Journal of Applied Physics

RESEARCH ARTICLE | APRIL 12 2023

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J. Appl. Phys. 133, 143906 (2023)
https://doi.org/10.1063/5.0145950

Journal of Applied Physics ARTICLE scitation.org/journal/jap

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Cite as: J. Appl. Phys. **133**, 143906 (2023); doi: 10.1063/5.0145950
Submitted: 12 February 2023 · Accepted: 27 March 2023 ·
Published Online: 12 April 2023

Yangkun He,[1,2,a)] J. M. D. Coey,[1,2] and Zsolt Gercsi[2]

AFFILIATIONS

[1]School of Materials Science and Engineering, Beihang University, Beijing 100191, China
[2]School of Physics and CRANN, Trinity College, Dublin 2, Ireland

[a)]**Author to whom correspondence should be addressed:** heyangkun@buaa.edu.cn

ABSTRACT

Fully compensated ferrimagnetic half metals have attracted great attention in spintronics. Unlike many previous calculations based on hypothetical ordered alloys, here we look for existing solid solution series taking as an example $Co_{1-x}Cr_xS_2$. Calculations find that a low-spin state for Cr that matches early experiments and a fully compensated ferrimagnetic half metal with Curie temperature above room temperature is found at $x \approx 0.33$. Our study demonstrates the method of combining two half metals with light and heavy 3*d* metals in a solid solution to achieve compensation, where atomic disorder does not destroy the desired properties.

I. INTRODUCTION

Ideal fully compensated ferrimagnetic half metals predicted by calculations have attracted recent attention, because high spin polarization combined with the absence of stray field is useful for high frequency spintronics.[1,2] There are a handful of systems predicted by density functional theory (DFT) calculations to be fully compensated ferrimagnetic half metals, such as Cr_2CoGa,[3] CrVTiAl,[4] Ti_2MnAl,[5] and Cr_2MnSb.[6] Unfortunately, none of them lived up to expectations due to phase instability[7,8] or the difficulty to achieve atomic ordering.[9,10] It is, therefore, desirable to be able to design fully compensated ferrimagnetic half metals based on the existing materials.

Up to now, there existed two promising methods to deliver materials with desired properties. The first method was doping a (near) half metal to shift the Fermi level (E_F) into the gap and aim for compensation. A good example is the inverse Heusler alloy Mn_2Ru_yGa,[11,12] where compensation and half metallicity are simultaneously achieved by Ru doping ($y = 0.5$). This method is difficult to generalize, because a narrow bandgap limits the range of useful doping where one can also obtain the desired magnetic compensation. E_F can also be shifted electrically by gate bias to induce half metallicity,[13] but this method is suitable when the density of states at the Fermi level is small—for semiconductors rather than metals.

The other method is to combine two known half metals with the intention of achieving magnetic compensation. An example is $Mn_2V_{1-z}Co_zAl$,[14] where the ternary end members, Mn_2VAl and Mn_2CoAl, are both half metals. By varying the V/Co ratio, the half metallic character is preserved across the whole series of materials. The composition with $z = 0.5$ is predicted to be a fully compensated ferrimagnetic half metal. This method guarantees compensation because of the wide half-metallic range of z from 0 to 1, and it decouples half-metallicity from magnetization over a wide range of magnetization of either sign, including zero. However, half metallicity also depends strongly on atomic order in Heusler compounds. In our example, Mn_2VAl ($L2_1$-type) and Mn_2CoAl (XA-type) have different crystal structures, and it is difficult to achieve the atomic order required experimentally in Heusler materials. Here, we propose a different class of alloys, where the sensitivity of electronic structure to atomic disorder is reduced.

II. METHODS

Ab initio calculations based on DFT were carried out using norm-conserving pseudopotentials and pseudo-atomic localized basis functions as implemented in the OpenMX software package.[15] Both local spin density approximation (LSDA)[16,17] and the generalized gradient approximation (GGA-PBE)[18] were

