Half-Metallic Ferromagnetism and Structural Stability of Zincblende Phases of the Transition-Metal Chalcogenides

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An accurate density-functional method is used to study systematically half-metallic ferromagnetism and stability of zincblende phases of 3*d*–transition-metal chalcogenides. The zincblende CrTe, CrSe, and VTe phases are found to be excellent half-metallic ferromagnets with large half-metallic gaps (up to 0.88 eV). They are mechanically stable and approximately 0.31–0.53 eV per formula unit higher in total energy than the corresponding nickel-arsenide ground-state phases, and therefore would be grown epitaxially in the form of films and layers thick enough for spintronic applications.

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Half-metallic ferromagnets are seen as a key ingredient in future high performance spintronic devices, because they have only one electronic spin channel at the Fermi energy and, therefore, may show nearly 100% spin polarization[1,2]. Since de Groot *et al*'s discovery [3] in 1983, many half-metallic ferromagnets have been theoretically predicted and some of them, furthermore, have been confirmed experimentally [4–7]. Much attention has been given to understanding the mechanism behind the half-metallic magnetism and studying its implication on various physical properties [8,9]. However, it is highly desirable to explore new half-metallic ferromagnetic materials which are compatible with important III-V and II-VI semiconductors. For this purpose, effort has be made on the metastable zincblende (B3) phases such as the transition-metal pnictides [10–20]. Although zincblende phases of MnAs [11], CrAs [12,13], and CrSb [14] have been successfully fabricated as nanodots, ultrathin films and ultrathin layers in multilayers, it has not been possible to grow the zincblende half-metallic ferromagnetic phases as high-quality layers or thick films. This is due to the metastable zincblende phases being about 1 eV per formula unit higher in energy than the ground-state nickel-arsenide ($B8_1$) phases. However, spintronic devices require thick films or layers. Therefore, it is important to explore theoretically other half-metallic ferromagnetic materials, which on the one hand are compatible with the binary tetrahedral-coordinated semiconductors, and on the other hand are not only low in energy with respect to the corresponding ground-state structures but also mechanically stable against structural deformations.

In this Letter we make use of an accurate full-potential density-functional method to study systematically transition-metal chalcogenides in the zincblende and nickel-arsenide structures in order to find half-metallic ferromagnetic phases which could be realized in the form of films and layers thick enough. We shall show that CrTe, CrSe, and VTe in the zincblende structure are excellent half-metallic ferromagnets with wide half-metallic gaps. They will be proved to be mechanically stable and approximately 0.31–0.53 eV per formula unit higher in energy than the corresponding ground-state phases, and therefore would be grown epitaxially in the form of films and layers thick enough for spintronic applications.

We make use of the Vienna package WIEN2K [21] for all our calculations. This is a full-potential (linear) augmented plane wave plus local orbitals method within the density-functional theory [22]. We take the generalized gradient approximation in Ref. [23] for the exchange-correlation potential. Relativistic effects are taken into account within the scalar approximation, but the spin-orbit coupling is neglected because it is proved to have little effect on our main conclusions. We use 3000 k points in the Brillouin zone for the zincblende structure and 2000 k points for the nickel-arsenide structure. When calculating the shear modulus constants of the zincblende phases we use 6000 k points. We set $R_{mt} \times K_{\max}$ to 8.0 and make the expansion up to $l = 10$ in the muffin tins. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}| dr$, between input charge density $[\rho_{n-1}(r)]$ and output $[\rho_n(r)]$ is less than 0.0001.

In order to search for the better half-metallic ferromagnets in zincblende structure, we explore systematically all zincblende phases of 3*d*–transition-metal chalcogenides. We find that among all these zincblende compounds only the CrSe, CrTe, and VTe phases are half-metallic ferromagnets. The ground-state phase of CrTe is a metallic ferromagnet in the hexagonal nickel-arsenide structure with experimental lattice constants $a = 3.998$ Å and $c = 6.254$ Å [24,25]. Its experimental Curie temperature is $T_c = 340$ K which decreases to zero at a pressure of 28 kbar[24]. In contrast, the ground-state phase of CrSe is an antiferromagnet in the nickel-arsenide structure with experimental lattice constants $a = 3.674$ Å and $c = 6.001$ Å [24,26]. Its Néel temperature was located at 320 K by specific heat measurement [27]. There has not been any experimental report on VTe, but it is shown by comparing the total energies of various phases that the nickel-arsenide ferromagnetic phase, with equilibrium lattice constants 4.13 and 6.07 Å, is the ground-state phase in this case. We predict the equilibrium lattice constants of the zincblende CrSe, CrTe, and VTe to be 5.833, 6.292, and 6.271 Å, respectively.

