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Half-metallicity and ferromagnetism of TcX (X=C, Si and Ge) in zinc blende structure

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ABSTRACT

We report results of a first-principles density-functional study of three binary transition-metal compounds TcX (X=C, Si and Ge) in the hypothetical cubic zinc blende (ZB) structure. Our calculations are based on the full potential linear augmented plane wave (FP-LAPW) plus local orbitals method, together with generalized gradient approximation for the exchange-correlation potential. Half-metallic (HM) ferromagnetism is observed in these binary compounds for their optimized cell volumes. In the HM state, these compounds possess an integer magnetic moment ($1.000\mu_B$) per formula unit, which is one of the important characteristics of half-metallic ferromagnets (HMFs). The ferromagnetic (FM) state is found to be stable for ZB TcC, TcSi and TcGe against the nonmagnetic (NM) and antiferromagnetic (AFM) states. Calculations show that half-metallicity can be maintained for a wide range of lattice constants in these binary compounds. Density functional calculations of exchange interactions and the Curie temperatures reveal similar trends for the three compounds with respect to the lattice parameter. These compounds are compatible with the traditional semiconductors, and could be useful in spin-electronics and other applications. The most important aspect of this work is to explore the possibility of not only magnetism, but HM ferromagnetism in compounds involving NM elements and $4d$ transition element Tc.

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1. Introduction

In recent years, a great deal of effort has been devoted to study the HM materials in view of their importance in the newly developing field of spin-based electronics or spintronics [1–3]. In 1983, de Groot et al., via density functional calculations, reported the existence of HM ferromagnetism in magnetic Heusler compounds such as NiMnSb [4]. HMFs are of immense interest because of 100% electron spin-polarization at the Fermi level. These materials are semiconductors with energy gaps for one spin direction, and metallic for electrons of opposite spin. Thus the electrons at the Fermi level, responsible for transport properties, are all spin-aligned. Subsequent to the study by de Groot et al., there have been numerous theoretical predictions and experimental studies on the HM materials such as NiMnSb, CrO_2, Fe_3O_4, manganite materials showing colossal magnetoresistance, and some transition-metal chalcogenides and pnictides [5–14]. Moreover, ZB Mn-IV binary compounds were also found to be HMFs [15–17].

The need for finding new HMFs which are more promising in basic properties and for applications [18] still remains paramount. The aim is to search for half-metals with simple structure, and high Curie temperature. Recently Liu et al. [19] and Bose and Kudrnovský [20] have presented extensive studies of exchange interactions and the Curie temperatures as a function of lattice parameter for some Cr-based chalcogenides and pnictides exhibiting half-metallicity. HM compounds which do not involve transition metals have also been considered. ZB Ca-based pnictides were predicted to be HMFs by Kusakabe et al. [21]. Very recently the HM ferromagnetism was found in many I–IV, I–V, II–IV and II–V ZB compounds [22–26], such as NaC and CaAs, where no transition metals are involved.

Almost all transition metal-based studies of half-metallicity involve elements from the $3d$ series. Though there are some works related to HM compounds containing no transition metal elements, those based on $4d$ transition elements are notably absent. The existence of the $4d$ transition element technetium was predicted by Mendeleev, who noted a gap in the periodic table indicating the missing element. The element was later discovered by Perrier and Segre in Italy in 1937. Nearly all technetium is produced synthetically and only minute amounts are found in nature. Technetium was the first element not found in nature (in any significant amount) to

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be produced artificially. It is a silvery-gray metal that tarnishes slowly in moist air, and its chemistry is supposed to be similar to that of its 5d counterpart, rhenium. Technetium's most stable isotopes, technetium-97 and technetium-98, have half-lives of 2.6 million years and 4.2 million years, respectively. Small amounts of technetium can retard the corrosion of steel. Technetium is used in a wide variety of diagnostic tools in medicine [27]. Until 1960s technetium was available only in small amounts. It can now be made in much larger quantities. Increase in technetium production is bound to follow as new applications of technetium and its compounds emerge. This work is a step in that direction.

Electronic properties of technetium are interesting. It has the second highest superconducting transition temperature among the elemental solids, surpassed marginally by niobium. Experiments as well as theoretical calculations reveal a high electron–phonon coupling [28]. Calculations for its close-packed hexagonal phase show that it has a moderately high Coulomb pseudopotential, moderate to high phonon frequencies and relatively low electron-spin fluctuation (paramagnon) coupling [28]. The latter is consistent with the observation that the exchange-enhancement of its spin susceptibility [29] is similar to its 4d neighbors, Ru and Rh, and relatively low compared to some of the 3d transition metals. However, under optimum conditions it can be driven toward magnetism. Magnetic properties of the transition metals in general, and especially the trends, can be understood to a large extent by noting that the d-band width decreases from left to right along a particular row and increases from 3d to 4d, and then to 5d along a particular column. Narrowness of a d-band results in a high density of states at the Fermi level, which drives the system toward Stoner instability and encourages lowering of energy via spin-polarization, i.e. magnetism. Wider d-bands are hard to spin-polarize, hence the absence of magnetism in the 4d counterparts of Mn, Fe, Co and Ni, namely Tc, Ru, Rh and Pd. However, the possibility of rendering these 4d elements, particularly Ru and Rh, magnetic via lattice dilation and/or reduced co-ordination, has been discussed in the literature and claims of experimental observation of such 4d magnetism have been made [30–32]. It should thus be possible to induce the same effect in Tc.

