

First-principles investigation of transition-metal-doped group-IV semiconductors: R_xY_{1-x} ($R=\text{Cr}, \text{Mn}, \text{Fe}$; $Y=\text{Si}, \text{Ge}$)

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A number of transition-metal- (TM) doped group-IV semiconductors, R_xY_{1-x} ($R=\text{Cr}, \text{Mn}, \text{Fe}$; $Y=\text{Si}, \text{Ge}$), have been studied by the first-principles calculations. The results obtained show that antiferromagnetic (AFM) order is energetically more favored than ferromagnetic (FM) order in Cr-doped Ge and Si with $x=0.03125$ and 0.0625 . In 6.25% Fe-doped Ge, the FM interaction dominates in all ranges of R - R distances, while for Fe-doped Ge at 3.125% and Fe-doped Si at both concentrations of 3.125% and 6.25%, only in a short R - R range can the FM states exist. In the Mn-doped case, the Ruderman-Kittel-Kasuya-Yoshida-like mechanism seems to be suitable for the Ge host matrix, while for the Mn-doped Si, the short-range AFM interaction competes with the long-range FM interaction. The different origin of the magnetic orders in these diluted magnetic semiconductors (DMS's) makes the microscopic mechanism of the ferromagnetism in the DMS's more complex and attractive.

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I. INTRODUCTION

Diluted magnetic semiconductors (DMS's) have stimulated a great deal of interest because of their potential applications in the spintronics, in which the electron spin becomes another degree of freedom in addition to the usual charge degree of freedom. Since the discovery of ferromagnetic (FM) order in Mn-doped III-V semiconductors such as InAs (Ref. 1) and GaAs (Refs. 2–4), the transition-metal magnetic impurities have been used as spin injectors, which are doped into the semiconductor hosts to cause ferromagnetism. But usually, the Curie temperatures of these materials are far below the room temperature, which, for example, is 35 K for $\text{In}_{1-x}\text{Mn}_x\text{As}$ and 110 K for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The Mn-doped II-VI semiconductors are less attractive because the superexchange interaction of the doped ions favors the antiferromagnetic (AFM) or spin glass configuration. However, in some DMS's based upon the transition-metal oxide, ferromagnetism has been observed at or even higher than room temperature, such as 280 K for ZnO (Ref. 5) and 400 K for TiO_2 (Ref. 6). On the other hand, in the group-IV semiconductor, Park *et al.*⁷ reported that Mn-doped Ge ($\text{Mn}_x\text{Ge}_{1-x}$) has a Curie temperature up to 116 K and then Cho *et al.* improved it to 285 K.⁸ So, if it were possible to make room-temperature FM $\text{Mn}_x\text{Si}_{1-x}$, the “spintronic semiconductor” industry would increase rapidly based upon now mature Si-based semiconducting technology and associated facilities.

The room-temperature FM DMS's discovered continuously in experiments brings a challenge to the theoretical work because their origin of ferromagnetism is still an open question. Though some different mechanisms, such as the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction,⁹ double exchange,¹⁰ double resonance,¹¹ the Zener tunneling model,¹² and the mean-field theory,¹³ have been proposed, none could give a conclusive interpretation. The strong p - d exchange interaction mediated by mobile holes is thought to be the origin of ferromagnetism in III-V-compound-based

DMS's,⁴ and carrier-induced ferromagnetism with the exchange interaction mediated by electrons was considered to be suitable for the Co-doped anatase TiO_2 system.⁶ While the first-principles calculation on the Mn-doped Ge made by Park *et al.* indicates that the FM order arises from a long-range FM interaction competing with a short-range AFM one. More detailed study¹⁴ by Zhao *et al.* shows that $\text{Mn}_x\text{Ge}_{1-x}$ is a RKKY-like FM semiconductor. In this paper, a similar study is extended to the Cr- (Fe-) doped Ge and Si. Since a Cr (Fe) atom has one electron less (more) than a Mn atom and Si is in the same column as Ge in the periodic table, comparison between these DMS's allows us to investigate variations of magnetic properties with a change of dopants and host semiconductors. In fact, there have been experiments to be done on the Cr- and Fe-doped Ge (Refs. 15 and 16) and also Mn-doped Si (Ref. 17). In Sec. II, we will introduce our calculation methods, and our numerical results are shown in Sec. III, from which some discussions and conclusions are made.

