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Magnetic moment collapse induced axial alternative compressibility of $\text{Cr}_2\text{TiAlC}_2$ at 420 GPa from first principle

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The electronic structure and thermodynamical properties of $\text{Cr}_2\text{TiAlC}_2$ are studied by first principles under pressure. The obtained results observed that the ferromagnetic order is the most stable ground state and the magnetic moment will collapse at about 50 GPa. As a result, the lattice a axis becomes stiffer above about 420 GPa, ultimately presenting the same axial compressibility trends with those of nonmagnetic compounds $\text{Mo}_2\text{TiAlC}_2$ and hypothetical $\text{Cr}_2\text{TiAlC}_2$. The elastic constants and phonon dispersion curves demonstrate the structural stability during the disappearance of magnetic moment and occurrence of axial alternative compressibility. The density of states and energy band calculations confirmed the existence of magnetic moment of $\text{Cr}_2\text{TiAlC}_2$ at 0 GPa and disappearance at high pressures above 50 GPa. Evolutions of magnetic moment collapse with pressure are confirmed by a variety of properties. The obtained Grüneisen parameter and thermal expansion coefficients show the maximum value among the known MAX phases, to date and to the author's knowledge.

The $\text{M}_{n+1}\text{AX}_n$ ($n = 1, 2, 3$, etc) belongs to nanolaminate crystal, in which M and A are transition and A-group elements, and X is C/N. MAX phases combine the advantages of metal and ceramics and thus present many excellent properties in the field of mechanics and thermodynamics. Many such crystals could be formed by substituting the Ti atoms to those unavailable structures at ambient conditions, such as $\text{Cr}_2\text{TiAlC}_2$ ¹, $(\text{Ti}_{2.5}\text{Nb}_{2.5})\text{AlC}_4$ ², $(\text{Cr}_{1.5}\text{Ti}_{2.5})\text{AlC}_3$ ³, $(\text{Ti}_{1-x}\text{Nb}_x)_2\text{AlC}$ ($x = 0 \sim 1.0$)⁴, $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}_5$ ($x = 0 \sim 1.0$), $\text{Mo}_2\text{TiAlC}_2$ ⁶ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ ⁷.

Formation energy⁸ computations on some titanium-doping stabilized structures confirm that the energy levels of Al/C species moving towards smaller-energy direction should be responsible for the synthesis of $\text{Mo}_2\text{TiAlC}_2$. Similarly, the novel $\text{Cr}_2\text{TiAlC}_2$ might also exist special properties. The possible origin⁹ of the Ti dopant stabilized Mo_3AlC_2 is explored, the introduced Ti atom presents smaller relative intensity at Fermi level in comparison with that of Mo atom, whereas the calculated energy levels of Al/C species immigrate to higher-energy side which should give negative contribution to the crystal stability. Despite the Ti-doping stabilized compounds have been studied by the density of states, the detailed bonding processes are still unclear, in particular at higher pressure.

Stimulated by the novel role of Ti doping stabilized nonmagnetic $\text{Mo}_2\text{TiAlC}_2$ ⁹, it is deservable to reveal the structural evolution of the similar magnetic compound $\text{Cr}_2\text{TiAlC}_2$. We therefore perform a systematical investigation to the newly synthesized $\text{Cr}_2\text{TiAlC}_2$ to determine its magnetically-related properties. First principles are accurate tool in the electronic structure calculations^{10–21}.

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Figure 1. Axial compressibilities of a , c , and volumetric shrinkage (inserted) of NM/FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$, where x represents a , c , and v at any pressures, x_0 represents a , c , and v at zero pressure. The other two inserted small figures mean the shift trends of internal coordinate u with pressure, where u_0 means the value u at 0 GPa for NM $\text{Mo}_2\text{TiAlC}_2$, NM/FM $\text{Cr}_2\text{TiAlC}_2$.