employed for our calculations, respectively. The cubic pyrite structure (Pa^{-3}, No. 205) was modeled with a 12-atom supercell with 4 Co atoms in the 4*a* (0,0,0) and 8 S atoms in the 8*c* (0.38,0.38,0.38) positions. Cr substitution for Co was realized gradually with $x = 0$, 0.25, 0.5, 0.75, and 1 in the $Co_{1-x}Cr_xS_2$ formula. A $15 \times 15 \times 15$ k-point mesh was used to evaluate the total energies and electronic density of states (DOS). Pre-generated fully relativistic pseudopotentials and pseudo-atomic orbitals (s3p3d3 with a cutoff radius of 6 atomic units (a.u.) for the metals and 7 a.u. radius with s3p3d2 for S) were used. An energy cutoff of 300 Ry was used for the numerical integrations. Results are presented with relaxed lattice parameters using a 10^{-5} Hartree/Bohr criterion for forces. The convergence criterion for the energy minimization procedure was set to 10^{-8} Hartree. The spin–orbit interaction (SOI) was not considered (turned off) in this work. In fixed spin moment (FSM) calculations presented in Fig. 2, the amplitude of the moments on Cr was constrained and the total energy was evaluated.

III. RESULTS AND DISCUSSION

A possible way to achieve highly ordered atomic structures is to alloy metallic elements with an electronegative nonmetallic counterpart such as O, S, or As. Examples with high spin polarization, confirmed by Andreev reflection experiments, include metallic CrO_2, dilute magnetic semiconductors such as Mn doped GaAs, and perovskite manganites such as $La_{0.7}Sr_{0.3}MnO_3$.[19]

The cubic pyrites TS_2 (T = Mn, Fe, Co, and Ni) with space group Pa^{-3} present an interesting opportunity to design such fully compensated ferrimagnetic half metals.[19] The transition metal atoms are located at the centers of regular sulfur octahedrons as illustrated in Fig. 1(a). The hybridization of 3*d* and sulfur 2*p* orbitals leads to a bandgap between t_{2g} and e_g orbitals of the 3*d* element in octahedral coordination, where the magnetic exchange splitting is usually ~1 eV,[19] as shown in Fig. 1(b). With partly covalent bonds due to the difference in electronegativity between the constituents, pyrites are partly ionic materials having formal valences T^{2+} and S_2^{2-}. Such a feature ensures that atomic order is maintained in both binary compounds and in ternary solid solutions with different transition metals. These pyrites are antiferromagnets when T = Mn [Fig. 1(c)] and Ni [Fig. 1(f)] with T in a high-spin state ($S = 5/2$ and 1, respectively). However, when T = Fe [Fig. 1(d)] or Co [Fig. 1(e)], the compounds are, respectively, paramagnetic or ferromagnetic in low-spin states with $S = 0$ or ½. Furthermore, compounds with T = Mn, Fe, and Ni are semiconductors and T = Co is a near half metal.[20,21] Therefore, alloying a lighter 3*d* element than Co can achieve half metallicity by lowering the Fermi level. Although binary CrS_2 does not crystallize in the pyrite structure, ternary pyrites $Co_{1-x}Cr_xS_2$ with $x < 0.4$ have been synthesized experimentally.[22] Unlike many previous papers based on hypothetical materials, here we look for a possible fully compensated ferrimagnetic half metal based on materials we know to exist.

Light 3*d* elements tend to couple antiferromagnetically with heavy 3*d* elements, forming ferrimagnets with a small net moment and large coercivity. This phenomenon has been used in Co–Cr alloys for perpendicular media for high-density magnetic recording.[23] Similarly, we expect to realize compensation in $Co_{1-x}Cr_xS_2$. However, first we have to consider the possibilities of either high-spin or low-spin states of Cr in $Co_{1-x}Cr_xS_2$ in order to judge the