II. CALCULATION METHOD

The software package VASP (Ref. 18) has been used in our calculations, which is based on a total energy pseudopotential plane-wave method within the local spin density approximation (LSDA). In the calculation, the interaction between ions and electrons is described by the projector-augmented wave method in the generalized gradient approximations (GGA).¹⁹ The initial crystal structures of R_xY_{1-x} ($R=\text{Cr}, \text{Mn}, \text{Fe}$; $Y=\text{Ge}, \text{Si}$) are taken as $2a \times 2a \times 2a$ supercell for $x=0.03125$ and $2a \times 2a \times 1a$ for $x=0.0625$ with two Y atoms replaced by two R atoms, among which the first is at the origin, and the other is put on a lattice position farther away from the origin indicated by three digits following N to represent its (x, y, z) coordinate in units of $a/4$.¹⁴ And the lattice constant a is taken as that of pure Ge and Si, i.e.,

TABLE I. Total energy of the FM phase (E_{FM}) in different configurations calculated relative to that with lowest FM energy, and the energy difference between AFM and FM state ($E_{AFM}-E_{FM}$) calculated for Cr-doped Ge and Si at $x=0.03125$. Also shown are the average magnetic moments on each Cr atom (muffin-tin radius = 1.32 Å) calculated from initial FM (M_{FM}) and AFM (M_{AFM}) configuration, respectively. Energies are all in units of meV/Cr and the magnetic moment are in units of μ_B/Cr .

System	$\text{Cr}_{0.03125}\text{Ge}_{0.96875}$				$\text{Cr}_{0.03125}\text{Si}_{0.96875}$			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	397.6	-387.3	2.10	± 2.78	237.3	-347.7	1.82	± 2.32
N220	34.0	-20.7	2.54	± 2.68	14.6	11.4	2.22	± 2.27
N400	0	-18.5	2.54	± 2.57	0	-10.8	2.22	± 2.22
N224	21.3	-28.4	2.53	± 2.61	22.8	-13.4	2.20	± 2.23
N440	39.4	-61.6	2.48	± 2.72	17.6	-23.2	2.18	± 2.29
N444	28.5	-31.3	2.51	± 2.61	15.6	-11.0	2.20	± 2.24

5.658 and 5.431 Å, respectively. In the spin optimization, the initial spin configuration in the AFM state is taken as 5 net spins on one R atom, and -5 on the other one, and in the FM state, 5 net spins are chosen for both R atoms. The same ground state is reached while increasing the value to 8 and 10. An energy of 350 eV is used for the plane-wave cutoff, and when the energy cutoff is increase to 550 eV, the total energy difference between the AFM state and the corresponding FM state changes no more than 0.05 meV/R. For the Brillouin zone sampling, we take the same k mesh as that in Ref. 14 for all the cases.

III. RESULTS AND DISCUSSION

The calculated FM total energies and the energy difference between AFM and FM states of the Cr-doped Ge and Si are presented in Tables I and II for $x=0.03125$ and 0.0625, respectively. Also shown are the averaged magnetic moments on the Cr atom. Obviously, for the Cr-doped Ge at both concentrations, the AFM order is energetically more favored than the FM order, which is consistent with the experimental measurement and theoretical calculation in Ref. 15. The fewer electrons of Cr than Mn in the Ge host matrix do not enhance the ferromagnetism in this system. And in the Si host matrix, independent of the doping concentration, only for the N220 configuration is the FM order slightly more favorable while the others tend take the AFM order. But in general the energy differences between AFM and FM decrease when x changes from 0.0625 to 0.031 25, indicating

that perhaps at lower enough x , the FM state would be lower than the AFM state in energy, which still needs more experiments to be confirmed.

