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. Since de Groot and Fermi's discovery in 1938, a lot of half-metallic ferromagnets have been theoretically predicted and some of them have been confirmed experimentally. Much attention has been paid to understanding the mechanism behind the half-metallic magnetism and to studying its implication on various physical properties. 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 been made on the metastable zincblende (B8) phases such as the transition-metal pnictides, 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.

An accurate density-functional method is used to study systematically half-metallic ferromagnetism and stability of zincblende phases of 3d-transition-metal chalcogenides. The zincblende CrTe, CrSe, and VTe phases are found to be excellent half-metallic ferromagnets with large 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 for all our calculations. This is a full-potential (linear) augmented plane wave plus local orbitals method within the density functional theory. 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 3d-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...
The Fermi energy there exist three $\Gamma_{15}$ bands. For the minority spin bands we see that just below the Fermi energy there exist two $\Gamma_{15}$ bands. Figure 2 shows the spin-dependent total and partial DOS of the three zinclblende phases. The zinclblende phases of CrTe, CrSe, and VTe have large half-metallic gaps, 0.88, 0.61, and 0.31 eV, respectively.

The binding energy curves for CrSe, CrTe, and VTe in the zinclblende structure are shown in Figure 3. All the three zinclblende 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 even lead to 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

![Figure 1](image1.png)

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

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 $c=6.07$ Å[24, 25]. Its Neel temperature was located at 320 K by specific heat measurement[27]. There has been not 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 zinclblende CrSe, CrTe, and VTe to be 5.833, 6.292, and 6.271 Å, respectively.

Figure 1 shows the band structures of the zinclblende 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 $\Gamma_{15}$ bands which result mainly from the Te (Se) $p$ electrons, whereas just above the Fermi energy there exist two $\Gamma_{12}$ bands which comprise mainly the Cr (V) $e_g$ electrons. For the majority-spin bands, there are also three $\Gamma_{15}$ bands below the Fermi energy originating mainly from the Te (Se) $p$ electrons, but the two $\Gamma_{12}$ bands mainly of the Cr (V) $e_g$ electrons are below the Fermi energy. The bands crossing the Fermi energy are the majority-spin $\Gamma_1$ and $\Gamma_{15}$.

The three $\Gamma_{15}$ 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 DOS of the three zinclblende phases. The zinclblende phases of CrTe, CrSe, and VTe have large half-metallic gaps, 0.88, 0.61, and 0.31 eV, respectively.

![Figure 2](image2.png)

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

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 the ob-

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) | $M$ ($\mu_B$) | $E_g$ (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       |

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.
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          |

served 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.

This work is supported in parts by Chinese Department of Science and Technology under the National Key Projects of Basic Research (No. G1999064509), by Nature Science Foundation of China (No. 60021403), and by British Royal Society under a collaborating project with Chinese Academy of Sciences.

* Corresponding author.

Email address: bgliu@aphy.iphy.ac.cn

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science 294, 1488 (2001); I. S. Osborne, Science 294, 1483 (2001); D. D. Awschalom and J. M. Kikkawa, Physics Today 52, No. 6, 33 (1999).

[2] W. E. Pickett and J. S. Moodera, Physics Today 54, No. 5, 39 (2001).

[3] R. A. de Groot, F. M. Mueller, P. G. van Engen and K. H. J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).

[4] J. W. Dong, L. C. Chen, C. J. Palmstrom, R. D. James, and S. McKernan, Appl. Phys. Lett. 75, 1443 (1999).

[5] S. M. Watts, S. Wirth, S. von Molnar, A. Barry and J. M. D. Coey, Phys. Rev. B 61, 9621 (2000).

[6] F. J. Jedema, A. T. Filip, B. van Wees, Nature 410, 345 (2001); S. Soeya, J. Hayakawa, H. Takahashi, K. Ito, C. Yamamoto, A. Kida, H. Asano, and M. Matsui, Appl. Phys. Lett. 80, 823 (2002).

