First-principles study of pressure-induced phase transition in the strongly correlated compound YCrO$_4$

Linyan Li,[1] Wen Yu,[1,2] and Changqing Jin[1,*]

[1]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
[2]*Physics Department, University of Science and Technology Beijing, Beijing 100083, China*

An accurate full-potential density-functional method is used to study zircon-type YCrO$_4$ as a function of pressure. The lattice parameters and oxygen positions of YCrO$_4$ in zircon-type and scheelite-type structures are investigated in theory. It is calculated by considering the on-site Coulomb interaction that a phase transition from the zircon phase to the scheelite phase takes place at a pressure of 2.9 GPa, which is in good agreement with the experimental observation. The bulk moduli evaluated from the Murnaghan equation as the relation of the total energies with unit cell volumes are 121.61 GPa and 141.28 GPa for the zircon phase and the scheelite phase, respectively. From the spin-dependent density of states and the energy bands, it is concluded that YCrO$_4$ is a ferromagnetic insulator with a magnetic moment of about $1\mu_B$ per formula for both phases.

I. INTRODUCTION

The phase transition of some ABX_4 compounds from the zircon-type structure to the scheelite-type structure has been studied extensively.[1–4] The magnetic properties of some RCrO$_4$ (R=Yb, Nd, Er, Tm, Sm, Dy, Eu, Lu, and Y) compounds have attracted more and more interests.[5–10] In ambient conditions, YCrO$_4$ is crystallized in a tetragonal zircon structure with space group $I41/amd$.[11–14] It has a long range ferromagnetic ordering below temperature 9.2 K.[10,13] Keitaro Tezuka *et al.* have studied the zircon-type structure of YCrO$_4$ from x-ray diffraction measurements.[14] Recently, the high-pressure properties of YCrO$_4$ have been studied through Raman scattering studies[15] and it was found that at about 3 GPa there exits a structural phase transition. It was concluded that the phase transition was from the zircon-type structure ($I41/amd$) to the scheelite-type structure ($I41/a$). In YCrO$_4$ compound, the Cr ions are of pentavalent state with one 3d electron, which has crucial effect on the magnetism. To our knowledge, there has been no theoretical study on YCrO$_4$ in the zircon-type and scheelite-type structures up to now.

In this work, we studied the structural, magnetic, and electronic properties of YCrO$_4$ in the zircon-type and scheelite-type structures by first-principles calculations. We optimized the lattice parameters and the oxygen positions. From the Murnaghan equation of state fit to the total energies as a function of the unit cell volume, we evaluated the bulk modulus and the phase transition pressure of YCrO$_4$ from the zircon phase to the scheelite phase. We investigated the spin-dependent density of states and energy bands of YCrO$_4$ in both structures.

II. COMPUTATIONAL DETAILS

All our calculations are performed using the WIEN2K package,[16] which is a full-potential linearized augmented plane waves (LAPW) method within the density functional theory (DFT).[17] From the spin-dependent density of states calculated with the generalized gradient approximation (GGA), YCrO$_4$ displays half-metallic property in zircon-type and scheelite-type structures. But from the experiment, it is an insulator.[18] These results indicate that the YCrO$_4$ compound is a strongly correlated system. So we use GGA+U method to explore the properties of YCrO$_4$. The GGA proposed in 1996 by Perdew, Burke, and Ernzerhof (PBE)[19] is adopted. The U is handled with the SIC method proposed by Anisimov *et al.*[20,21] and in this method the U is the Coulomb parameter and the J is the exchange parameter, which is zero. U is added on the Cr 3d orbital and is set to be 7.08 eV. Relativistic effects are taken into account in the scalar approximation. Muffin-tin (MT) sphere radii of 1.85, 1.65, and 1.5 bohr are used for Y, Cr, and O atoms, respectively. The valence wave functions inside the MT spheres are expanded into spherical harmonics up to l=10 and $R_{mt}K_{max}$ are taken to be 8.0. We use 1500 k points in the Brillouin zone for the zircon-type structure and 1000 k points for the scheelite-type structure. The self-consistent calculations are considered to be converged only when the integrated magnitude of the charge density difference between input and output, $\int|\rho_n(\vec{r}) - \rho_{n-1}(\vec{r})|d\vec{r}$, is less than 0.000 01. In this work, all our calculations, including the optimization and the oxygen relaxation, are performed by the GGA+U method using the same U and k points as the above.