Tables III and IV give the results of Mn-doped Ge and Si with $x=0.031\ 25$ and 0.0625, respectively. It is clear that our results of $\text{Mn}_x\text{Ge}_{1-x}$ are the same as those in Ref. 14, indicating that it is a RKKY-like FM semiconductor. However, it is totally different for $\text{Mn}_x\text{Si}_{1-x}$ although both Ge and Si are in the same column in the periodic table. Independent of the doping concentration, the $\text{Mn}_x\text{Si}_{1-x}$ tends to be FM even when the Mn-Mn distance is as long as 9.41 Å in the N444 case, except that the N111 shows AFM order. The AFM interaction between Mn ions exists only in a short range (the nearest neighbor, about 2.35 Å), which competes with the long-range (all beyond the nearest-neighbor) FM interaction. This mechanism was once thought to be the origin of the FM order in the $\text{Mn}_x\text{Ge}_{1-x}$ system,⁷ which now seems to be responsible for the FM order in Mn-doped Si. So, it is plausible that the FM order would be easier in the Si host matrix than in Ge for Mn doping. When $x=0.031\ 25$, the lowest FM energy is found in the N440 configuration for Ge and in N220 for Si, and the corresponding energy differences between AFM and FM states ($E_{AFM}-E_{FM}$) are 103.92 and 74.88 meV/Mn in these two configurations. Increasing x to 0.0625, the lowest FM energy configuration becomes N220 for both Ge and Si, and the corresponding $E_{AFM}-E_{FM}$ increases to 122.2 and 84.6 meV/Mn, respectively. So, in the same doping concentration, the Curie temperature of $\text{Mn}_x\text{Ge}_{1-x}$ will be higher than that of $\text{Mn}_x\text{Si}_{1-x}$, and in both

TABLE II. The same as Table I except at $x=0.0625$.

System	$\text{Cr}_{0.0625}\text{Ge}_{0.9375}$				$\text{Cr}_{0.0625}\text{Si}_{0.9375}$			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	370.6	-381.3	2.09	± 2.78	237.2	-351.0	1.84	± 2.33
N220	10.6	-36.5	2.50	± 2.69	8.7	5.8	2.21	± 2.27
N400	0.0	-69.8	2.45	± 2.69	0.0	-32.2	2.17	± 2.29
N440	12.1	-67.7	2.44	± 2.72	6.0	-25.0	2.17	± 2.29

TABLE III. The same as Table I, except for the Mn-doped Ge and Si, in which the muffin-tin radius of Mn is 1.32 Å.

System	Mn _{0.03125} Ge _{0.96875}				Mn _{0.03125} Si _{0.96875}			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	263.3	-257.4	3.06	±3.20	26.2	-181.1	1.18	±2.69
N220	10.2	76.4	3.17	±3.22	0.0	74.9	2.83	±2.48
N400	60.6	-17.5	3.16	±3.21	137.0	5.4	2.81	±2.81
N224	70.4	-3.9	3.18	±3.23	142.6	23.7	2.82	±2.80
N440	0.0	103.9	3.16	±3.23	22.3	125.1	2.83	±2.59
N444	94.3	-27.0	3.16	±3.25	153.1	15.6	2.81	±2.83

TABLE IV. The same as Table III except at $x=0.0625$.

System	Mn _{0.0625} Ge _{0.9375}				Mn _{0.0625} Si _{0.9375}			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	279.0	-219.9	3.03	±3.18	158.5	-258.5	2.40	±2.69
N220	0.0	122.2	3.15	±3.15	0.0	84.6	2.80	±2.55
N400	4.9	104.9	3.14	±3.19	23.3	109.8	2.76	±2.63
N440	32.7	98.2	3.13	±3.19	42.5	108.4	2.81	±2.65

TABLE V. The same as Table I except for Fe-doped Ge and Si, in which the muffin-tin radius of Fe is 1.30 Å.