Figure 1 shows the band structures of the zincblende CrSe, CrTe, and VTe phases at their equilibrium volumes. For the minority spin bands we see that just below the Fermi energy there exist three Γ_{15} bands which result mainly from the Te (Se) p electrons, whereas just above the Fermi energy there exist two Γ_{12} bands which comprise mainly the Cr (V) e_g electrons. For the majority-spin bands, there are also three Γ_{15} bands below the Fermi energy originating mainly from the Te (Se) p electrons, but the two Γ_{12} bands mainly of the Cr (V) e_g electrons are below the Fermi energy. The bands crossing the Fermi energy are the majority-spin Γ_1 and Γ'_{15}. The three Γ'_{15} bands are mainly of Cr (V) t_{2g} character. There is strong interaction between the Te (Se) p bands and the Cr (V) t_{2g} bands. Figure 2 shows the spin-dependent total and partial density of state (DOS) of the three zincblende phases. The zincblende phases of CrTe, CrSe, and VTe have large half-metallic gaps, 0.88, 0.61, and 0.31 eV, respectively.

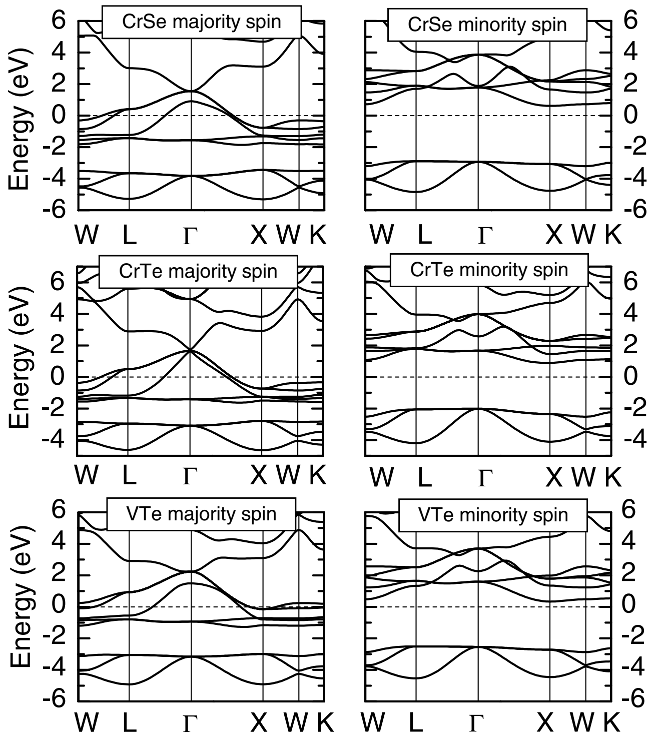

FIG. 1. The band structures of the zincblende phases of CrSe (upper panels), CrTe (middle panels), and VTe (lower panels) at their equilibrium lattice constants. The left-hand panels are the majority-spin bands and the right-hand panels are the minority-spin bands.

The binding energy curves for CrSe, CrTe, and VTe in the zincblende structure are shown in Fig. 3. All the three zincblende phases are ferromagnetic because the antiferromagnetism with the modulation vector [001] makes their equilibrium total energy per formula unit increase by 0.07, 0.12, or 0.13 eV, respectively, and other antiferromagnetic modulation vectors lead to even higher total energies. We summarize our main results in Table I. The metastable energy of a phase is defined as its total energy per formula unit minus that of the corresponding ground-state phases. There have been previous predictions of half-metallic ferromagnetism in transition-metal pnictides or chalcogenides from DOS calculations [28]. However, no detailed discussion of their energetics has been given. It is clear that the metastable energies of the