One way to put Tc atoms in an under-coordinated environment and thus render it magnetic would be to consider Tc-based alloys, where the hybridization between Tc 4d-orbitals is drastically reduced. Tc-based alloys in open (i.e. not close-packed) Zinc blende structure provide this opportunity. The binary transition-metal compounds TcX (X=C, Si and Ge) are structurally compatible with the group IV semiconductors, and share the zinc blende crystal structure with the typical semiconductor materials such as GaAs. It should be possible to grow films of ZB TcX directly on other ZB semiconductors substrates. The existence of large number of such ZB semiconductors and semiconducting substrates provides the opportunity to tune the lattice parameter and hence the band gap. Thus it is of interest to study the electronic and magnetic properties of these compounds. We have carried out a search of TcX compounds in order to ascertain the possibility of half-metallicity in these systems. It is hoped that the practical issues related to growth and physical property measurements of these compounds will be settled in near future. Successful fabrication of these materials offers exciting possibilities for the spintronic industry.

In this paper, we report systematic FP-LAPW calculations of binary ZB transition-metal compounds TcX (X=C,Si,Ge). We find HM ferromagnetism in these binary compounds at their optimized (equilibrium) cell volumes. We have thus investigated the electronic and magnetic properties for lattice parameters at and around these optimum (equilibrium) values. The remainder of this paper is organized as follows: In Section 2 we present the details of our calculations; in Section 3 we investigate the electronic and magnetic properties of these zinc blende binary Tc compounds TcX, where

X stands for C, Si and Ge. Exchange interactions and the Curie temperatures of these compounds are discussed in Section 4. Section 5 presents a summary of our results and conclusions.

2. Computational details

The ZB structure has the space group ($F\overline{4}3m$, or T_d^2, No. 216). The unit cell of TcX (X=C, Si and Ge) ZB structure may be viewed as an *fcc* lattice with four atoms per unit cell: Tc located at (0, 0, 0), X atoms at (0.25, 0.25, 0.25) and the two vacant sites at (0.5, 0.5, 0.5) and (0.75, 0.75, 0.75). We use the type-I AFM ordering [33] for the AFM calculations.

We used the WIEN2k [34] code, based on the full potential linear augmented plane wave plus local orbitals method and the density functional theory (DFT) [35]. The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (GGA-PBE96) was used for exchange and correlation [36] potentials. We consider full relativistic effects for the core states, and use the scalar approximation for the valence states. We have neglected the spin–orbit coupling because of its marginally small effect on the main results. We use 3000k points for the full Brillouin-zone integrations, using $14 \times 14 \times 14$ mesh of k-points in the irreducible wedge of Brillouin zone according to the Monkhorst–Pack scheme [37]. Convergence was checked by increasing the number of k points. We set $R_{mt}*K_{max}$ to 8.0 and considered angular expansion up to $l_{max} = 10$ in the muffin tins. The self-consistent calculation was allowed to stop only after the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}| \, dr$, for the input and output charge densities ρ_{n-1} and ρ_n became less than 10^{-4}.

## 3. Electronic structure of the binary compounds

We have carried out structural optimization of ZB TcX. For each of the binary compounds, we calculate total energy as a function of cell volume and thereby determine the equilibrium volume and lattice constant. Electronic densities of states (DOS), bands, and moments are then calculated for the equilibrium lattice constants. The equilibrium lattice constants *a*, moments per magnetic atom, the gaps G*MAJ* of majority-spin bands, and the HM gaps G_{HM} of these binary compounds, are summarized in Table 1. Of all the binary Tc compounds based on IV we find three HMFs. Table 1 shows the energy gaps of the majority-spin bands. The total magnetic moment is mainly contributed by the Tc atoms, being the same as in ZB binary transition-metal compounds. A certain amount of magnetic moments is found in the interstitial region too. Unfortunately, no experimental or theoretical data of elastic constants are available for comparison.

Fig. 1 shows the spin-dependent total DOS of FM ZB TcX (X=C, Si and Ge) at their equilibrium lattice constants. We remark that all three compounds exhibit energy gap. X-p states occupy the part from −3.5 to −1.5 eV below the Fermi level, while X-s states

Table 1

The calculated equilibrium lattice constants *a* (Å), bulk modulus *B* (GPa), first order pressure derivative of bulk modulus *B′*, energy difference (meV) $\Delta E_1 = E_{PM} - E_{FM}$ (between NM and FM states) and $\Delta E_2 = E_{AF} - E_{FM}$ (between AFM and FM states), majority-spin gaps G_{MAJ} (eV), and HM gaps G_{HM} (eV) for the TcX compounds. The results are done with the predicted equilibrium lattice constant, respectively.