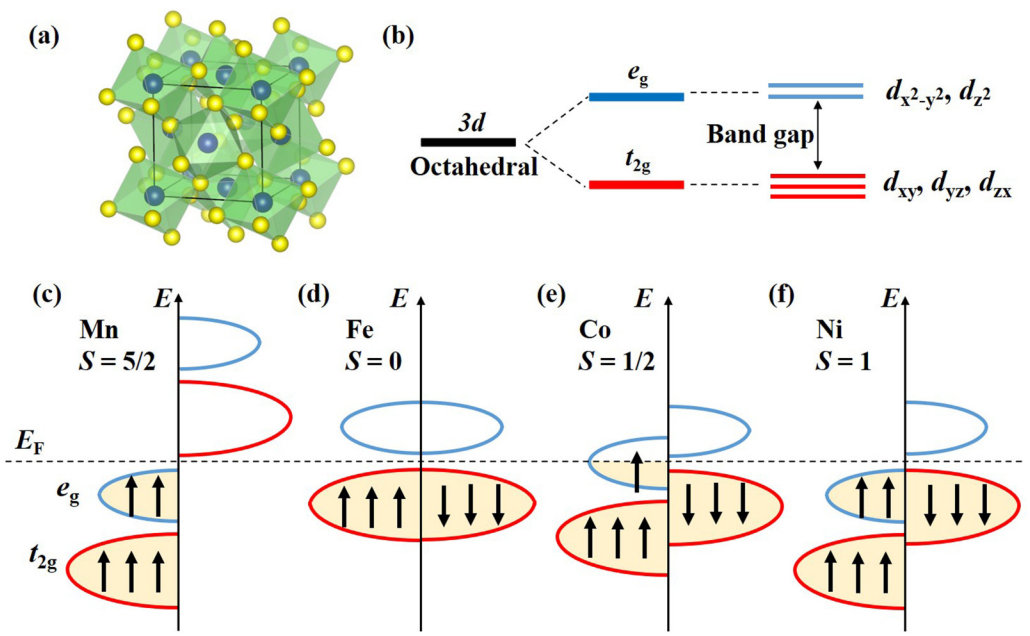

FIG. 1. (a) Crystal structure of pyrite. Blue and yellow atoms are transition metal and sulfur, respectively. (b) The splitting of the 3*d* orbitals in octahedral coordination. (c)–(f) Schematic views of the band structure of Mn, Fe, Co, and Ni in pyrite. The left and right parts refer to spin-up and spin-down channels, respectively.

correct concentration x. In the hypothetical pyrite CrS_2, Cr^{2+} would have four $3d$ electrons. In the high-spin state, all four occupy the same spin channel, giving a moment of 4 μ_B, as shown in Fig. 2(a). In this case, a full compensation would occur at $x = 0.2$, and the alloy would be a normal metallic magnet due to the presence of a Fermi level in both spin channels. On the other hand, if Cr is in a low-spin state, three electrons populate the spin-down channel with only one in the spin-up channel as shown in Fig. 2(b). Then, with 2 μ_B for Cr, magnetic compensation would be achieved for $Co_{0.67}Cr_{0.33}S_2$. This composition will also be half metallic with a gap in the same spin channel for both Co and Cr. Indeed, our fixed spin moment (FSM) calculations confirm that the low-spin state of Cr is energetically favored over the high-spin state by more than 3.5 meV for every composition studied, as shown in Fig. 2(c). Indeed, this also agrees with experimental observations that 4 μ_B is rarely ever found in Cr-based material.

The calculated electronic density of states of $Co_{1-x}Cr_xS_2$ is shown in Fig. 3(a). Calculations carried out using the GGA-PBE[18] scheme predict the entire composition range to be half metals,