III. RESULTS AND DISCUSSION

A. Structural properties

Figure 1 shows the zircon-type and scheelite-type structures of YCrO$_4$. It is well known that the ABO$_4$ zircon-type and scheelite-type structures are body-centered tetragonal. The B ions are tetrahedrally coordinated by O ions, but with different bond lengths and angles. The A ions are eight-coordinated by O ions. The conventional unit cells of the zircon-type (space group $I41/amd$, No. 141) and scheelite-type (space group $I41/a$, No. 88) structures contain four formula units. A primitive cell is defined to contain only two formula units. As shown in Fig. 1, the Cr positions are set to be the origins of the unit cells. The atoms in unit cell occupy
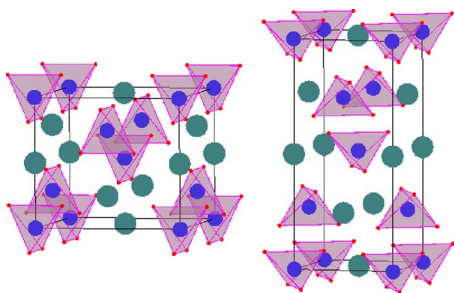
FIG. 1. (Color online) The zircon-type structure and scheelite-type structure of $YCrO_4$, highlighting the Y-O tetrahedron coordination. The left-hand side is zircon-type structure and the right-hand side is the scheelite-type structure.

the following positions: in the zircon-type structure, Y at $(0, 3/4, 1/8)$ on the $4a$ Wyckoff sites, Cr at $(0, 1/4, 3/8)$ on the $4b$ Wyckoff sites, O at $(0, y_1, z_1)$ on the $16h$ Wyckoff sites, where y_1 and z_1 are internal parameters. In the scheelite-type structure, Y at $(0, 1/4, 5/8)$ on the $4b$ Wyckoff sites, Cr at $(0, 1/4, 1/8)$ on the $4a$ Wyckoff sites, O at (x_2, y_2, z_2) on the $16f$ Wyckoff sites, where x_2, y_2, and z_2 are internal parameters.

The zero-pressure structural parameters of $YCrO_4$ in the zircon-type and the scheelite-type structures are shown in Table I. The calculated lattice parameters of zircon-type $YCrO_4$ are about 1.3% larger than the experimental results

from Ref. 14. It is known that calculations within the generalized gradient approximation (GGA) typically overestimate (0–3 %) the lattice parameters. In order to obtain the zero-pressure structural parameters, the following procedure was done; first, propose an initial unit cell Volume; second, optimize c/a ratio with the given oxygen positions; third, relax the oxygen positions with the optimized c/a; fourth, repeat the second and the third steps until the c/a ratio and the oxygen positions have no change. Fifth, with fixed c/a and oxygen positions, the corresponding energy is obtained with the volume given by the first step. By iterating the above procedure for several times, the E-V relation is formed. The optimized volume, synchronously, the zero-pressure lattice parameters, are obtained with the minimum energy and the corresponding c/a ratio and the oxygen positions are also obtained. The calculated c/a ratio is 0.8759 and 2.2325 at the optimized volume for the zircon-type structure and the scheelite-type structure, respectively. With the volume decreasing, the c/a ratio increases a little for the zircon-type structure but decreases a little for the scheelite-type structure, indicating that in the zircon-type structure the a axis is easier to be compressed than the c axis under pressure while reverse in the scheelite-type structure. But the change of c/a related to the unit cell volume is so little that it has no influence on the total energies and other properties. In the structural calculation, the nonzero value of U has almost no effect on the lattice parameters. When U equals zero, i.e., GGA method is taken, the lattice parameters of zircon phase are

TABLE I. The zero-pressure structural parameters of $YCrO_4$ in zircon-type structure and scheelite-type structure.