Compounds	a	B	B′	ΔE_1	ΔE_2	G_{MAJ}	G_{HM}
TcC	4.630	247.284	4.486	45.18	46.67	0.75	0
TcSi	5.450	110.417	3.848	96.68	83.03	0.49	0.24
TcGe	5.613	95.560	4.499	138.14	82.27	0.38	0.02
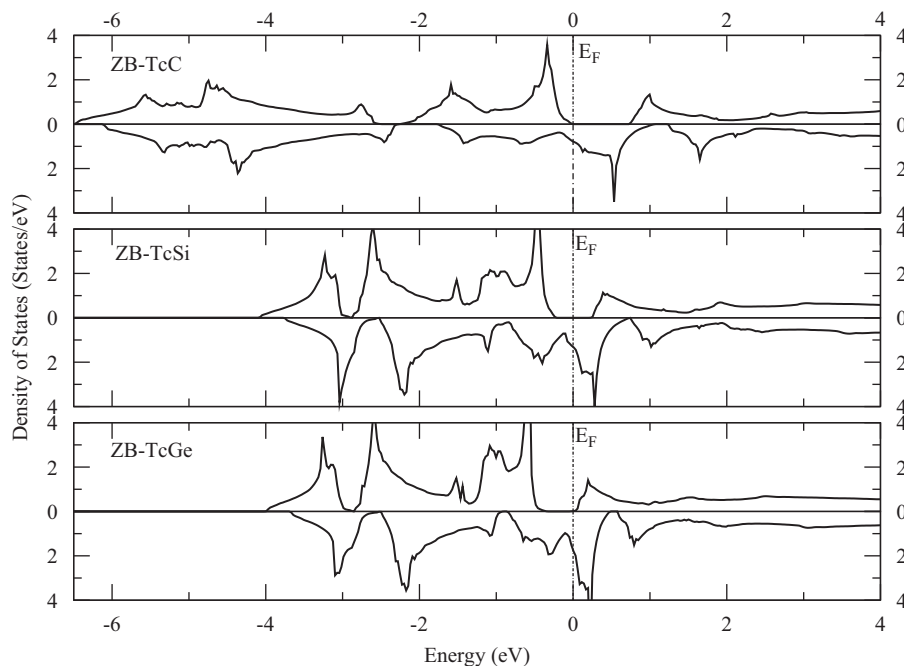
Fig. 1. Spin-dependent total DOS of the four ZB binary compounds: TcC, TcSi and TcGe. The upper or lower part of every panel is the majority-spin DOS or the minority-spin DOS. In each row, the panel is the calculation with volume optimization. In all cases, E_F lies within the majority-spin gap, i.e., the systems are HM.

are located about from -8.5 to -6.5 eV below the Fermi level, not shown in the figure. It can be clearly seen that all of these binary compounds keep their HM character at their respective equilibrium lattice constants. There is an energy gap of about 0.75, 0.49, and 0.35 eV in the majority-spin channel for TcC, TcSi and TcGe, respectively. The minority-spin channel shows a metallic character, as also observed in ZB MnC, MC (M=Ca, Sr, Ba), CaSi, and CaGe [24]. We note that the HM gap, which is defined as the minimum of the difference between the Fermi level and (in this case) majority-spin conduction/valence band edges, is too small for TcC. This makes TcC a nearly spin-gapless semiconductor [38]. The HM gaps are 0, 0.24 and 0.04 eV for TcC, TcSi and TcGe, respectively. Compared to other ZB HMFs, these values are relatively small. We have verified that the energies of NM and AFM states are higher than that of the FM state for all these compounds, confirming the stability of FM states. Although there are no experimental data available for comparison, similar studies of FM HM ZB transition-metal pnictides and chalco-genides have shown that the ZB structure usually does not have the lowest total energy compared with other crystal structures. How-ever, the ZB films of CrAs, CrSb, MnAs, and CrTe have been fabricated on appropriate ZB semiconductor substrates [39–44]. In the follow-ing, we will discuss the electronic structure and the magnetism of ZB TcSi in some detail, as a prototype of the group TcX (X=C, Si, Ge). Similar discussion should be applicable to the other two compounds as well.

As for the trends with the atomic number of X, we note that the Tc magnetic moment increases slightly along the C–Si–Ge series; this can be ascribed to the increasing lattice constants of the Tc sublattice, which results in a smaller d–d overlap (and smaller band width) and a consequently larger exchange inter-action. On the other hand, the X magnetic moment increases as the anion atomic number increases, keeping the global magnetic moment very close to $1.0\mu_B$.

In Fig. 2 we show the partial DOS of TcSi projected on Tc and Si. The corresponding spin-polarized band structures of TcSi in the ZB structure with Tc d-character are shown in Fig. 3. It is clear that the band structure is semiconducting for the majority spin electrons (spin up) and metallic for the minority spin electrons (spin down),

revealing the HM character of ZB TcSi. For both majority and minority spin bands the three lowest bands originate primarily from hybri-dized Si p states and Tc d states. The three lowest majority spin bands are fully filled, while the minority spin bands are partly filled because of the interaction between the Si p states and the Tc d states. It can be explained from the electronic arrangements: in ZB TcSi, seven valence electrons (Tc:$4s^23d^1$; Si:$3s^23p^2$) contribute to bond formation and magnetism; two of them occupy the Si s states (about -6.5 to -8.5 eV). Three of the remaining five valence electrons occupy the majority spin p states of Si and d states of Tc, respectively, which results in the three majority spin fully filled bands. The three minority spin bands are partly filled, and provide the main magnetic moment. Moreover, because of tetrahedrally coordinated environ-ment in the ZB structure, these bands from -4 to 0 eV below the Fermi level for both majority and minority spin channels are mainly formed by the Tc d states.