Computational Methods

The geometric relaxation is completed by the Vanderbilt-type²² ultrasoft pseudopotential with a generalized gradient approximation of Perdew–Burke–Ernzerh (GGA/PBE²³) function. A 350.0 eV energy cut-off is used for the wavefunction computation, and the k -point is defined using $10 \times 10 \times 2$ Monkhorst-Pack mesh^{24,25}. Electronic configuration simulations are carried out for Cr $3s^2 3p^6 3d^5 4s^1$, Ti $3s^2 3p^6 3d^2 4s^2$, Al $3s^2 3p^1$, and C $2s^2 2p^2$, respectively. The energetic iteration criterion is 5.0×10^{-7} eV/atom. All the simulations were finished by CASTEP²⁶.

Results and Discussion

Structural properties. Previous investigations for Cr_2AlC , Cr_2GaC , and Cr_2GeC ²⁷ demonstrated these Cr-containing MAX compounds are weak correlated materials, if applicable it should be $U < 1$ eV and therefore it is unnecessary to use LDA + U method (localized density approximation), our detailed test calculations for its usability are shown in Table S1. The atomic arrangement and Brillouin zone (BZ) orientation of $\text{Cr}_2\text{TiAlC}_2$ are same⁹ with that of $\text{Mo}_2\text{TiAlC}_2$. Therefore, several collinear magnetic configurations of $\text{Cr}_2\text{TiAlC}_2$ are considered to search for its ground state, including non-magnetic (NM), ferromagnetic (FM), various antiferromagnetic (AFM), and two in-plane AFM, in which no correlation effect of the Cr d electrons is applied. These magnetic orders are same¹³ with that of Mo_2GaC , we here ignore the schematic illustrations for simplicity. Relative to the minimum energy of the NM unit cell, the comparison for all the considered magnetic states of $\text{Cr}_2\text{TiAlC}_2$ is presented in Figure S1. With the results of Table S2 and Figure S1, it is reasonable to consider FM configuration as the ground phase, consisting with the theoretical calculations¹.

The space group of FM $\text{Cr}_2\text{TiAlC}_2$ is $P6_3/mmc$ with twelve atoms per unit cell constituting of two formula units, the atomic coordinate is: $(2/3, 1/3, u)$ of Cr, $(0, 0, 0)$ of Ti, $(0, 0, 1/4)$ of Al, $(1/3, 2/3, v)$ of C. The obtained structural constants are: $a = b = 2.9392 \text{ \AA}$, $c = 17.8341 \text{ \AA}$, $u = 0.130617$, $v = 0.074795$, consistent with the experimental data $(2.906, 2.9139, 17.803, 17.805 \text{ \AA}, 0.13095, 0.07501)^1$, $(2.921, 2.91, 17.878, 18.56 \text{ \AA})^3$.

Usually, the contraction of c axis under pressure is faster than that of a axis, such as NM $\text{Mo}_2\text{TiAlC}_2$ ⁹, whereas our simulations observe that the compressibility along a axis is faster than that of c axis within 0–420 GPa in FM $\text{Cr}_2\text{TiAlC}_2$. Interestingly, an alternative case occurs with pressure continuous increasing, as is shown in Fig. 1. For comparison purpose we also simulate the structural evolution for the hypothetical NM $\text{Cr}_2\text{TiAlC}_2$ and find that the two axial compressibilities are almost identical below about 100 GPa, henceforth the stiffer a axis occurs. The detailed structural evolutions for FM/NM $\text{Cr}_2\text{TiAlC}_2$, and NM $\text{Mo}_2\text{TiAlC}_2$ are shown in Table S3. The rapidest shift of Cr atom in FM $\text{Cr}_2\text{TiAlC}_2$ among the three compounds might resist the c -axis contraction. The NM $\text{Cr}_2\text{TiAlC}_2$ present almost identical c -axis contractions with that of NM $\text{Mo}_2\text{TiAlC}_2$, the slightly larger a -axis compressibility of NM $\text{Cr}_2\text{TiAlC}_2$ might originates from its smaller atomic radials. The magnetic moment definitely decelerates the c -axis but accelerates the a -axis contractions in FM $\text{Cr}_2\text{TiAlC}_2$ in comparison with those of NM $\text{Cr}_2\text{TiAlC}_2$. In addition, the volumetric compressibility of NM $\text{Mo}_2\text{TiAlC}_2$ is evidently smaller than that of NM $\text{Cr}_2\text{TiAlC}_2$ due probably to the larger Mo radius, the largest volumetric compressibility of FM $\text{Cr}_2\text{TiAlC}_2$ due mainly to the fact of its easily compressed a axis.

