Nature of charge transport and p-electron ferromagnetism in nitrogen-doped ZrO₂: An ab initio perspective

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Zirconium dioxide provides an exceptional prototype material for studying the redistribution of the polaron holes and its magnetic coupling with their nearby anions owning to the difference oxygen binding behavior in the monoclinic phase. Here, we perform a comprehensive study of the p-electron magnetism in the nitrogen doped 2 × 2 × 2 monoclinic ZrO₂ based on spin-polarized density functional theory. Nitrogen substitutions make the system display half-metallic properties, and the origin of room temperature ferromagnetism ascribes to the p-p coupling interaction between N 2p and the host 2p states. The charge density difference and Mulliken population analyses provide evidences of charge redistributions. Our results reveal that the polaron transfer may alter the magnetic properties and it is greatly facilitated ferromagnetic coupling if the polaron holes are localized around a single anion dopant.

The defect-induced magnetism involving only s- and p-electron elements have captured great interest and exhibited promising potential applications in spintronics devices. Doping 2p light elements (LE) into oxide semiconductors, what is known as a model system of diluted magnetic semiconductors (DMSs)¹⁻⁴, the room temperature ferromagnetism (RTFM) can be achieved. For instance, RTFM was reported in C- or N-doped ZnO⁵⁻⁸, TiO₂⁹⁻¹¹ thin films and Li-doped ZnO¹² nanorods. Theoretically, possible ferromagnetism (FM) was also predicted in C-, or N-doped TiO₂¹³⁻¹⁴, ZnO¹⁵⁻¹⁶, CaO¹⁷⁻¹⁸ and MgO¹⁹⁻²² by density functional theory (DFT) or self-interaction correction (SIC) calculations. Compared to the conventional 3d transition-metal (TM)-doped DMSs²³⁻²⁷, LE-doped DMSs can provide a novel way to exclude the problem of clusters or secondary phases formed by doping 3d TM elements. Moreover, the spatially extended p states of the host and the impurities may able to extend the magnetic interaction to longer range. Various experimental and theoretical explorations have shown that the exchange interactions between the structural defects are believed to be responsible in establishing the magnetic moment. However, it remains obstacle that the relationship between valence band holes and origin of stable magnetic ordering in these materials. Therefore, a comprehensive understanding on the p-electron magnetism is essential for further exploring other potential DMSs.

The reasons we choose zirconium dioxide (ZrO₂) as a prototypical DMS are as follows. (i) ZrO₂ as a promising candidate for gate dielectric material²⁸⁻³², has attracted much attention due to its relatively large dielectric constant (~25), wide band gap (5.1–7.8 eV), high breakdown field, and good thermal stability. Introducing ferromagnetism into the nonmagnetic (NM) ZrO₂ may open a new avenue for its applications. (ii) Due to difference oxygen binding behaviors in monoclinic ZrO₂ (m-ZrO₂), it is an exceptional prototype material for understanding of the relationship between electronic structure and the p-electron characters in these DMSs. Inspired by the prediction of Ostanin et al.³³ that cubic ZrO₂ should have a high Curie temperature (~500 K) by doping Mn, lots of efforts have focused on Mn-doped cubic ZrO₂ but rare attentions were paid to LE-doped m-ZrO₂, especially for doping N³⁴⁻³⁶. Unlike TiO₂, CeO₂ and SnO₂, oxygen sites in the m-ZrO₂ can be divided into two types according to their binding behavior, one is bonded with three Zr atoms (labeled as O3) and the other is bonded with four Zr atoms (labeled as O4) [see Figs. 1(a) and 1(b)]. The projected density of states (PDOS) of the 2p orbitals for the O3 and O4 are presented in Fig. 1(d). At the first glance, the 2p orbitals of O3 can accommodate more holes than that in
the 2p orbitals of O4 near the Fermi level. It implies that the O4 2p shell should be first fully occupied compared to the O3 2p shell while sufficient holes are injected. It can be anticipated that the redistribution of the induced holes and the interaction with their nearby atoms will have a significant impact on establishing the RTFM.