A so-called "rule of 8" seems to operate for transition metal-based ZB pnictides and chalcogenide HM compounds (Slater-Pauling-type behavior) [10]. For these compounds the total magnetic moment per formula unit, M, and the total number of valence electrons in the unit cell Z_{tot} are expected to be related as

$$M = (Z_{tot} - 8)\mu_B \tag{1}$$

This relation assumes that the exchange splitting is sufficient to push the minority e_g states above the Fermi level E_F, leading to a situation where the minority anion-s and p–t_{2g} hybrid states are fully occupied and all higher minority states are unoccupied, resulting a total minority state occupation of 4. In general

$$M = (N_{maj} - N_{min})\mu_B = (N_{maj} + N_{min} - 2 \times N_{min})\mu_B = (Z_{tot} - 2 \times N_{min})\mu_B \tag{2}$$

where $N_{maj}(N_{min})$ is the number of occupied majority (minority) states. Eq. (1) follows from a total minority state occupation of 4. The situation in the case of the TcX (X=C, Si, Ge) HM compounds, however, is similar to that of MnC ($3d$ counterpart of TcC) discussed by Pask et al. [15]. Since the exchange splitting in the case of the TcX compounds considered is not sufficient to push the minority e_g states completely above the Fermi level in TcX,
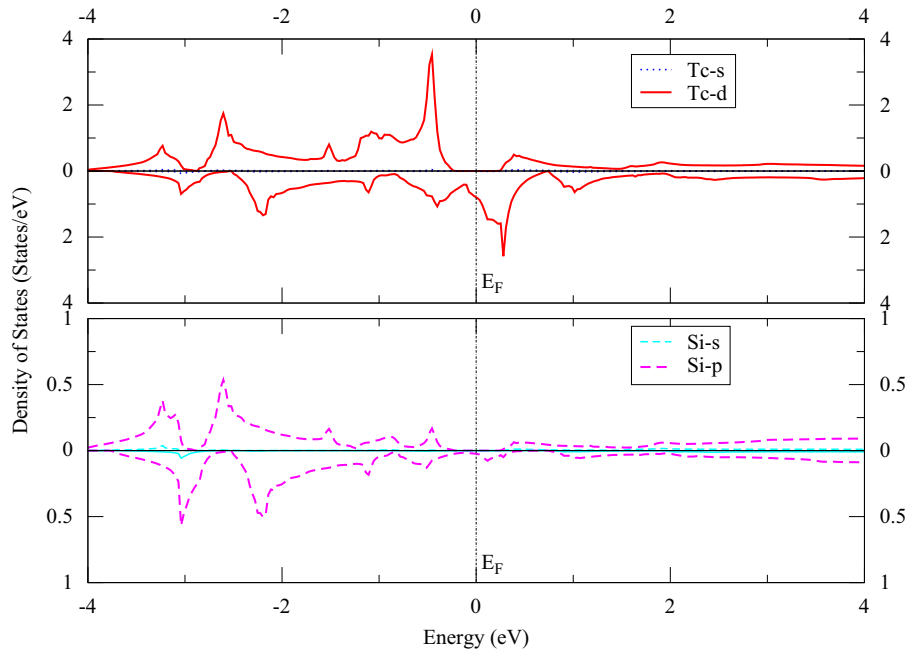
Fig. 2. Spin-dependent partial DOS of the ZB binary compound TcSi projected on two atoms at the equilibrium crystal constants.
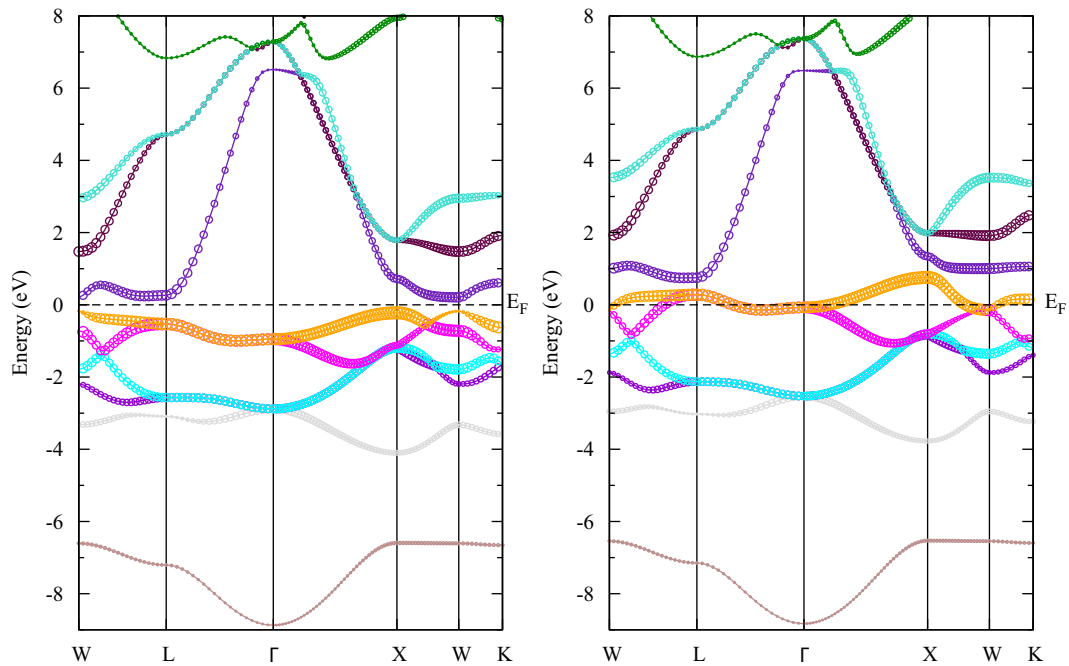