Our calculated elastic constants are listed in Figs 2 and S2. Using the stability criteria²⁸, i.e.

$$C_{12} > 0, C_{33} > 0, (C_{11} - C_{12})/2 > 0, C_{44} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \quad (1)$$

It is found that FM $\text{Cr}_2\text{TiAlC}_2$ is mechanical stable up to 500 GPa. To confirm this conclusion, we calculate the phonon spectra at 0, 420, and 500 GPa by the finite displacement method using a cutoff radius of 5 Å with a supercell volume of 16 times larger than the unit cell under the same precision settings with that of geometrical relaxation, as is shown in Figure S3. The results indicate that FM $\text{Cr}_2\text{TiAlC}_2$ is dynamic stable within 0–500 GPa.

Figure 2. Elastic constants c_{ij} and mechanical moduli consisting of bulk modulus (B), shear modulus (G), Lamé coefficients (Lame), and axial Young's moduli ($E_{x,y}$, E_z) of NM/FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$, respectively.

Figure 3. Magnetic moment evolution of FM $\text{Cr}_2\text{TiAlC}_2$ and AFM Cr_2AlC per unit cell. The Spin Density is the sum of spin-up plus spin-down, whereas the $|\text{Spin Density}|$ is the sum of each absolute value of $|\text{spin-up}|$ and $|\text{spin-down}|$.

The calculated elastic constants of FM/NM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$ ⁹ are shown in Fig. 2, in which the discrepancy between the FM/NM $\text{Cr}_2\text{TiAlC}_2$ tends to zero with pressure increasing to about 40 GPa, suggesting that the magnetic moment are totally collapsed.

Previous calculations for Cr_2GeC ²⁹ observed a magnetic moment collapse phenomenon at about 25 GPa, which is far smaller than the present 50 GPa, indicating that the Ti atom probably resists the collapse process and therefore could stabilize the lattice⁹, as is shown in Fig. 3. In addition, it is about 40 GPa in Cr_2AlC from our simulations. The difficult collapse evolution possibly means the existence of more complex intermediate transition

magnetic configurations. This magnetic transition (from FM to NM) of $\text{Cr}_2\text{TiAlC}_2$ should be the internal driven force of axial alternative compressibility at about 420 GPa.