System	Fe _{0.03125} Ge _{0.96875}				Fe _{0.03125} Si _{0.96875}			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	0.0	170.5	2.22	±2.17	0.0	95.3	1.96	±1.43
N220	246.6	-81.6	0.001	±2.47	129.3	0.0	-0.001	±0.111
N400	184.6	43.5	-0.005	±2.13	81.7	0.0	0.000	±0.000
N224	204.6	39.6	-0.011	±2.11	104.6	0.0	0.000	±0.001
N440	198.1	7.9	-0.006	±2.62	86.4	0	0.0	±0.006
N444	211.9	45.7	-0.004	±2.15	97.7	0	0.0	±0.000

TABLE VI. The same as Table V except at $x=0.0625$.

System	Fe _{0.0625} Ge _{0.9375}				Fe _{0.0625} Si _{0.9375}			
	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}	E_{FM}	$E_{AFM}-E_{FM}$	M_{FM}	M_{AFM}
N111	0.0	156.0	2.23	±2.22	0.0	109.0	1.98	±1.51
N220	114.4	38.5	2.45	±2.39	249.4	-95.0	1.57	±0.21
N400	97.8	94.6	2.50	±2.06	101.7	0.0	0.004	±0.02
N440	129.5	70.2	2.55	±2.05	106.9	0.0	0.02	±0.02

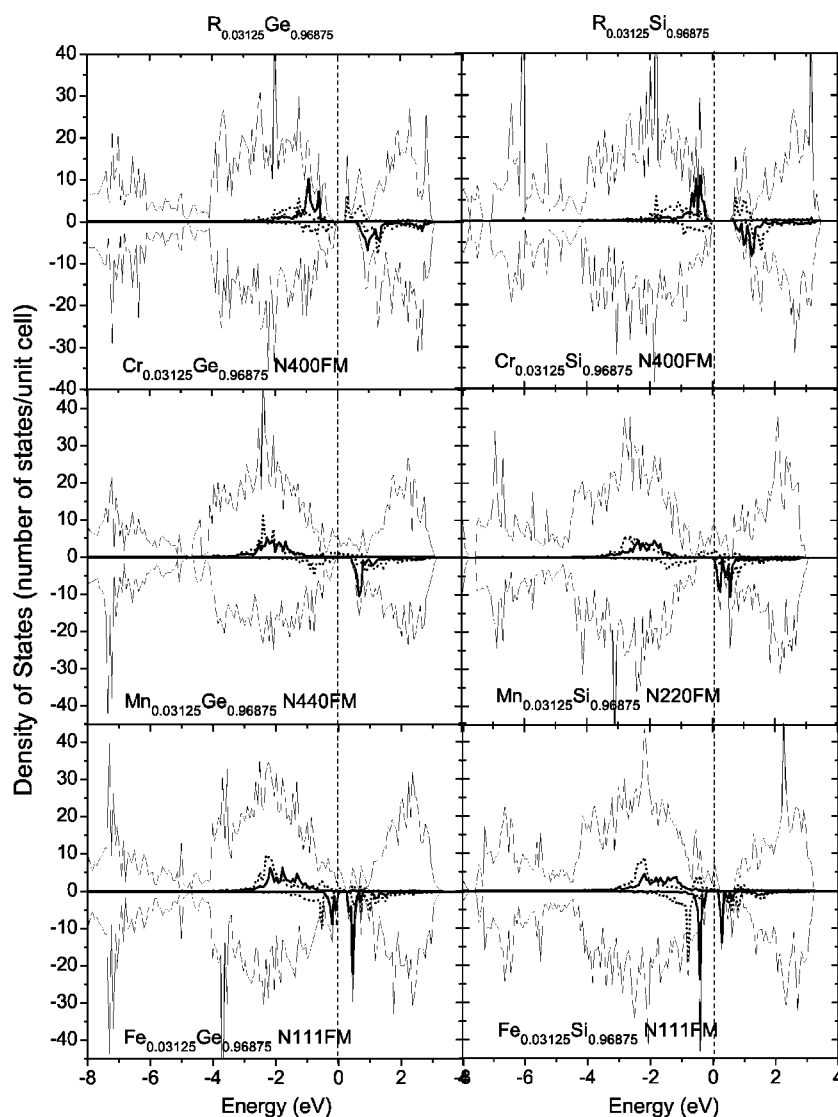


FIG. 1. The total DOS (thin line), and the three times magnified projected $3d\ e_g$ (bold line) and t_{2g} (dotted line) partial DOS for the lowest FM configurations at 3.125% doping concentration. The positive DOS value means that of spin up while negative is for spin down. The vertical dashed line represents the Fermi level.