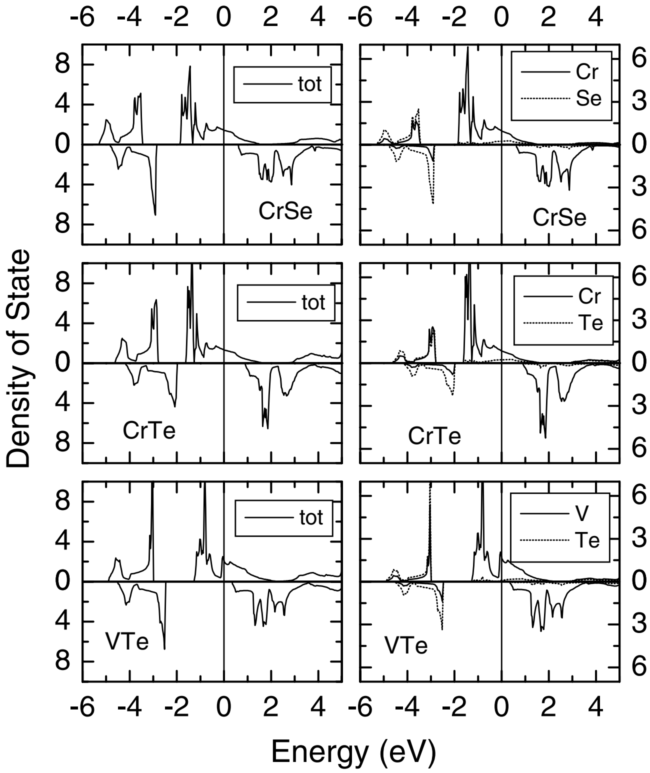

FIG. 2. Spin-dependent total (tot) and partial DOS (per eV per formula unit) of CrSe, CrTe, and VTe in the zincblende structure. The upper-left panel shows the total DOS of the CrSe phase, and the upper-right panel shows the Cr (solid lines) and Se (dotted lines) partial DOS; the middle-left panel shows the total DOS of the CrTe phase, and the middle-right panel shows the Cr (solid lines) and Te (dotted lines) partial DOS; the lower-left panel shows the total DOS of the VTe phase, and the lower-right panel shows the V (solid lines) and Te (dotted lines) partial DOS.

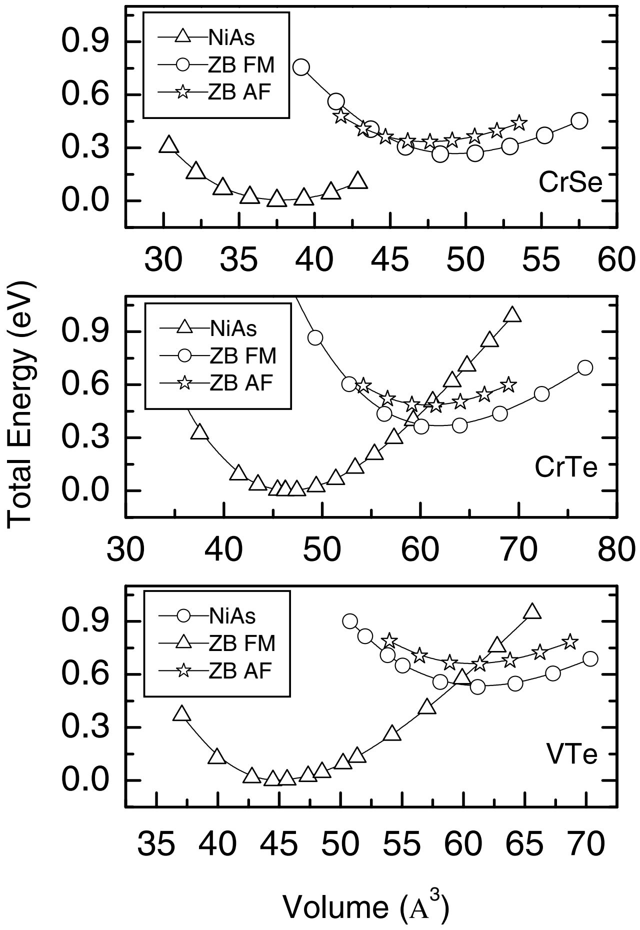

FIG. 3. The total energies of the zincblende (ZB) phases, with respect to the corresponding NiAs (triangles) ground-state phases, as functions of the volume per formula unit for CrSe (upper panel), CrTe (middle panel), and VTe (lower panel). The half-metallic ferromagnetism in the ZB ferromagnetic phases (ZB FM, circles) persists to be nonzero up to a compression of 12%, 22%, or 10% about the equilibrium volume, respectively. The ZB antiferromagnetic phases (ZB AF, stars), which are lowest in energy among all the antiferromagnetic ZB structures we can construct, are presented for comparison.