**Results**

**Structure stability.** Let us first consider a Zr$_5$O$_6$N supercell with a single N substituted at an O site, accompanying a formation of a doped hole. After a structural relaxation, the N substituted at O3 site (N$_{O3}$) model system is found to have a lower energy of 65.4 meV than that of the N substituted at O4 site (N$_{O4}$) model system. This should be due to the fact that N$_{O3}$ has a more freedom to relax than the N$_{O4}$. In addition, both spin-polarized and non-spin-polarized states are calculated to check the stability of the magnetization. The results reveal that both the model system of N$_{O3}$ and that of N$_{O4}$ favor the energy differences of about 387.5 and 293.1 meV between the spin-polarized state and the non-spin-polarized state respectively. The probability of incorporating a defect in a crystal is determined by the formation energy. The calculated formation energy of N$_{O3}$ (or N$_{O4}$) is 3.92 eV (or 3.99 eV) and $-1.56$ eV (or $-1.49$ eV) for the O-rich condition and Zr-rich condition, respectively.

**Electronic properties.** The calculated total density of states (TDOS) and PDOS for the N 2p, the neighboring Zr 4d and O 2p states are shown in Fig. 2. It is found there exist significant hybridization between the N 2p states and O 2p states around the Fermi level ($E_F$), suggesting a strong p-p coupling interaction between them. Such a strong p-p interaction makes the energy levels near the $E_F$ spin split. The partially filled spin-down band split off from the fully occupied spin-up band via Hund exchange, resulting typical FM half-metallic character, which is important for the spintronics applications. Additionally, nitrogen substituting for oxygen introduces some hole states peaked about 1.0 eV above $E_F$, which are mainly originated from N 2p, O 2p and Zr 4d orbitals. The total magnetic moment of the supercell is 1.00 $\mu_B$ corresponding to the single excess p electron provided by the N dopant. This is consistent with the previous results of N-doped ZnO$^{13}$, TiO$_2$$^{44}$, In$_2$O$_3$. The moments are mainly localized on the N 2p orbital ($-0.86$ $\mu_B$), with minor contributions of the O (0.18 $\mu_B$) and the neighboring Zr atoms is polarized antiferromagnetically with a magnetic moment of $-0.04$ $\mu_B$ (See the Supplementary Information for more details).

The band structure calculations suggest that the localized holes induced by N dopant mediate the FM interaction. The carriers, i.e. holes, which were introduced by the substitution of N at O sites, reside not only on the N 2p orbitals but also on its near neighboring O atoms. The holes near each anion impurity tend to align parallel to the moment of the impurity ion under the p-d hybridization-like p-p coupling interaction$^{35,39}$. Sufficient spin-polarized holes can mediate the spin alignment of the N dopant atoms, resulting in an indirect strong FM coupling among them. Therefore, the mechanism responsible for the FM coupling in the N-doped ZrO$_2$ can be classified as the p-p coupling interaction between the impurity 2p states and the host 2p states.

**Magnetic coupling.** Next, we examine the magnetic coupling of these magnetic moments. To understand this issue, we calculate four nonequivalent structural configurations of Zr$_5$O$_6$N$_2$, which are constructed by replacing two O atoms by N with various N-N distances. Here, the “dimer” of N-Zr-N configuration is only considered because we find the magnetic coupling to be negligible small when the N-N pair is well separated. The (i, j) configuration is adopted to denote an N-N pair, in which two O sites are replaced by N at i and j sites, as shown in Fig. 1(c). This amounts to the doping concentration of 3.13%. The magnetic coupling strength can be obtained from the energy difference between FM and AFM states ($\Delta E_{FM-AFM} = E_{FM} - E_{AFM}$). A positive value means the FM state is favored and vice versa. $\Delta E$ is the relative energy with respect to the (a, b) configuration which has the lowest total energy. The results are summarized in Table 1. It is found that the $\Delta E$ becomes smaller when the N-N distance gets larger, and hence the doped N atoms do not have a tendency of clustering. It is noteworthy that the FM states always exhibit a lower energy than the AFM states except for the (a, d) configuration in which the N-N distance is 2.8 Å with the bond angle $\angle$N-Zr-N near 90°. It is well known that the Curie temperature in the mean field approximation (MFA) $T_c$ is calculated as $k_B T_c = (2/
Table 1 | Summary of the calculated results for all configurations of \( \text{Zr}_{32}\text{O}_{62}\text{N}_2 \). \( d_{N-N} \) is the N-N distances. The relative energy \( \Delta E \) is referred to the \([a, b]\) configuration and the most stable state (either FM or AFM) is used for each configuration. The magnetization energy \( \Delta E_{FM-AFM} \) is the energy difference between the FM and AFM states, and \( M \) is the total magnetic moment for the FM state.