host matrices, the Curie temperature will increase with Mn doping concentration.^{8,14,17,20}

The results of the 3.125% and 6.25% Fe-doped two group-IV semiconductors are listed in Tables V and VI, respectively. For both concentrations of Fe-doped Ge and Si, the lowest-energy states are all *N111* configurations with FM order, and all other configurations have much higher energies than the *N111*. So, there would be ferromagnetism in Fe-doped group-IV semiconductors, and the recent experimental result shows that $\text{Fe}_x\text{Ge}_{1-x}$ (Ref. 16) is an *n*-type FM semiconductor with a Curie temperature as high as 233 K while the ferromagnetism in Fe-doped Si still needs further experimental observations. It is found from Table V that for the Ge host matrix, all other configurations, except the *N111* and *N220*, converge to the nonmagnetic state even from the initial FM one, and their energies are lower than that of the AFM state. In contrast, the *N220* configuration favors the AFM state rather than the nonmagnetic. However, for the Si host matrix, all configurations, except only *N111*, favor the nonmagnetic, being independent of the initial magnetic state. Comparing these results with those at 6.25% in Table VI, we found that the higher Fe concentrations will enhance the fer-

romagnetism. For example, the FM state in all $\text{Fe}_{0.0625}\text{Ge}_{0.9375}$ configurations are more favorable in energy than the AFM. So in the Fe-doping cases, the FM interaction is a very short-range one, and would become longer range by increasing the doping concentration.

It is generally thought that the *d* orbital on the *R* atom is much more hybridized with the *p* orbital of Si than with that of Ge, which would cause a smaller local magnetic moment on *R* in the Si matrix than that in Ge one.²⁰ From our calculated magnetic moments on *R* atoms listed in the above-mentioned tables it can be seen that at the same concentrations, in general, the magnetic moment on *R* in the Ge host matrix is a little larger than that in the Si one. We have also checked that if the lattice constant of Ge is compressed compared to that of Si, i.e., increasing the mixing of the *p* orbital of Ge with the *d* orbital of the *R* atom, the magnetic moment on the *R* atom would decrease in all cases. Especially in the case of 6.25% Fe doping, the decrease of the Ge lattice constant will cause the Fe atom to be nonmagnetic like that in $\text{Fe}_{0.0625}\text{Si}_{0.9375}$ listed in the right part of Table VI. And vice versa, enlarging the Si lattice constant to that of Ge causes the *N111* and *N220* configurations of the Fe-doped Si to be