Previous measurements^{30,31} confirmed that Cr_2GeC and Cr_2AlC exist net magnetic moments and the magnitudes nearly vanish at about 100 K, whereas the crude estimation of the magnetic moment of per Cr atom is $0.05^{30}/0.02^{31} \mu_B$ in Cr_2AlC and $0.02^{30} \mu_B$ in Cr_2GeC , far smaller than available calculations such as FM $\text{Cr}_2\text{AlC}^{32}$ ($0.9 \mu_B$ at $U = 1.95$ and $2.5 \mu_B$ at $U = 2.95$), AFM $\text{Cr}_2\text{AlC}^{33}$ ($0.7 \mu_B$), AFM $\text{Cr}_2\text{GeC}^{34}$ ($1.4 \mu_B$). However other measurement³⁵ for AFM Cr_2AlC obtained a value of $0.64 \mu_B$. Our computed sum of the absolute magnetic moment of spin-up and spin-down directions is $5.3749 \mu_B$ in AFM Cr_2AlC in one unit cell (four Cr atoms, $0.6719 \mu_B$ per Cr atom), consisting well with previous calculations²⁷, in particular with the calculations FM $\text{Cr}_2\text{AlC}^{36}$ ($0.7 \mu_B$), $\text{Cr}_2\text{AlC}^{27}$ ($0.7 \mu_B$ at $U = 0$ eV), $\text{Cr}_2\text{GaC}^{37}$ ($0.75 \mu_B$). A value of about $0.8 \mu_B$ is observed in present FM $\text{Cr}_2\text{TiAlC}_2$. The difference between the present FM $\text{Cr}_2\text{TiAlC}_2$ and AFM Cr_2AlC is about $0.13 \mu_B$, whereas they are nearly identical in a recent calculation³⁸, with values of $0.99 \mu_B$ in FM $\text{Cr}_2\text{TiAlC}_2$ and $1.0 \mu_B$ in AFM Cr_2AlC , respectively. The slab of Ti-C between the two nearest Cr_2AlC stack blocks in unit cell of $\text{Cr}_2\text{TiAlC}_2$ possibly affect the atomic moment as the Ti atom could strongly stabilize the unavailable Cr_3AlC_2 ³⁹.

The calculated bond length compressibility and bond population of FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$ are shown in Figures S4 and 5, through which a clear correlation between the bond population of Al-Cr and *a*-axis stiffening above 420 GPa is undoubtedly seen. The abnormal increase of bond population in Al-Cr bond above 420 GPa means that the antibonding interaction becomes stronger again after it approaches the first local minimum.

Electronic properties. The bond populations of C-Cr are $1.35 e$ at 0 GPa and $1.01 e$ at 500 GPa in FM $\text{Cr}_2\text{TiAlC}_2$, which are always larger than those of C-Mo in NM $\text{Mo}_2\text{TiAlC}_2$, with individual values of $1.21 e$ at 0 GPa and $0.79 e$ at 500 GPa, revealing stronger covalent bonding of C-Cr and its degree of covalence decreases with pressure. The value of strong C-Cr bond is apparently larger than that of diamond ($1.08 e$)⁴⁰ at ambient conditions, meaning the extreme stability of the lattice.

The respective bond populations of C-Ti are $0.65 e$ at 0 GPa and $-0.15 e$ at 500 GPa in FM $\text{Cr}_2\text{TiAlC}_2$, which are always smaller than those of counterparts of C-Ti in NM $\text{Mo}_2\text{TiAlC}_2$, with individual values of $0.76 e$ at 0 GPa and $0.32 e$ at 500 GPa. Both the C-Ti bonds, belonged respectively to the FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$, present smaller bond populations than their respective C-Cr and C-Mo bonds, showing the smaller covalence and larger ionicity within a large pressure range.

The bond population of Al-Cr are $0.41 e$ at 0 GPa and $-2.6 e$ at 500 GPa in FM $\text{Cr}_2\text{TiAlC}_2$, whereas the values of Al-Mo are $0.4 e$ at 0 GPa and $-2.23 e$ at 500 GPa in NM $\text{Mo}_2\text{TiAlC}_2$, the critical pressures of Al-Cr and Al-Mo are about 50 and 70 GPa from positive to negative values, respectively, which means that the electronic transition from bonding to antibonding states. Conclusively, a harder ‘M-X’ and softer ‘M-A’ bond in M_3AX_2 phase appears. After substitution of one Mo by one Ti from the four corners of the in-plane sites, the reduction of bond population are $0.7 e$ from C-Cr to C-Ti in FM $\text{Cr}_2\text{TiAlC}_2$ and $0.45 e$ in NM $\text{Mo}_2\text{TiAlC}_2$, reduced from C-Mo to C-Ti. These large reductions might benefit the stabilization of unavailable Cr_3AlC_2 ³⁹ through substitution doping of Ti atom. Analysis to the bond population variations of Cr-Ti detects an antibonding state interaction at 0 GPa and the degree of interaction increases with pressure, whereas such interaction caused a stiffest bond in FM $\text{Cr}_2\text{TiAlC}_2$, with lowest contraction within the four bonds.