| Configuration \([i, j]\) | \( d_{N-N} \) (Å) | \( \Delta E \) (meV) | \( \Delta E_{FM-AFM} \) (meV) | \( M \) (\( \mu_B \)) | Coupling |
|--------------------------|------------------|-----------------|------------------------|-----------------|--------|
| \([a, b]\)               | 4.4              | 0               | -372.7                 | 2.0             | FM     |
| \([a, c]\)               | 3.4              | 66.1            | -355.3                 | 2.0             | FM     |
| \([a, d]\)               | 2.8              | 163.3           | 2.6                    | 2.0             | NM     |
| \([d, e]\)               | 2.6              | 286.9           | -32.7                  | 2.0             | FM     |

Table 2 | Atomic charge densities from Mulliken population analysis of Zr, O and N atoms.

| Atomic charge densities | Zr     | O(2p) | N(2p) |
|-------------------------|--------|-------|-------|
| \( \text{Zr}_{32}\text{O}_{62}\text{N}_{1.46} \) | 1.47   | 0.74  | N/A   |
| \( \text{Zr}_{32}\text{O}_{62}\text{N}_{3} \)  | 1.46   | 0.75  | -0.65 |

Figures:

Figure 3 | The charge density differences for the \([d, e]\) and \([a, b]\) configurations are shown in \((a)\) and \((b)\). The schematic energy level diagram of pair interaction between \( \text{O}^+ \) ions and \( \text{N}^2+, \text{N}^+ \) and \( \text{N}^0 \) ions are illustrated in \((c)\), \((d)\) and \((e)\), respectively.

3c) \( \Delta E_{FM-AFM} \) where \( k_B \) is Boltzmann constant. The MFA estimates \( T_c \) for DMSs with low concentrations within 5~10% errors. The \( T_c \) is always very lower than the room temperature, due to the short-range magnetic exchange interaction of deep impurity states in wide band-gap semiconductors, percolation of the ferromagnetic coupling is difficult to achieve for small concentrations. However, in the case of \([a, b]\) configuration, the \( \Delta E_{FM-AFM} \) value reaches 372.7 meV, larger than that of N-doped TiO\(_2\) and N-doped In\(_2\)O\(_3\) which are known to be RTFM. Therefore, such a strong ferromagnetic interaction implies that the RTFM for N-doped ZrO\(_2\) is quite feasible considering the simple estimate. Though not shown here, our additional similar calculations for Zr\(_{32}\)O\(_{62}\)N\(_2\) with a long N-N distance (7.4 Å) reveal that the FM and AFM state are degenerate, whereas the total energy is 412.3 meV higher compared to the ground state of \([a, b]\) configuration (See the Supplementary Information for more details). For comparison, let’s focus on the largest and shortest N-N distances. The relative energy \( \Delta E \) and \( \Delta E_{FM-AFM} \) are given in Table 2. To start with, we calculate the number of electrons on each atom in bulk ZrO\(_2\), which results in charge states of Zr and O atoms of \(+1.50e\) and \(-0.74e\), respectively. Note that these values are far from the formal ones corresponding to the ideal ionic situation (Zr\(^{4+}\) and O\(^{2-}\)), owing to the spatial division and the partial covalent feature of the Zr-O bonds. For \([d, e]\) configuration, a Mulliken population analysis indicates that the local charges of N1 and N2 ions are \(-0.65e\) and \(-0.64e\), whereas the neighboring of Zr and O remain essentially unchanged. Similar calculation for \([a, b]\) configuration reveals that the N-N pair is strongly polarized, with charge states of \(-0.88e\) and \(-0.45e\) on the N4 and N3 sites, respectively. Given the above observations, the N1 (N2), N3 and N4 ions should have their electron configuration like N\(^2+\) (\(2p^6\)), N\(^+\) (\(2p^5\)) and N\(^0\) (\(2p^4\)), respectively. Due to the coupling interaction between N 2p and O 2p, ppp and ppr states are formed. The schematic energy level diagram of the p-p hybridization between O\(^2-\) and the above three kinds of N charge configurations (N\(^2+\), N\(^+\), N\(^0\)) are illustrated in Figs. 3(c), 3(d) and 3(e). The nearly degenerate ppp antibonding states are half-filled, 3/4 filled and fully filled, resulting 1.0 \( \mu_B \), 2.0 \( \mu_B \) and 0.0 \( \mu_B \) total magnetic moment, consistent with the DOS in Figs. 4(a)–4(c).
In order to further understand the nature of magnetic coupling in Zr$_{32}$O$_{62}$N$_2$, the spin charge density (SCD) distribution of (\(a, b\)) and (\(d, e\)) configurations in the FM states and the AFM states are shown in Fig. 5. As can be seen, in (\(d, e\)) configuration, the \(p\)-like shape spin charge resides mainly on both the two N impurities and they have identical spin direction in the FM states while opposite direction in the AFM states. It indicates that there existed a strong FM coupling interaction induced by the N 2p orbitals [see also Fig. 4(b)]. Meanwhile, the lobes of N 2p orbitals are towards the lobes of O 2p orbitals to maximize the overlaps, which manifests that the \(p-p\) interaction does extend to the neighboring O ions, similar to the case of single N doping. In great contrast, for (\(a, b\)) configuration in the FM states, the main features are that the spin charge is mostly contributed by the N4 dopant and N-N pair coupling interaction nearly vanished [see also Fig. 4(c)]. This can be understood by noticing that the N-N distance is 4.4 Å, almost double of the distance in (\(d, e\)) configuration. Such a long distance effectively degenerate the N-N pair coupling interaction.