Fig. 3. Spin-dependent energy bands of the ZB TcSi at equilibrium volume, with the thickness of the lines showing the (Tc)d-character of the bands: left panel, majority spin; right panel, minority spin.

Eq. (1) is inapplicable. Additionally, in TcX, as in the case of MnC [15], the majority rather than minority channel is insulating, so Eq. (2) is not valid either. A relation, that is valid for TcX (X=C, Si, Ge), follows more naturally from an equivalent expression in terms of majority occupation:

$$M = (N_{maj} - N_{min})\mu_B = (2N_{maj} - Z_{tot})\mu_B \tag{3}$$

In TcX, the bonding–antibonding splitting is sufficient to push the majority antibonding states completely above the Fermi level, leaving the majority anion-s, p–t_{2g} hybrid, and e_g states fully occupied, and all higher majority states unoccupied, yielding a total majority occupation of (4). So the appropriate relation for such compounds is

$$M = (8 - Z_{tot})\mu_B \tag{4}$$

For TcX, $Z_{tot} = 7$, and Eq. (4) predicts a magnetic moment of $1\mu_B$, in agreement with our *ab initio* results (see Table 2). An interesting implication of Eq. (4) is that as the cation atomic number decreases, the magnetic moment should increase, precisely opposite to the pnictide compounds. And indeed, *ab initio* results result show exactly this, i.e., $M = 2\mu_B$ and $M = 3\mu_B$ for ZB CaSi, CaGe [24], and ZB NaC, KC, respectively.

Table 2
The calculated spin magnetic moments in the unit of μ_B using the equilibrium lattice constants a, the Tc atom moment, X atom moment and the unit cell magnetic moments, for the TcX ZB compounds. The results are done with the predicted equilibrium lattice constant, respectively.

Compounds	Tc	X	Int	Tot
TcC	0.845	−0.034	0.189	1.000
TcSi	0.894	−0.030	0.136	1.000
TcGe	0.931	−0.046	0.115	1.000
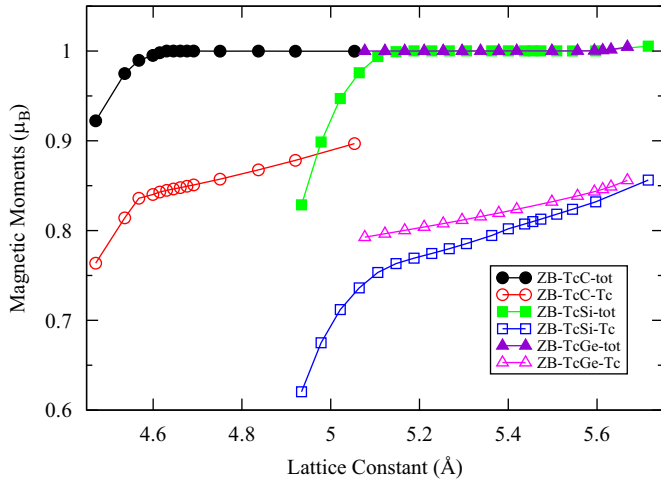
Fig. 4. Total magnetic moment of ZB compounds as a function of the lattice constants for TcC, TcSi and TcGe.

The basic ferromagnetism, as usual, is induced by the exchange splitting of the d bands of the magnetic atoms, which, in this case, happens to be the Tc atoms. The minority-spin energy gaps are formed between the p-dominated bands and the e_g bands of Tc. The HM gaps are formed when the Fermi level, with a favorable DOS distribution of the minority-spin bands, falls in the energy gaps of the majority-spin bands. Take TcSi as an example. The Tc d states play a role similar to that of the transition metal atoms ZB binary transition-metal compounds. The elements C, Si and Ge play an important role for the creation of a gap at the E_F in these binary Tc-based compounds. An Si atom has four valence electrons ($3s^2 3p^2$) and Tc has valence configuration $3d^1 4s^2$. The bands between 6.5 and 8.5 eV below the Fermi level are provided by the s electrons of Si. The favorable DOS distribution of the minority-spin bands makes the Fermi level fall at the right position, rendering all these three compounds HMFs.