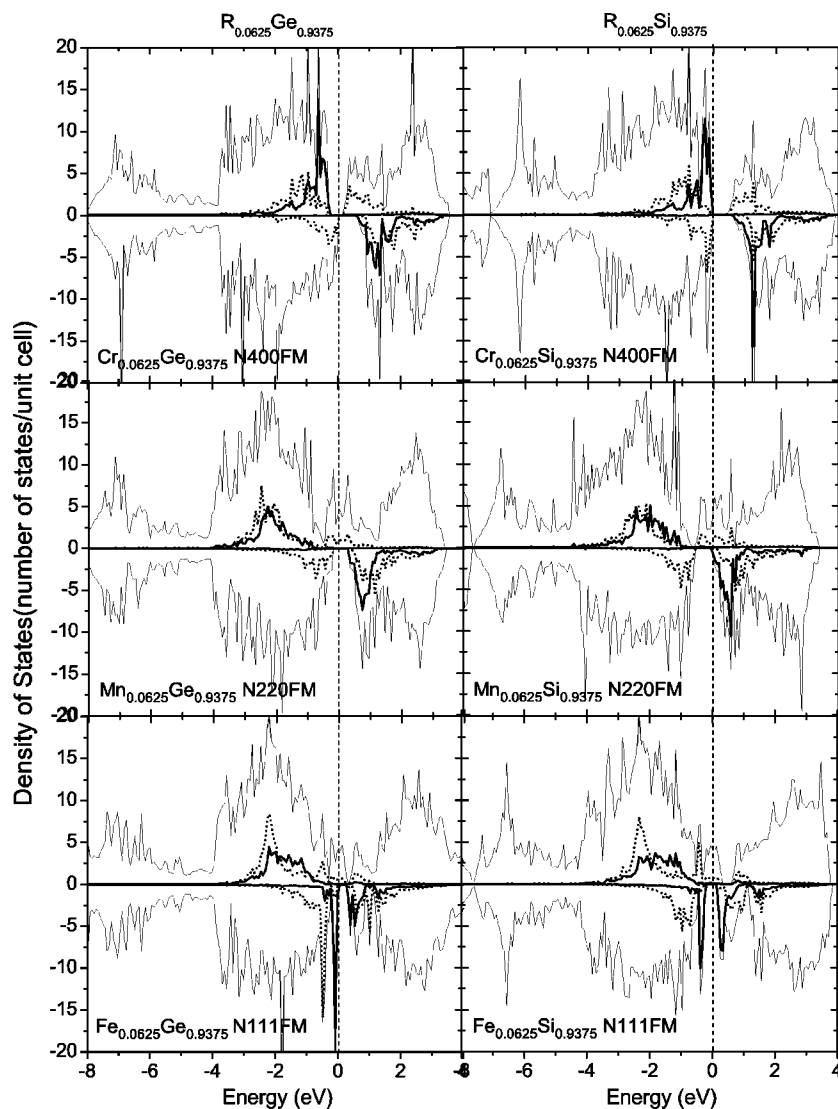


FIG. 2. The same as Fig. 1 but at 6.25% doping concentration.

in FM order although $N400$ and $N440$ remain in the nonmagnetic order. So, compressing (enlarging) the lattice would decrease (enhance) the FM order of the TM-doped group-IV semiconductor, which is consistent with the theoretical calculation on the Mn-doped diamond, another group-IV element with the same crystal structure, in which the absence of ferromagnetism had been predicted.²¹

To further investigate the transition-metals-doped group-IV semiconductors, we have also studied the electronic structures of these systems, and focused our attention on the lowest-energy FM states in all the configurations. The obtained total density of states (DOS) and 3d partial DOS on R atoms in the systems under study are shown in Figs. 1 and 2 for $x=0.031\,25$ and 0.0625 , respectively. Since Cr (Fe) has one electron less (more) than the Mn atom, a careful analysis of the total DOS of $\text{Cr}_x\text{Y}_{1-x}$ ($\text{Fe}_x\text{Y}_{1-x}$) in both figures shows that the Fermi level is a little downshifted (upshifted) compared with that of $\text{Mn}_x\text{Y}_{1-x}$. Moreover, from the 3d partial DOS and the magnetic moment of R atoms listed in Tables I to VI, we can deduce that one absent (redundant) electron in Cr (Fe) compared to Mn is in the spin-up (-down) state, which can also be seen from the opening (narrowing) of the