Structural type		Zircon	Scheelite
Lattice parameters	a(Å)	7.20995	5.07534
		7.1162(5)[a]	
	c(Å)	6.31520	11.33070
		6.2543(4)[a]	
	c/a	0.8759	2.2325
Unit cell volume	V_0(Å³)	328.28544	291.86836
Bulk modulus	B(GPa)	121.61	141.28
		139[b]	
	$B\prime$	4.54	4.49
Atomic positions	Y	$(0, 3/4, 1/8)$	$(0, 1/4, 5/8)$
	Cr	$(0, 1/4, 3/8)$	$(0, 1/4, 1/8)$
	O	$(0, 0.56609, 0.79829)$	$(0.24286, 0.60608, 0.54749)$
Bond lengths and angles	Y-O(Å)	2.330(4×)	2.357(4×)
		2.453(4×)	2.423(4×)
	Cr-O(Å)	1.719(4×)	1.734(4×)
	O-O(Å)	2.652(2×)	2.749(2×)
		2.882(4×)	2.991(4×)
	O-Cr-O(°)	100.93(2×)	119.15(2×)
		113.90(4×)	104.86(4×)

[a]Reference 14.
[b]Reference 15.
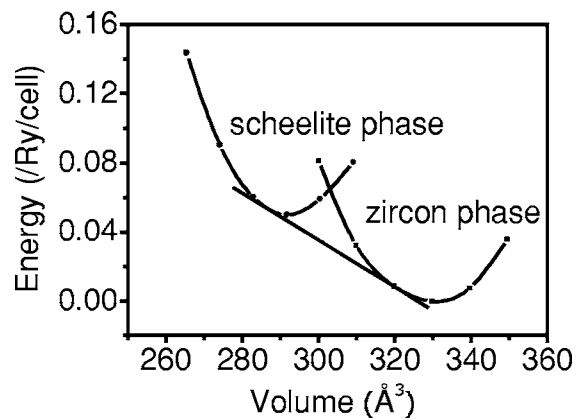
FIG. 2. Total energy as a function of unit cell volume for zircon phase and scheelite phase of $YCrO_4$.

$a=7.1775$ Å and $c=6.2867$ Å, which are about 0.5% smaller than those from $U=7.08$ eV, as listed in Table I.

B. Phase transition

The relation of the total energies with the volumes of unit cell for the zircon phase and the scheelite phase is shown in Fig. 2. The energy of the zircon phase is taken as reference value. It is well known that the structural phase transition would occur at a pressure when the Gibbs energies of the two structures are equal. On the comment tangent line of Fig. 2, the Gibbs free energies of the two phases are equal. Since all our calculations are preformed at $T=0$ K, the Gibbs free energy becomes the enthalpy $H=E+PV$, so the comment tangent line to the energy curves of the phases indicates the phase transition pressure. In this work, the bulk modulus and the phase transition pressure are evaluated from the Murnaghan equation as the relation of the total energies with unit cell volumes:

$$E = B \times \frac{V}{B'} \times \left(\frac{(V_0/V)^{B'}}{B'-1} + 1 \right),$$

$$P = \frac{B}{B'} \times \left[\left(\frac{V_0}{V} \right)^{B'} - 1 \right],$$

where V_0 is the volume at zero pressure; E is the total energy, and P is the pressure corresponding to the unit cell volume V; B is the bulk modulus and B' is the pressure derivative of bulk modulus, $B'=dB/dP$, which is assumed to be constant. The bulk moduli evaluated from the Murnaghan equation are 121.61 GPa and 141.28 GPa for zircon phase and scheelite phase and the corresponding B' are 4.54 and 4.49, respectively, as shown in Table I. Furthermore, when we use "third-order" Birch equation of state[22] these results are not changed. The bulk modulus of the scheelite phase is larger than that of the zircon phase, revealing that the scheelite phase is more difficult to compress than the zircon phase. This is reasonable since the unit cell volume of the scheelite phase is smaller than that of the zircon phase, indicating that the scheelite phase is more closely packed than the zircon phase. From the Table I, the Cr-O and O-O distances in scheelite-

type structure are larger than those in zircon-type structure, indicating the decreasing of volume is mainly from the shrinking of the voids among Y-O and Cr-O polyhedrons. The calculated phase transition pressure from the zircon phase to the scheelite phase is about 2.9 GPa, which is in good agreement with the experimental value 3 GPa.[15] In our calculations, we found that the phase transition pressure vary very little with the value of U. It is known that some other scheelite-type compounds, such as $CaWO_4$ and $SrWO_4$, can undergo a phase transition from the scheelite-type structure to the fergusonite-type structure under high pressure[23,24] The same kind of phase transition maybe occur in the $YCrO_4$ compound under much higher pressure.