To deep understand the axial compressibility of FM $\text{Cr}_2\text{TiAlC}_2$, we systematically studied the bond rotation angle variations under pressure and the obtained results are shown in Table S4. Apart from the contributions of the bond nature to the axial compressibility, the number of bonds rotating towards orientation with increasingly larger projection angle to the *ab* plane is also more than the cases of opposite rotations, *i.e.*, three (C-Cr, C-Ti, and Cr-Ti) versus one (Al-Cr). The three rotations contribute larger to *c* axis than to *a* axis. Owing to the rapid immigration of Cr atom along *c* axis, all of the four bonds rotate far larger angles in FM $\text{Cr}_2\text{TiAlC}_2$ than those of NM $\text{Mo}_2\text{TiAlC}_2$, particularly for the low pressure range below 50 GPa. These behaviors might be one reasonable explanation to the stiffer *c* axis of FM $\text{Cr}_2\text{TiAlC}_2$ at low pressure.

For understanding the chemical bonding of FM $\text{Cr}_2\text{TiAlC}_2$, we calculate the band structure and density of states (DOS) at 0 and 50 GPa, respectively, comprising of spin-up (alpha) and spin-down (beta) components, as is seen in Figs 4 and 5. These spin-up/down levels shift their profiles towards higher/lower-energy sides as a whole. However, as far as the orbitals with energies crossing the Fermi level are concerned, the average covered energy ranges (the broadened width of each orbital) of all the spin-down orbitals decrease with pressure below about 50 GPa firstly and increase with pressure above 50 GPa subsequently, as is shown in Figure S6, which also provides correlation to the magnetic moment collapse behavior at about 50 GPa. Still, the minimum range of average covered beta orbital approximately equals to the energy threshold of alpha orbital at 0 GPa. In addition, the variation slopes of the two different curves present synchrotron responses to the external compression below 50 GPa, explaining the existence of magnetic moment below 50 GPa. The two values ultimately become equal to each other at 500 GPa, demonstrating the fact that driving the spin orbital overlap is extremely difficult. This is also the reason why the axial alternative compressibility happens at extreme high pressure (about 420 GPa) other than at about 50 GPa.

To explore the shift trend of the whole beta orbitals under pressure, we further test all of the orbitals crossing the Fermi level, as is shown in Figure S7. As expected, the Cr *3d* dominant orbitals present substantial discrepancies between alpha and beta spin orbitals at 0 GPa, whereas such discrepancies are rapidly reduced under pressure. Their contrary shift tendencies illustrated the energy evolution shown in Figure S6.

Both the t_{2g} and e_g states are half-filled, whereas the low-spin states provide six more unoccupied orbitals and high-spin states fill in five more valence orbitals and therefore they provide the net magnetic to the system. Analysis to all the orbitals observed that the low-lying energy levels are contributed mainly by Cr *3d* (t_{2g}) states in the vicinity of Fermi level, whereas the high-lying energy levels are composed mainly by Cr *3d* (e_g). Energy levels

Figure 4. Electron density of states of of FM $\text{Cr}_2\text{TiAlC}_2$ at 0 GPa.

Figure 5. Electron density of states of of FM $\text{Cr}_2\text{TiAlC}_2$ at 50 GPa.

crossing Fermi level present highly hybridized characters. Energy levels sited in the conduction band are contributed mainly by Cr $3d$ (e_g) and Ti $3d$ (e_g) states. These distributions consist with the bond population features shown in Figure S5 such as the antibonding Cr-Ti population.