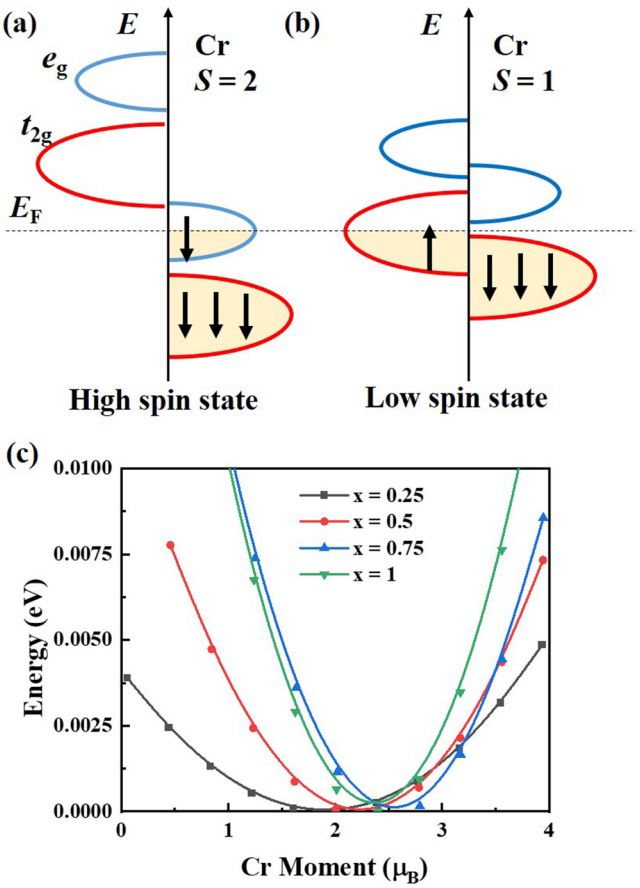

FIG. 2. Band structure of Cr in (a) high- and (b) low-spin states in pyrite. (c) Fixed spin moment (FSM) calculations by GGA-PBE method showing that Cr moment is around 2 μ_B (low-spin state).

with an ~1.1 eV bandgap in the spin-down channel [Fig. 3(b)]. Cobalt exhibits a moment of ~1 μ_B and Cr has an opposing moment of about 2 μ_B (low-spin state). We also plot the calculated magnetic moments on the $3d$ metal sites together with the net moment as a function of x in Fig. 3(c). The net moment decreases from 1 μ_B for $x = 0$ to 0.25 μ_B for $x = 0.25$ and once again increases back to 2 μ_B for the hypothetical CrS_2 ($x = 1$). These findings confirm our hypothesis that compensation can be tailored for $x = 0.33$.

It should be noted that there has been a long debate whether the GGA or the LSDA method better captures the experimental findings for the parent CoS_2.[20] The main difference between the results for the two methods lies in the spin-down channel when x is small. Using LSDA, we find a small density of states of the E_F in the spin-down channel when $x < 0.25$ as shown in Fig. 3(d), which is similar to a previous result.[20] The position of the conduction band and the valence band in the spin-down channel as a function of x is plotted in Fig. 3(e) and half metallicity is achieved when $x > 0.25$. Calculated magnetic moments of Co and Cr are plotted together with the net moment as a function of x in Fig. 3(f). The net moment changes linearly with x. Compensation is achieved for $x = 0.33$ for both GGA and LSDA methods. Therefore, our prediction of magnetic compensation and half metallicity for $x > 0.25$ stands regardless of the flavor of the DFT.

Predictions of half metallicity and full spin polarization from DFT calculations must be treated with caution when applied to real materials.[24,25] The calculations are for zero temperature, they do not take into account quasiparticle excitations such as magnetic polarons and often neglect spin–orbit coupling.[26] At finite temperatures, low-energy magnon modes will reduce the spin polarization well below 100%. That said, our calculations may serve as a guide to the design of compensated half metals with substantial polarization.

Experimental data for $Co_{1-x}Cr_xS_2$ ($x < 0.4$) reported in Ref. 22 are replotted in Fig. 4. The lattice constant increases linearly from 0.5535 to 0.5558 nm with x increasing from 0 to 0.39 due to the larger atomic radius of Cr than Co. The net moment drops with increasing x and reaches a minimum for $x = 0.31$. Further Cr addition leads to an increased net magnetic moment. These data also confirm the low-spin state of Cr with a slope of −2.9 μ_B/Cr and, thus, fully support our speculation about its half-metallic nature. In addition, T_C increases with x and reaches the maximum of 350 K at the compensation composition.

The method of alloying two half metals to find a fully compensated ferrimagnetic half metal can also be applied in other systems. However, to design new materials with heavy-light $3d$ metal pairs that couple antiferromagnetically for compensation, both high T_C and atomic ordering should be considered. Therefore, neither weakly magnetically coupled V and Ni nor Mn–Fe with consecutive atomic numbers is recommended. The best choices could be Cr–Co, Cr–Fe, and Mn–Co. Indeed, an attempt to solve the problem of order in the quaternary Mn–V–Co–Al Heusler system mentioned in Sec. I, alloys of two $L2_1$ half metals Mn_2VAl and Co_2VAl were designed[27] with antiferromagnetically coupled Mn and Co atoms. Full compensation was successfully achieved when $w = 1$ in $Mn_{2-w}Co_wVAl$, but only with a low magnetic ordering temperature.[28]