### Discussion

Now we turn to address the question of what stabilizes the ferromagnetic ground state of (\(a, b\)) configuration. Spontaneous ferromagnetism can be evaluated according to the “Stoner Criterion” [43, 44]:

\[ D(E_F) J > 1, \]

where \(D(E_F)\) is the DOS at the Fermi level and \(J\) denotes the strength of the exchange interaction. The \(D(E_F)\) is proportional to \(m^{3/2}(E_{VBM}-E_F)^{-1/2}\), where \(m\) is the effective mass and \(E_{VBM}\) is the energy of the valence band maximum (VBM). Due to the stronger N3-Zr than N4-Zr bonds in the (\(a, b\)) configuration as indicated by their bond length (N3-Zr ~ 2.05 Å, N4-Zr ~ 2.22 Å), the N3 spin-up states are occupied and the occupation of the spin-down states will decrease. Thus the spin charge tend to accumulate around the N3 atom, which makes the defect level deeper and wave function more localized, resulting in a larger \(D(E_F)\), and a larger spin-exchange splitting \(J\) of the band, as can be seen in Figure 4(a). The enhanced

![Figure 4](https://www.nature.com/scientificreports/)

**Figure 4** The spin-resolved TDOS and PDOS for the (\(d, e\)) and (\(a, b\)) configurations. (a) TDOS. The N 2p PDOS of (\(d, e\)) and (\(a, b\)) configurations in the FM states are illustrated in (b) and (c) respectively. The Fermi level is indicated by the dashed vertical line.

![Figure 5](https://www.nature.com/scientificreports/)

**Figure 5** The isosurface SCD of (\(a, b\)) and (\(d, e\)) configurations in the FM states and the AFM states. The cyan, red and blue balls represent Zr, O and N atoms, respectively. The green (yellow) isosurface correspond to positive (negative) spin charge densities. The isovalue is set to 0.02 e/Å$^3$. 

In order to further understand the nature of magnetic coupling in Zr$_{32}$O$_{62}$N$_2$, the spin charge density (SCD) distribution of (\(a, b\)) and (\(d, e\)) configurations in the FM states and the AFM states are shown
exchange splitting stabilizes the FM state, it can cause the system to be ground state. These results therefore indicate that it will be easier to obtain stable ferromagnetism if the injected holes are not shared by several neighboring anion atoms, but localize around a single anion. A similar situation was observed in the different system of C-doped ZnO\(^{45}\).

In summary, our \textit{ab initio} calculations result indicate that the substitutional N induces spin-split impurity states near the Fermi level and leads to the half-metallic property. The total magnetic level and leads to the half-metallic property. The total magnetic...
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Author contributions
H.Z. carried out calculations, J.L. and F.G. took analyses and discussion. H.Z. and J.L. wrote the manuscript. K.C., X.Y. and S.C. discussed and reviewed the manuscript.

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