The values (per unit cell) of the spin-up DOS at Fermi level are 4.74, 4.27, 3.51, 1.08 states/eV for 0, 20, 50, and 500 GPa, respectively. The correspondent values of spin-down counterparts are -2.41 , -2.73 , -3.39 , and -1.08 states/eV. The total DOS value⁹ is 5.58 states/eV at 0 GPa in NM $\text{Mo}_2\text{TiAlC}_2$, far smaller than the current 7.15 states/eV of FM $\text{Cr}_2\text{TiAlC}_2$, denoting the significant influence of magnetic moment. In Figure S8, the energy band of FM $\text{Cr}_2\text{TiAlC}_2$, particularly for its spin-up components, present similar metallic and energy-level features with that of NM $\text{Mo}_2\text{TiAlC}_2$ at 0 GPa⁹, indicating the possibility of whole disappearance of the magnetic influence under pressure.

Electron density difference (EDD) shown in Fig. 6 correlates well with that of Mulliken charge variations. C atom gains charges ($-0.59 e$) mainly from Ti ($0.81 e$) and Al ($0.32 e$) atoms, respectively. Moreover, Cr atom loses its minor charges ($0.03 e$) at ambient conditions in FM $\text{Cr}_2\text{TiAlC}_2$. However the number of charges in C atoms keeps almost unchanged even under higher pressure, which is important to sustain the extensive stability of C-Cr and C-Ti bond populations under pressure. The Al atoms lose its charge firstly and gain charge from others subsequently under pressure, which is just contrary with that of Cr atom, whereas Ti atoms monotonically lose its charges with pressure. These charge transfer direction forms significantly larger bond populations along Al-Cr orientation and relatively small values along C-related bonds including C-Cr and C-Ti, which probably means the strong charge saturation of C atoms.

Electron localization function (ELF) generally reflects the general and total orbital bonding features and the charge transfer trends as well as the atomic charge distributions, as is shown in Fig. 7. The C atom attracts substantial charges around it and builds polarized bonding along C-Cr direction with ionic dominance and partial covalent participation character. At pressures below 50 GPa, the charge distributions of Cr d states present strong anisotropy feature, whereas such feature rapidly decreased under pressure, indicating the strong hybridization of Cr d states. Moreover, the partial-filling feature of Cr d states is undoubtedly shown, such as the prominent t_{2g} (d_{xy}) at low pressure and e_g (d_{z^2}) at high pressure. However, less Mo $3d$ orbital feature is discernible⁹ in NM

Figure 6. Electron density difference (EDD) of FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$ with color range of $-0.4 \sim 0.15$ and starts from blue to green and red in turn. The horizontal axes x or y represent lattice a or b directions, vertical axis z means c direction.

$\text{Mo}_2\text{TiAlC}_2$ at any pressures. Al (Ti) presents similar variations under pressure with its counterpart in the two compounds FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$.

Under pressure, the giant reduction of ELF value in NM $\text{Mo}_2\text{TiAlC}_2$ ⁹ means the weakening of bonding at 20 GPa. With pressure continuous increasing, the inter-atomic bonding of NM $\text{Mo}_2\text{TiAlC}_2$ behaves similar variations with those of FM $\text{Cr}_2\text{TiAlC}_2$. The large electron localization could be seen in the region between adjacent atoms in NM $\text{Mo}_2\text{TiAlC}_2$, indicative of nearly completely filled and slightly stronger covalent bonding, consisting well with its relatively larger mechanical quantities. Both FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$ show similar polarized bonding features with directional orientations around the C atoms at high pressure, which means the anisotropic bonding characters and different chemical bonding styles. The small ELF value between C and Cr and the nearly spherically symmetry distribution of Cr sites in FM $\text{Cr}_2\text{TiAlC}_2$ demonstrate the mixture bonding character. A directional bonding between Cr and Al is polarized towards the Cr sites judged from an arc shape. There is a maximum value between C and Ti, indicative of covalent bonding. The nearly square distribution around C means its partially ionic constitutions. In addition, a predominantly antibonding orbital along Cr-Ti is built.