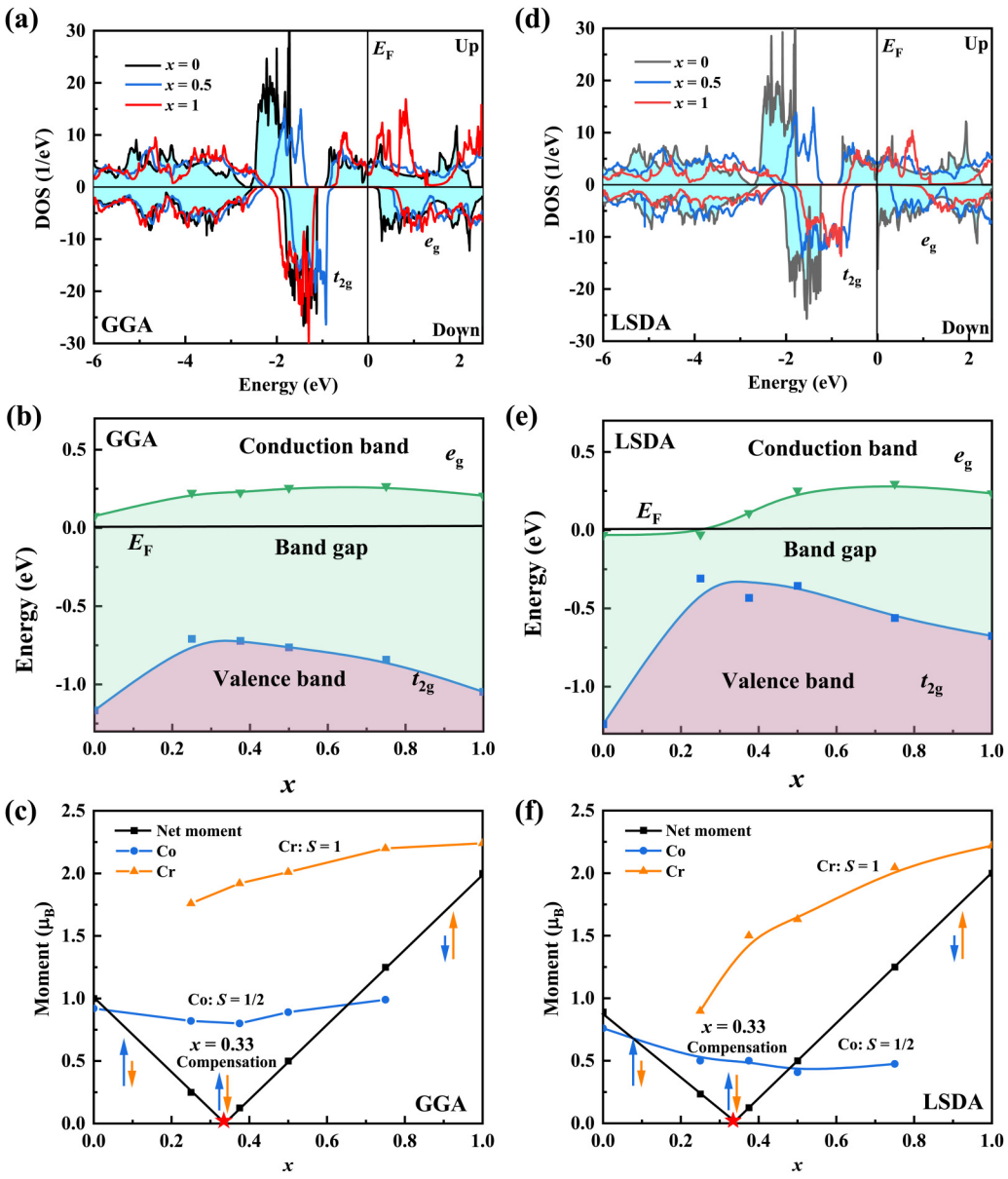

FIG. 3. (a) Density of states of $Co_{1-x}Cr_xS_2$ ($x = 0$–1) calculated by GGA-PBE method. (b) The position of the conduction band and the valence band in the spin-down channel as a function of x. (c) Calculated magnetic moment of Co and Cr plot together with the net moment as a function of x. (d) Density of states of $Co_{1-x}Cr_xS_2$ ($x = 0$–1) calculated by LSDA method. (e) The position of the conduction band and the valence band in the spin-down channel as a function of x. There is a small DOS in the spin-down channel for a small x and half metallicity is achieved when $x > 0.25$. (f) Calculated magnetic moment of Co and Cr plot together with the net moment as a function of x for $Co_{1-x}Cr_xS_2$ ($x = 0$–1) calculated by LSDA. DFT data for $x = 0.375$ are for a 24-atom supercell, where the original cell was doubled along the c-axis.