C. Magnetic properties

It is known that the $YCrO_4$ compound has a long range magnetic ordering and it is ferromagnetic below temperature 9.2 K.[10,13] We calculated the total energies of $YCrO_4$ for paramagnetic and ferromagnetic configurations in the zircon-type and scheelite-type structures, respectively. From the difference of the total energies, $YCrO_4$ should be stabilized in the ferromagnetic state for both structures. For one formula of $YCrO_4$, in the zircon-type structure, the calculated magnetic moment contribution from Y, Cr, and O atoms is $0.006\,22\mu_B$, $0.977\,67\mu_B$, $-0.025\,61\mu_B$, respectively, and the interstitial contribution is $0.118\,56\mu_B$. In the scheelite-type structure, it is $0.005\,99\mu_B$, $0.980\,81\mu_B$, $-0.028\,63\mu_B$, and $0.127\,74\mu_B$, respectively. In both structures, the calculated magnetic moment per formula of $YCrO_4$ is about $1\mu_B$. It is obvious that the magnetic moment of $YCrO_4$ is mainly from the Cr^{+5} ions for both structures. In the $YCrO_4$ compound, the Y ion is trivalent and its outer-shell electronic configuration is $4d^05s^0$ and so the Y^{+3} ions have little contribution to the total magnetic moment of $YCrO_4$ because of no d electrons in the outer shell. However the Cr ion in $YCrO_4$ is of pentavalent state and its outer-shell electronic configuration is $3d^14s^0$. In such case, the magnetic Cr^{+5} ions play a dominant role in determining the overall magnetic moment. The saturated moment of Cr^{+5} ions is $1\mu_B$ if there is no covalent effect in the Cr-O bond. The calculated magnetic moment of Cr^{+5} ions of $YCrO_4$ in zircon-type structure and scheelite-
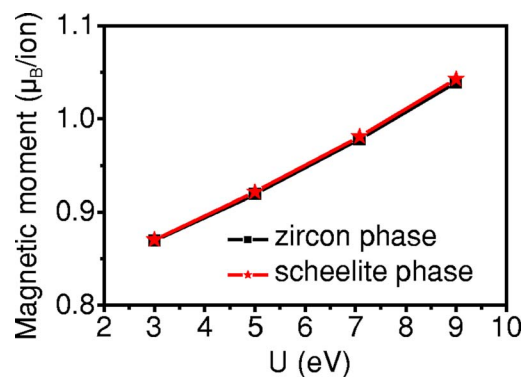

FIG. 3. (Color online) The magnetic moment of Cr^{+5} ions in zircon phase and scheelite phase of $YCrO_4$ with different values of U.
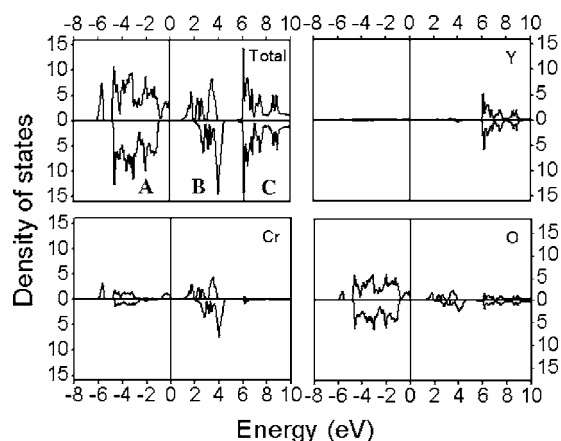
FIG. 4. Total and partial spin-dependent density of states of $YCrO_4$ in the zircon-type structure (space group $I41/amd$, No. 141).