We have investigated the robustness of half-metallicity with respect to the variation of lattice constants in these compounds. Fig. 4 shows that the total magnetic moments of all three binary compounds retain their integer values with the compression and expansion of the lattice parameter around the equilibrium values until the compression reaches a critical value, beyond which the moment drops rapidly. Half-metallicity of TcX, with X=C, Si and Ge, is found to persist up to contraction of the lattice constant by 6%, 8%, and 21%, respectively.

The calculated magnetic moments are found to be dependent on the magnetic configuration. The lower the available volume per Tc atom, the more susceptible the magnetic moment on the magnetic configuration. For example, the FP-LAPW calculation, for the same lattice parameters as shown in Table 1, produces Tc magnetic moments of 0.259, 0.549 and 0.828μ_B for TcC, TcSi and TcGe, respectively, in the AFM [001] configuration. The corresponding numbers for the AFM [110] configuration are 0.375,

0.609 and 0.813μ_B. Comparing with the corresponding values of 0.845, 0.894 and 0.931μ_B for the FM configuration shown in Table 2, we see that the magnetic moment is most robust in TcGe and least so in TcC. As discussed in the next section, we have employed the tight-binding linear muffin-tin orbital (TB-LMTO) method [45,46] to study the exchange interaction in these compounds. Magnetic moments obtained with this method are similar to those given by the FP-LAPW method for the FM phase. To study the robustness of the magnetic moments, we have studied the disorder local moment (DLM) [47] states in these compounds using the TB-LMTO method. In the DLM state the Tc sublattice is populated randomly by Tc atoms of equal but oppositely directed magnetic moments. The randomness is treated within the coherent potential approximation. The Tc moment in this state is found to be most robust for TcGe, being as high as in the FM state. The DLM moments for TcSi and TcC are of the order of 0.5 and 0.2μ_B at lattice parameters corresponding to the onset of half-metallic FM phase in these compounds. Thus both FP-LAPW calculations and the TB-LMTO calculations show that the magnetism is most robust in TcGe among these three compounds. This result is understandable in view of the fact that the volume per Tc atom is the highest in TcGe.

4. Exchange interactions and Curie temperatures

We have employed the tight-binding linear muffin-tin orbital (TB-LMTO) method [45,46], within the atomic sphere approximation (ASA), to compute the exchange interactions between the various atoms. To this end we first compare the electronic structure and magnetic moment results from the TB-LMTO-ASA with those given by the FP-LAPW (WIEN2K code) method. TB-LMTO calculations employ exchange–correlation potential of Vosko et al. [48], an s, p, d, f basis set, relativistic treatment of core electrons and scalar-relativistic treatment of valence electrons. Radii of the atomic spheres are chosen according to their Hartree potentials, and the radii of the empty spheres are chosen so as to minimize the sphere overlaps according to the prescription of the atomic sphere approximation and as implemented in the Stuttgart TB-LMTO code [49]. The results, particularly with respect to half-metallicity, are found to be similar to those from WIEN2k. The gap values are marginally lower and can be ascribed to the differences between LDA (in TB-LMTO-ASA) and GGA (in FP-LAPW). The equilibrium lattice parameters are 2–5% higher in TB-LMTO LDA calculations. The computation of exchange interaction is based on the mapping [50,51] of the zero temperature band energy onto a classical Heisenberg model:

$$H_{\text{eff}} = -\sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j. \tag{5}$$

The justification of replacing the total energy by the band energy is given by the magnetic variant of the 'Andersen force theorem' [52,53], which asserts that the differences in the total energies of various magnetic configurations can be approximated by the differences in their band energies alone [54–56]. Several details/issues related to this mapping appear in our previous publications [19,20]. The representation of the total energy via an effective Heisenberg model itself can be and has been justified [51,57] for metallic (itinerant) ferromagnets as follows. The magnetic excitations in itinerant ferromagnets are of two different types: Stoner excitations, in which an electron from the majority-spin band is excited across the Fermi level (surface) to an unoccupied minority-spin band, creating an electron–hole spin-triplet pair and collective spin-wave excitations (magnons). The former are associated with longitudinal fluctuations of the magnetization and the latter are associated with the collective transverse

fluctuations of the direction of magnetization. The application of the Heisenberg model can be justified to the extent the magnetic properties are dominated by magnons, and the Stoner excitations can be neglected. This is certainly the case at low temperatures, where the density of states is dominated by magnons. The Heisenberg model approximation is decidedly good for strong ferromagnets such as Fe and Co with large exchange splittings [58], and less justifiable for Ni which has a smaller exchange splitting. However, even for Ni the results turn out to be quite acceptable [51]. In view of the results related to the magnitude of the moments in various different magnetic configurations in the ZB TC-X (X=C, Si, Ge) alloys, it should be noted that the Heisenberg model description should be a good approximation for TcGe and increasingly less reliable for TcSi and TcC. However, even for the latter two cases, Heisenberg model would not be entirely unreasonable to use. Note that for fcc Ni the DLM moment is zero, and yet the Heisenberg model produces reasonable results [51].