TABLE I. The predicted equilibrium lattice constant (a), magnetic moment per formula unit (M), half-metallic gap (E_g), and metastable energy (E_t) of the transition-metal pnictides and chalcogenides with zincblende structure.

Name	a (Å)	M (μ_B)	E_g (eV)	E_t (eV)
MnAs [16]	5.70	3.5	⋯	0.9
MnSb [20]	6.18	4.000	0.20	0.9
MnBi [20]	6.399	4.000	0.42	1.0
CrAs	5.659	3.000 [18]	0.46	0.93
CrSb [19]	6.138	3.000	0.77	1.0
VTe	6.271	3.000	0.31	0.53
CrSe	5.833	4.000	0.61	0.31
CrTe	6.292	4.000	0.88	0.36

three transition-metal chalcogenides are substantially smaller than those of the transition-metal pnictides.

An important question to address is whether these zincblende phases are mechanically stable, so that they would be grown experimentally [29]. In order to investigate this we have evaluated the tetragonal and trigonal shear constants, C' and C_{44}, respectively, by computing the change in energy of the zincblende phases under small volume-conserving strains (see Fig. 4). Their values are given in Table II together with the bulk modulus B for comparison. We see that all the zincblende phases are stable against the tetrahedral and rhombohedral deformations. The three zincblende transition-metal chalcogenides have slightly smaller bulk moduli, but larger tetragonal shear moduli than the zincblende CrAs phase. They are softer than GaAs, which has bulk and tetragonal shear modulus of 61.3 and 59.7 GPa, but are harder than the zincblende CrAs phase which has already been fabricated successfully epitaxially. Importantly, however, their metastable energies are much smaller than that of the zincblende CrAs phase. Therefore, the zincblende phases of CrSe, CrTe and VTe would be realized in the near future by means of epitaxial growth.

In summary, using the accurate density-functional method we have made a systematic computation of all the $3d$–transition-metal chalcogenides in the zincblende and nickel-arsenide structures and found the zincblende CrSe, CrTe and VTe to be excellent half-metallic ferromagnets. These zincblende phases have very large half-metallic gaps (up to 0.88 eV) and are approximately 0.31–0.53 eV per formula unit higher in energy than the corresponding nickel-arsenide ground-state phases. Moreover, they are mechanically stable and harder than

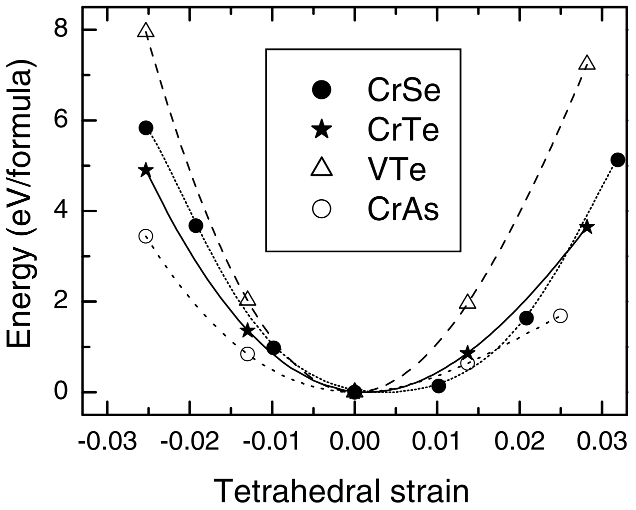

FIG. 4. Total energies of the equilibrium zincblende phases of CrSe (dotted line with solid circles), CrTe (solid line with stars), VTe (long dashed line with triangles), and CrAs (dashed line with open circles) as functions of tetrahedral strain at fixed atomic volume.

TABLE II. The predicted bulk modulus (B) and shear moduli (C' and C_{44}) of the zincblende transition-metal chalcogenides with half-metallic ferromagnetism. CrAs is presented for comparison.

Name	B (GPa)	C' (GPa)	C_{44} (GPa)
VTe	50.3	9.9	30.5
CrSe	59.5	5.6	50.7
CrTe	45.9	5.5	36.4
CrAs	71.0	5.1	46.1

the observed zincblende CrAs phase. Therefore, they would be grown epitaxially in the form of films and layers thick enough, and useful in spintronics and other applications.

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