type structure is $0.977\,67\mu_B$ and $0.980\,81\mu_B$, respectively, which is nearly equal to the saturated moment $1\mu_B$. In the two structures, the magnetic moments of O^{-2} ions, which are induced local magnetic moments, are negative and this result can be understood as follows: there is some hybridization from the majority p states of O^{-2} ions with the majority d states of Cr^{+5} ions and more are shared with the d atoms, whereas the minority p states of O^{-2} ions are more localized; this results in opposite magnetic moments of the O^{-2} ions. In addition, the interstitial contribution to the total magnetic moment comes from the valence electrons, which are not included in the muffin tins. Since the total magnetic moments of $YCrO_4$ for both structures are mainly from the Cr ions, we studied the relation of the magnetic moment of Cr ions with U, as shown in Fig. 3. When U equals to 9.0 eV, the magnetic moment of one Cr^{+5} ion is more than $1\mu_B$, which is an unreasonable value.

In order to know whether the magnetic moment of $YCrO_4$ varies under higher pressure, we calculated the magnetic moment of scheelite-type $YCrO_4$ under about 17 GPa and found that the total and atomic magnetic moments per formula are the same with those of zero-pressure scheelite-type $YCrO_4$. We concluded that the magnetic properties of $YCrO_4$ in
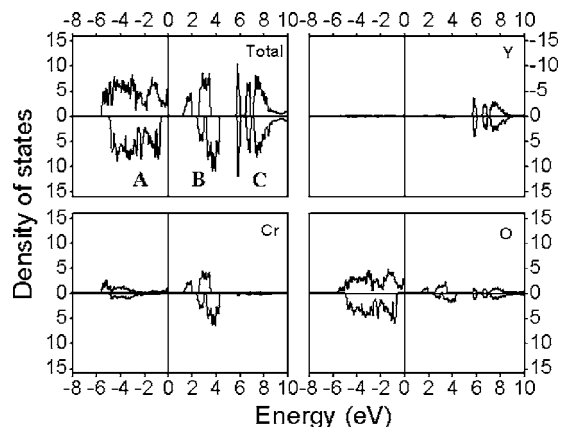

FIG. 5. Total and partial spin-dependent density of states of $YCrO_4$ in the scheelite-type structure (space group $I41/a$, No. 88).

zircon-type and scheelite-type structures are not sensitive to pressure at least to 17 GPa and the magnetic moment is determined by the Cr^{+5} ions.

D. Electronic properties

The experiment shows that $YCrO_4$ is an insulator.[18] We use GGA+U method and the U is set to be 7.08 eV to calculate the electronic structures. The spin-dependent density of states of the zircon-type and the scheelite-type structures are shown in Figs. 3 and 4, respectively. The Fermi level is located at $E=0$. There are energy gaps near the Fermi level for majority spin and minority spin of both structures, indicating that $YCrO_4$ is an insulator. Partial density of states is very important to study the bonding of the compounds. In Figs. 4 and 5, the energy ranges are divided into three parts labeled A, B, and C. The Y states are mainly located at the C part, which is far from the Fermi level and has little effect on the electronic properties. Most of the Cr states are located at the B part near the Fermi level, dominating the bottom of the conduction band and some are located at the A part, contributing to the valence band. The O states are mainly distributed at A part and dominate the character of the valence bands. As a whole, the O states distributed in the total energy range, indicating that the O ions have some hybridization with the Cr ions and Y ions.

The spin-dependent energy bands of $YCrO_4$ in the zircon-type and scheelite-type structures are presented in Figs. 6 and
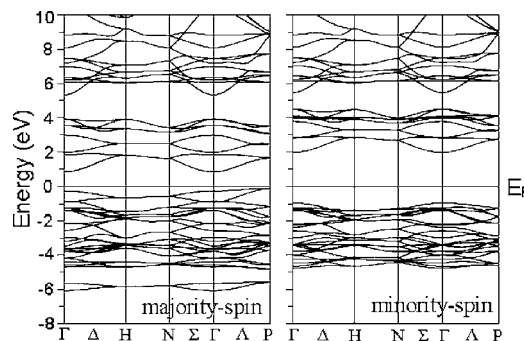