In Eq. (5) i, j are site indices, $\mathbf{e}_i$ is the unit vector pointing along the direction of the local magnetic moment at site i, and J_{ij} is the exchange interaction between the moments at sites i and j. The mapping procedure was first given by Liechtenstein et al. [54–56], who used multiple-scattering formalism to show that the exchange integrals in Eq. (5) can be written as

$$J_{ij} = \frac{1}{4\pi} \lim_{\epsilon \to 0^+} \mathrm{Im} \int \mathrm{tr}_L[\Delta_i(z)g_{ij}^{\uparrow}(z)\Delta_j(z)g_{ji}^{\downarrow}(z)]\,dz, \qquad (6)$$

where $z = E + i\epsilon$ represents the complex energy variable, $L = (l, m)$, and $\Delta_i(z) = P_i^{\uparrow}(z) - P_i^{\downarrow}(z)$, representing the difference in the potential functions for the up and down spin electrons at site 'i'. $g_{ij}^{\sigma}(z)(\sigma = \uparrow, \downarrow)$ represents the matrix elements of Green's function of the medium for the up and down spin electrons. It should be noted that the spin magnetic moments are included in the above definition of J_{ij}. Positive and negative values of J_{ij} imply FM and AFM couplings, respectively, between the atoms at sites i and j.

In Fig. 5 we show the exchange interactions between the Tc atoms as a function of lattice parameter for the three compounds around their respective equilibrium values. Note that the TB-LMTO-ASA equilibrium lattice parameters are 2–5% higher than those given by the FP-LAPW method (WIEN2k). There are induced moments associated with the nonmetallic atoms (C, Si, Ge) and the empty spheres and therefore non-zero exchange interactions between them and the Tc atoms (atomic spheres). Although, these are somewhat dependent on the choice of the radii, we can safely conclude that the interaction among the non-Tc spheres and between them and the Tc atoms is about three orders of

magnitude smaller than those between the Tc atoms themselves. This results in the simplification that the Curie temperature can be calculated reliably by considering the interactions between the Tc-atoms alone. As shown in Fig. 5, for TcC and TcSi the interactions (primarily the nearest neighbor interaction) increases with increasing lattice parameter or volume per atom, and saturates (temporarily) at a value somewhat above the equilibrium lattice parameter. For TcGe the equilibrium lattice parameter is already at a value corresponding to this saturation plateau and the nearest neighbor interaction increases only when the lattice parameter is increased to a high value close to 6.0 Å. For all the three compounds the nearest neighbor interaction dominates.

We calculate the Curie temperature T_c using both the mean-field approximation (MFA) and the more accurate random-phase approximation (RPA) [20]. If the magnetic sublattice consists only of the magnetic atoms X, and all interactions involving the induced moments can be neglected, then in the MFA, the Curie temperature is given by

$$k_B T_c^{\mathrm{MFA}} = \frac{2}{3} \sum_{i \neq 0} J_{0i}^{X,X}, \qquad (7)$$

where the sum extends over all the neighboring shells and involves the exchange interactions between the magnetic atoms X. MFA is known to grossly overestimate T_c. A much more improved description of finite-temperature magnetism is actually provided by the RPA. The expression for RPA T_c, valid under the same conditions as stated above, is

$$(k_B T_c^{\mathrm{RPA}})^{-1} = \frac{3}{2} \frac{1}{N} \sum_{\mathbf{q}} [J^{X,X}(\mathbf{0}) - J^{X,X}(\mathbf{q})]^{-1}. \qquad (8)$$

Here N denotes the order of the translational group applied and $J^{X,X}(\mathbf{q})$ is the lattice Fourier transform of the real-space exchange interactions $J_{ij}^{X,X}$. In the present situation the magnetic atom X is Tc for all the three compounds. The computed RPA T_c values as a function of lattice parameter are shown in Fig. 6. For the equilibrium lattice parameters we estimate the T_c values to be around 100 K, 200 K, and 300 K for TcC, TcSi and TcGe, respectively. These values are relatively lower than those estimated for some of the 3d-transition metal based chalcogenides and pnictides [20,19], which have 3–4 times larger [10] magnetic moments.

The initial decrease in T_c with increasing lattice parameter, followed by an increase, may warrant a few comments. As a matter of fact, such non-monotonic variation of T_c, including local maximum/minimum, with volume/lattice parameter is not unique to TcGe. The exchange interactions in metallic systems have an oscillatory character, resulting from the sharp cutoff at the Fermi level (wave vector). The oscillations can be seen as a function of volume as well as inter-atomic distances for a given volume. As a result, a non-monotonic variation of T_c with lattice parameter is not surprising. For TcGe the second neighbor interaction turns antiferromagnetic at higher lattice parameter (Fig. 5), and this may cause the initial decrease. However, as the second neighbor interaction turns more negative, the positive nearest neighbor interaction increases in magnitude as well, and this increase may eventually cause T_c to increase again. With further changes in the lattice parameter, both TcC and TcSi may also show trends similar to that of TcGe, perhaps to a lesser extent as far as magnitude of variation is concerned. A behavior similar to that of TcGe with regard to volume dependence of T_c has also been predicted for CrTe in a rock-salt structure. [19]. An explanation of the change in exchange interaction and T_c with pressure/volume can be constructed by considering the variation in the magnetic moment and the bare exchange interactions separately. This has been discussed in detail in a recent publication by one of the present authors [59].
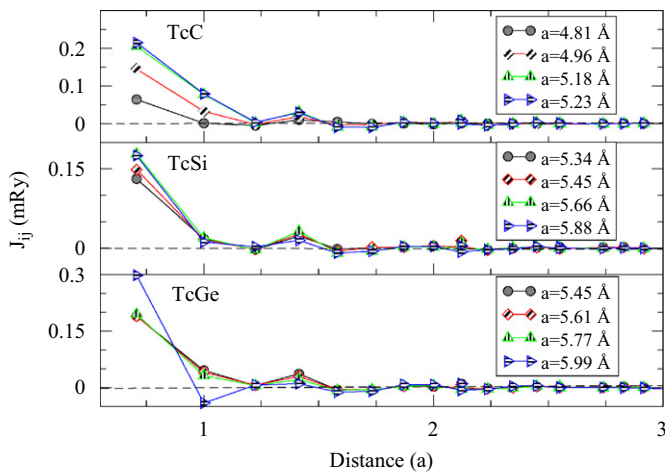