On the other hand, the suggested counterions should maintain itinerant rather than localized d electrons; otherwise, Mott or charge transfer insulators are likely to form, rather than half metals. Pyrite, marcasite, and arsenopyrite-type compounds are recommended, as most of them exhibit itinerant 3d electrons.[29] The rich combinations for $(X_2)^{2-}$, $(XY)^{3-}$, and $(Y_2)^{4-}$, where X is a chalcogen and Y is a pnictogen, offer abundant choices for the design of compensated half metals.

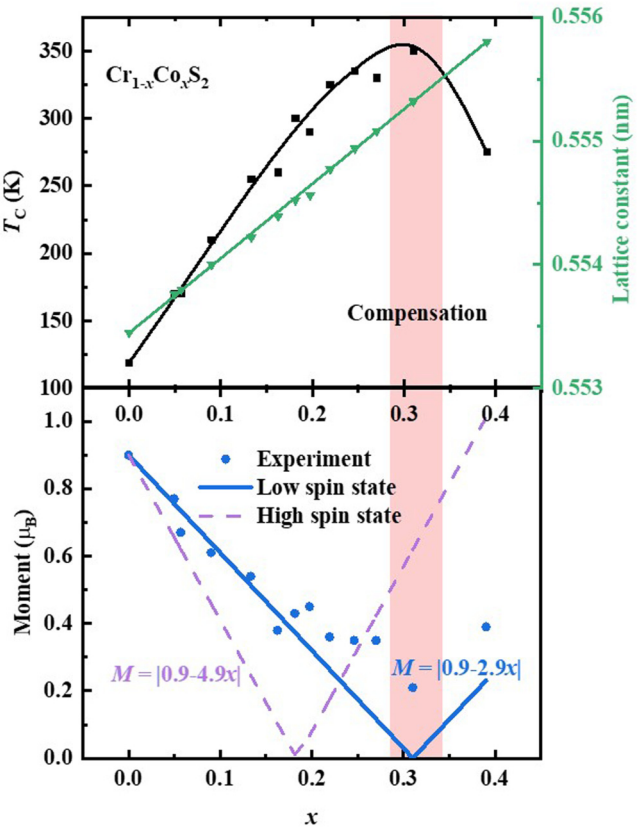

FIG. 4. Experiment measured net moment, T_C and lattice constant as a function of x in $Co_{1-x}Cr_xS_2$ reproduced from Ref. 22. [Reproduced with permission from Donohue *et al.*, Mater. Res. Bull. **6**, 231–237 (1971). Copyright 1971 Elsevier Ltd.] The data suggest compensation at $x = 0.33$ with the highest T_C of ~350 K. The net moment as a function of x for high-spin states for Cr is shown by the dashed lines.

IV. CONCLUSIONS

In summary, we have designed a fully compensated ferrimagnetic half metal based on the pyrite $Co_{1-x}Cr_xS_2$ solid solution. The magnetic moments of Co and Cr couple antiparallel and Cr are confirmed to be in a low-spin state from DFT calculations that are in agreement with the experiment. Full magnetic compensation exists when $x \approx 0.33$, where T_C lies above room temperature. Theoretical results on the parent CoS_2 strongly depend on the functional used but half metallic electronic structure is predicted for $x > 0.25$, regardless of the DFT flavor.

Our study provides an example for a method of combining two metals with heavy or light 3*d* metal pairs in a series of alloys to achieve compensation and half metallicity, where atomic disorder does not pose a risk to these desired properties. The best choices are Cr–Co, Cr–Fe, or Mn–Co with nonmetallic counterparts that possess a large electronegativity.

ACKNOWLEDGMENTS

This work was supported by the Science Foundation Ireland, under the MANIAC, SFI-NSF China project (No. 17/NSFC/5294) and ZEMS project (No. 16/IA/4534).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yangkun He: Data curation (lead); Writing – original draft (lead); Writing – review & editing (lead). **J. M. D. Coey:** Project administration (lead); Writing – review & editing (supporting). **Zsolt Gercsi:** Data curation (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

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

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