FIG. 6. Spin-dependent energy bands of $YCrO_4$ in the zircon-type structure. The left-hand panel is for majority-spin and the right-hand panel for minority spin.
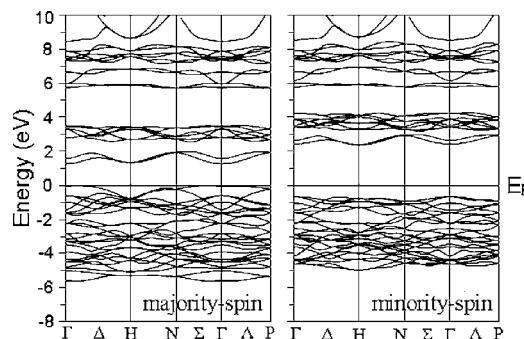

FIG. 7. Spin-dependent energy bands of $YCrO_4$ in the scheelite-type structure. The left-hand panel is for majority-spin and the right-hand panel for minority spin.

TABLE II. The spin-dependent energy gaps of $YCrO_4$ in zircon-type structure and scheelite-type structure.

	Majority spin (eV)	Minority spin (eV)
Zircon	0.93834	2.93783
Scheelite	1.26201	3.02223

7. The spin-dependent energy gaps of both structures are shown in Table II. In the zircon-type structure, for majority spin there is an indirect band gap of 0.938 34 eV with the maximum of the valence band at the Λ direction and the minimum of the conduction band at the Γ point; for minority spin there is a direct band gap of 2.937 83 eV with the maximum of the valence band and the minimum of the conduction band at the Γ point. In the scheelite-type structure, for majority spin there is an indirect band gap of 1.262 01 eV with the maximum of the valence band at the Σ direction and the minimum of the conduction band at the Γ point; for minority spin there is an indirect band gap of 3.022 23 eV with the maximum of the valence band at the Γ point and the minimum of the conduction band at the H point. In the calculation, we found that the energy gaps have direct relation with the U value, as shown in Fig. 8. When U is 3.0 eV, the minority spin of zircon phase is insulator but the majority spin is metallic, indicating the half-metallic nature of zircon $YCrO_4$. In fact, $YCrO_4$ is an insulator from experiment.[18] When U is 5.0 eV, the gap of zircon phase is so small that it is easy to become half-metallic under high pressure. When U is 7.08 eV and 9.0 eV, the corresponding differences of the respective energy gaps are not large. In Sec. III C, we have reported that the magnetic moment is unreasonable when U equals to 9.0 eV. Based on these results, we think the value of U taken in all our calculations, 7.08 eV, is reasonable. Actually, the value of U can be more accurately adjusted to fit the measured energy gaps when some optical or photo-emission experiments are performed later.
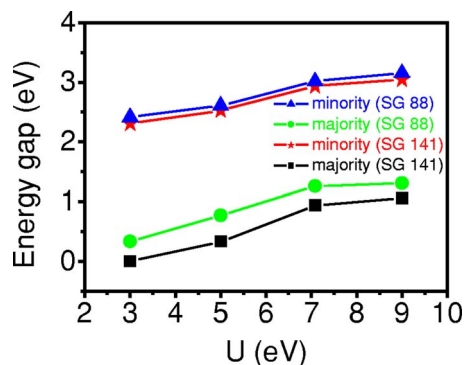

FIG. 8. (Color online) The energy gaps of $YCrO_4$ in zircon phase and scheelite phase with different values of U.

IV. CONCLUSION

We have investigated the structural properties, magnetic properties, and electronic properties of $YCrO_4$ in the zircon-type and scheelite-type structures using first-principles method. The lattice parameters and the oxygen positions of $YCrO_4$ in both structures are studied in theory. With the Murnaghan equation, the evaluated phase transition pressure from the zircon phase to the scheelite phase is about 2.9 GPa, which is consistent with the experiment value 3 GPa. The calculated bulk moduli are 121.61 GPa for the zircon phase and 141.28 GPa for the scheelite phase. From the spin-dependent density of states and energy bands, $YCrO_4$ is a ferromagnetic insulator for both phases. The magnetic moment of $YCrO_4$ per formula is about $1\mu_B$ for both phases and the Cr^{+5} ions play a dominant role in determining the total magnetic moment.

*Electronic address: jin@aphy.iphy.ac.cn

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