gap in spin-up (-down) channel in the case of Cr (Fe) doping compared to that of the Mn doping. These changes of total DOS around the E_F in the spin-channels will lead to different spin polarized conductivity in these systems. As shown obviously in Figs. 1 and 2, the Cr- (Fe-) doped Ge and Si system is nearly semiconducting (metal) in the total DOS structure, which is consistent with its tendency to be in the AFM (FM) ground state because the decreasing (increasing) carrier mobility would suppress (enhance) the FM order in the system. The 3d partial DOS of the R atoms are mostly distributed around E_F in the range from -3 to $+2$ eV. And in the spin-up channel, the main peaks of Cr in its valence band are centered at about -1 eV, while those of Mn and Fe are at -2.3 eV,²⁰ which are mostly contributed by e_g^\uparrow and t_{2g}^\uparrow . But for the spin-down part, the occupied peaks of Cr and Fe are mainly located at -0.5 eV and that of Mn is at about -1 eV, all of which are mostly composed of t_{2g}^\downarrow , whereas the unoccupied state around 0.5 eV for Mn and Fe and that at 1.2 eV for Cr have e_g^\downarrow character. So it is known from the above results that in general the crystal field splitting $\Delta_{e_g-t_{2g}}$ is about 0.5 , 1.3 , and 1.8 eV and the exchange splitting of e_g orbital is about 2.2 , 2.8 , and 2.8 eV for Cr, Mn, and Fe, respectively.

Clearly the exchange splitting energy is larger than the crystal field splitting energy in these systems, leading to their quite strong spin ordering and few changes in host's geometrical structure when doped with TM's.^{8,17} And above all, we can see that for Mn in Ge (Si), the local magnetic moment is contributed by three electrons in the t_{2g}^{\uparrow} orbital, and the e_g^{\uparrow} orbital is occupied by about one electron. With a small crystal field splitting, both of them are hybridized with the p orbital of Ge (Si) strongly, which enhances the carrier mobility and reduces the magnetic moment on the Mn atom. For Cr, the lack of the one t_{2g}^{\uparrow} electron makes this system semiconducting and thus it prefers more to stay in the AFM order. In the Fe-doped cases, one more electron occupies the e_g^{\downarrow} orbital, near the Fermi level, hybridizing with the p electrons, which makes the gap in the spin-down channel narrower or disappear, causing the magnetic moment on Fe to be smaller than that on Mn.

According to Anderson's s - d mixing model,²² the local magnetic moment on the transition-metal atom doped into the host matrix is determined by three factors: the on-site Coulomb interaction U of d electrons, the mixing of the d orbital with the delocalized orbital s of the host, and the energy difference between the d orbital and the Fermi level of the system. So, we have also done LSDA+ U calculations within VASP, which show that the on-site U will enhance the local magnetic moment on R , especially for 6.25% Fe-doped Si. $U=3.0$ eV would cause a magnetic moment as large as $3.02\mu_B$ on the Fe atom in the $N400$ configuration and the corresponding FM state is energetically lower than the AFM one by about 31.67 meV/Fe compared with the nonmagnetic state without U . And the total DOS of its FM state is nearly half-metal, which is consistent with the nearly integer magnetic moment on Fe. The same calculation of $\text{Mn}_{0.0625}\text{Ge}_{0.9375}$ in the $N220$ configuration shows that the

system remains a half-metal²³ though the magnetic moment on Mn is increased to $3.77\mu_B$. The reason why the half-metal feature is kept even including U is due to the strong s - d mixing in these TM-doped group-IV semiconductors. Furthermore, the LSDA+ U calculation of 6.25% Cr-doped Si in $N220$ and $N400$ configuration shows that the AFM state is still more stable than the FM one in energy.

IV. CONCLUSION

In summary, we have studied the transition-metal-doped group-IV semiconductors R_xY_{1-x} ($R=\text{Cr, Mn, and Fe}$; $Y=\text{Si and Ge}$) by the first-principle calculations in LSDA and GGA formalism. The obtained results show that there exist different ground states for different R elements. The one fewer electron of Cr than in Mn seems to disfavor the FM ordering in the doping system. In contrast, Fe doping makes the group-IV semiconductors more FM than Mn doping. It is also found that enlarging the lattice constant would decrease the p - d mixing and benefit FM order, which perhaps is another way to get a higher-Curie-temperature magnetic group-IV semiconductor in experiments. These systems seem to have different mechanisms of FM order, although their R elements are in the same row and both Si and Ge are in the same column in the periodic table, which still needs much more experimental and theoretical efforts to make clear.

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