Fig. 5. Distance dependence of exchange interaction in ZB TcX (X=C, Si, Ge) compounds.
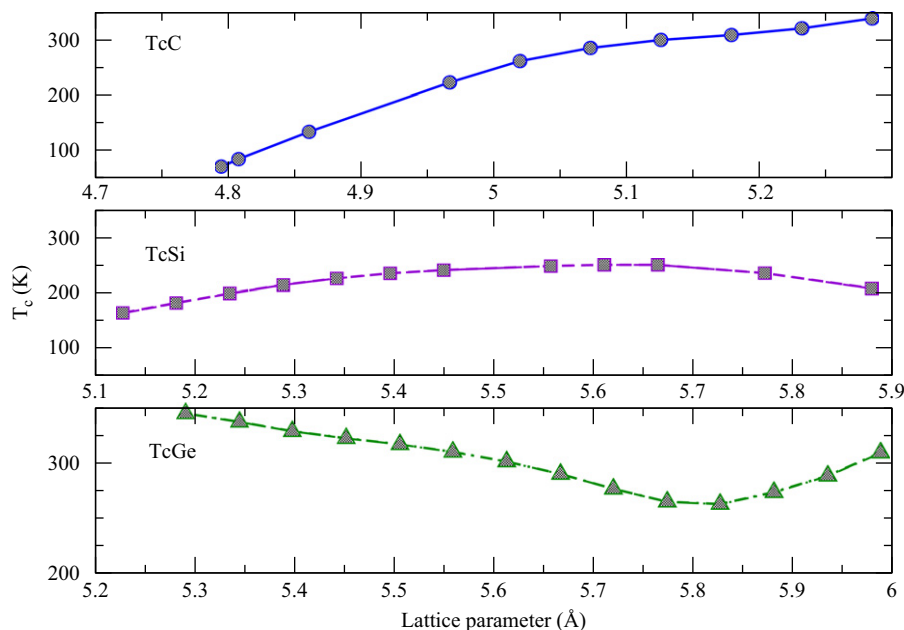
Fig. 6. Variation of the Curie temperature with lattice parameter in ZB TcX (X=C, Si, Ge) compounds.

5. Summary and conclusions

The most important aspect of this work has been to study the possibility of not only magnetism, but HM ferromagnetism in compounds involving NM elements and the 4d transition element Tc. To this end, using an accurate full-potential density-functional method, we have performed a systematic study of the electronic and magnetic properties of ZB binary transition-metal compounds TcX, where X represents group IV elements: C, Si and Ge. Via cell volume optimization, these three compounds are predicted to be robust HMFs around their respective equilibrium lattice parameter values with a magnetic moment of $1.000\mu_B$ per formula unit. The FM state is found to be energetically favorable to the NM and the AFM states. The FM ordering of the binary compounds is produced by a strong p–d hybridization. These binary compounds are compatible with the II–VI semiconductors both with respect to structure and lattice parameters.

Among the three compounds studied, magnetism is found to be most robust in TcGe, in the sense that the magnitude of the moment for a given lattice parameter in TcGe is more or less independent of the magnetic configuration. This conclusion is based on our study of the AFM [100] and AFM [110] configurations as well as the DLM configuration, where the Tc sublattice is supposed to be randomly occupied with Tc atoms of equal but opposite magnetic moments. For TcSi and TcC the moments are smaller in AFM and DLM configurations than their corresponding FM values. Our results based on the Heisenberg model study should definitely hold for TcGe. Although the results are less reliable for TcSi and TcC than TcGe, they should be considered reasonably accurate.

Exchange calculations show that the magnetism is dominated by nearest neighbor interaction. Estimated Curie temperatures lie in the range of 100 K, 200 K and 300 K for TcC, TcSi and TcGe, respectively. The relatively lower values of T_c compared with some Cr- and Mn-based chalcogenides and pnictides [20,19] are due to the magnetic moment for TcX (X=C, Si, Ge) being 3–4 times lower than the latter compounds [10]. However, these Tc-based compounds do show robust half-metallicity at and around their equilibrium volumes, with estimated T_c values that go as high as the room temperature. These results and observations render them worthy of further studies with regard to their potential application in spintronic devices.

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