[7] J. M. D. Coey, M. Viret, S. von Molnár, Adv. Phys. 48, 167 (1999).

[8] T. Akimoto, Y. Moritomo, A. Nakamura, and N. Furukawa, Phys. Rev. Lett. 85, 3914 (2000); J. M. D. Coey and M. Venkatesan, J. Appl. Phys. 91, 8345 (2002); I. Galanakis, P. H. Dederichs, and P. Mavropoulos, Phys. Reb. B 66, 134428 (2002).

[9] C. M. Fang, G. A. de Wijs and R. A. de Groot, J. Appl. Phys. 91, 8340 (2002).

[10] T. Plake, M. Ramsteiner, V. M. Kaganer, B. Jenichen, M. Kästner, L. Diweritz, and K. H. Ploog, Appl. Phys. Lett. 80, 2523 (2002); S. Sugahara and M. Tanaka, Appl. Phys. Lett. 80, 1969 (2002).

[11] K. Ono, J. Okabayashi, M. Mizuguchi, M. Oshima, A. Fujimori, and H. Akinaga, J. Appl. Phys. 91, 8088 (2002).

[12] H. Akinaga, T. Manago and M. Shirai, Jpn. J. Appl. Phys. Part 2 39, L1118 (2000).

[13] M. Mizuguchi, H. Akinaga, T. Manago, K. Ono, M. Oshima, M. Shirai, M. Yurii, H. J. Lin, H. H. Hsieh, and C. T. Chen, J. Appl. Phys. 91, 7917 (2002).

[14] J. H. Zhao, F. Matsukura, E. Abe, D. Chiba, and H. Ohno, Appl. Phys. Lett. 79, 2776 (2001).

[15] P. Radhakrishna and J. W. Cable, Phys. Rev. B 54, 11940 (1996).

[16] S. Sanvito and N. A. Hill, Phys. Rev. B 62, 15553 (2000); A. Continenza, S. Picozzi, W.T. Geng and A. J. Freeman, Phys. Rev. B 64, 085204 (2001); Y. J. Zhao, W. T. Geng, A. J. Freeman and B. Delley, Phys. Rev. B 65, 113202 (2002).

[17] P. Ravindran, A. Delin, P. James, B. Johansson, J. M. Wills, R. Ahuja and O. Eriksson, Phys. Rev. B 59, 15680 (1999).

[18] M. Shirai, Physica E 10, 143 (2000); I. Galanakis, Phys. Rev. B 66, 012406 (2002).

[19] Bang-Gui Liu, cond-mat/0206485; Phys. Rev. B 67, 172411 (2003).

[20] Y.-Q. Xu, B.-G. Liu and D. G. Pettifor, Phys. Rev. B 66, 184435 (2002).

[21] P. Blaha, K. Schwarz, P. Sorantin and S. B. Trickey, Comp. Phys. Comm. 59, 399 (1990).

[22] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[23] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[24] G. I. Makovetski, Sov. Phys. Solid State 28, 447 (1986).

[25] J. Dijkstra, H. H. Weitering, C. F. van Bruggen, C. Haas and R. A. de Groot, J. Phys. CM 1, 9141 (1989); J. Dijkstra, C. F. van Bruggen, C. Haas and R. A. de Groot, J. Phys. CM 1, 9163 (1989).

[26] F. K. Lotgering and E. W. Gorter, J. Phys. Chem. Solids 3, 238 (1957); L. M. Corliss, N. Elliott, J. M. Hastings, and R. L. Sass, Phys. Rev. 122, 1402 (1961).

[27] I. Tsubokawa, J. Phys. Soc. Jpn. 15, 2243 (1960).

[28] H. Shoren, F. Ikemoto, K. Yoshida, N. Tanaka and K. Motizuki, Physica E 10, 242 (2001); I. Galanakis and P. Mavropoulos, Phys. Rev. B 67, 104417 (2003).

[29] P. J. Craievich, M. Weinert, J. M. Sanchez, and R. E. Watson, Phys. Rev. Lett. 72, 3076 (1994).