) Powder x-ray diffraction (PXRD) patterns of various $Ni_{1-x}Co_xPS_3$ NS samples in comparison with the standard monoclinic $NiPS_3$ (PDF #33-0952) and $CoPS_3$ (PDF #78-0498). The broad peak at 2θ ~26o in all PXRD patterns comes from the carbon cloth. a.u., arbitrary units. (C) Energy-dispersive spectroscopy (EDS) mapping and (D) the corresponding spectrum of a $Ni_{0.68}Co_{0.32}PS_3$ NS show uniform distribution of constituent elements. (E) HAADF-STEM image of a

$Ni^{0.68}Co_{0.32}PS_3$ nanosheet collected from the $Ni_{0.68}Co_{0.32}PS_3$ NS sample on carbon cloth shown in the inset SEM image. (F) SAED pattern of the $Ni_{0.68}Co_{0.32}PS_3$ nanosheet along the [001] zone axis. (G) Atomic force microscopy image of a $Ni_{0.68}Co_{0.32}PS_3$ NS transferred onto Si/SiO_2 substrate, showing a thickness ~5.6 nm. (G) Raman spectra of various $Ni_{1-x}Co_xPS_3$ ($0 \leq x$

A weak ferromagnetic (FM) ground state at low temperature in few-layered van der Waals (vdW) magnetic $Ni_{1-x}Co_xPS_3$ nanosheets containing sulfur vacancies (S_v) was discovered by a research team led by Prof. He Jun from National Center for Nanoscience and Technology (NCNST) of the Chinese Academy of Sciences (CAS), in collaboration with Prof. Jin Song from the University of Wisconsin-Madison. This work was published in *Science Advances*.

Transition metal phosphorus trichalcogenides (MPX_3, X= S or Se; M = Mn, Fe, Co, Ni, etc.), as the representatives of two-dimensional (2D) vdW magnetic materials, have gained wide attention in various fields, including superconductivity, optoelectronics and catalysis. In particular, $NiPS_3$ exhibits intriguing quantum properties owing to the intrinsic strong charge-spin correlation effects. It is an antiferromagnetic (AFM) material with a model Hamiltonian of the XXZ type.

In this study, researchers found that the existence of crystal defects in chemically synthesized $Ni_{1-x}Co_xPS_3$ nanosheets, i.e., sulfur vacancies (S_v), could suppress the strong intralayer antiferromagnetic exchange interaction (J3) in $NiPS_3$, and the Co substitution decreases the formation energy of S_v during the synthesis process.

Besides, they found that the conversion synthesis process for the $Ni_{1-x}Co_xPS_3$ nanosheets are necessary to promote the formation of S_v. S_v do not seem to exist in sufficient quantity in chemical vapor transport grown single crystal. The presence of S_v in $Ni_{1-x}Co_xPS_3$ nanosheets led to the suppression of long-range AFM correlations while other competing ferromagnetic exchange interactions dominate at low temperatures, creating a magnetically frustrated system.

As a consequence, the magnetic field required to tune this defect mediated ferromagnetic state (several thousand oersted), which made these nanosheets more appealing for spintronic applications.

Theoretically, in correlated $NiPS_3$, the half-filled Ni e_g orbitals coupled with half-filled S $3p$ orbitals, which mediates the electron hooping between neighboring Ni sites through superexchange interaction. Owing to the negative charge transfer energy, the S ligand transfers one electron to the half-filled e_g Ni $3d$ orbital to form a d^9L ground state, namely negative charge transfer (NCT) state. NCT state also dominates between antiferromagnetically aligned neighboring Ni atoms. In this case, the presence of S_v could affect the electronic correlation and then tune the magnetic ordering in correlated $NiPS_3$.

These findings provide a less explored route for controlling competing correlated states and magnetic ordering by defect engineering in 2D vdW magnets.

More information: Fengmei Wang et al, Defect-mediated ferromagnetism in correlated two-dimensional transition metal phosphorus trisulfides, *Science Advances* (2021). DOI: 10.1126/sciadv.abj4086

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