The calculated Fermi surfaces (FS) of orbitals crossing Fermi level are shown in Figure S9. The FS evolution provides a direct evidence for the magnetic moment collapse under pressure. Alpha orbitals with higher energies locate at nearer distance from the center of the Brillouin zone (BZ), whereas beta orbitals with higher energies locate at farer distance from the center of BZ. In particular, the spatial orientations of the alpha and beta orbitals are extremely different. This is the typical anisotropy of the energy level distribution features, meaning the existence of the residual net magnetic moment.

The whole FS profiles of orbitals 51 and 52 are shifted to first BZ at 20 GPa. Meanwhile, the higher energy of the orbital exists, the nearer distance of its FS to the center of the first BZ will be, which is just contrary to the case of beta spin at 0 GPa. Orbitals 49 and 50, with beta spin belonging to higher-energy orbitals in comparison with the other orbitals crossing Fermi level, site farer from the center of the first BZ relative to the other ones at 0 GPa, whereas they transform to the lower-energy orbitals with same orbital sites at 20 GPa, meaning the huge shift of the beta orbital towards lower-energy side under 20 GPa. Such orbital energy shift is about 0.6 eV, far larger than the case of alpha orbital which shows a global shift of about 0.2 eV towards higher-energy side. The just opposite shift tendencies will cause more overlap between them and ultimately induce them are totally overlapped at 500 GPa. Despite the magnetic moment has already been disappeared at 50 GPa, the orbital energies and the FS profiles are not totally merged, still existing an energy discrepancy of about 0.1 eV between the different spin orbitals.

Elastic properties. The small c_{33} means that the c -axis direction is relatively soft, which is partially inconsistent with the axial compressibility. An evident dip of c_{33} corresponds to the c -axis softening above 420 GPa in FM $\text{Cr}_2\text{TiAlC}_2$, as is shown in Figure S2. Anisotropic parameter $A = c_{33}/c_{11}$, $A = 1$, denoting isotropic crystal, any ratio higher or lower than 1 means an elastic anisotropy. The obtained A are 1.1671 at 0 GPa and 0.9978 at 500 GPa, respectively. The

Figure 7. Electron localization function (ELF) of FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$, with color range of 0–0.03 and starts from blue to green and red in turn. With deep blue signifying one extreme of almost no localization (nearly free electrons) and red signifying regions where electrons are completely localized. The horizontal axes x or y represent lattice a or b directions, vertical axis z means c direction.

Figure 8. The pressure dependences of the anisotropic factor A , A_1 and A_2 .

judgment of the anisotropy in shear is obtained by $A_1 = 2c_{44}/(c_{11} - c_{12})$. When $c_{44}/c_s = 1$, a crystal is isotropic. The FM $\text{Cr}_2\text{TiAlC}_2$ presents anisotropic nature at 0 GPa, whereas the degree of anisotropy decreases with pressure, with results of 0.4259 at 0 GPa and 1.2231 at 500 GPa, respectively. Another shear anisotropy ratio is $A_2 = (c_{11} + c_{33} - 2c_{13})/4c_{44}$, a crystal is isotropic when $A_2 = 1$. The variation range of A_2 is 0.9803–0.3822 within 0–500 GPa in FM $\text{Cr}_2\text{TiAlC}_2$. The detailed variation trends are shown in Fig. 8 and S10, in which an evident critical point is clearly seen at about 50 GPa. A behaves oscillation phenomenon within 0.9–1 in the pressure range 50–500 GPa, which is different with the other two shear anisotropic factors. In comparison with the cases of NM $\text{Mo}_2\text{TiAlC}_2$, all of the three factors of FM $\text{Cr}_2\text{TiAlC}_2$ behave significant variations at low pressures below about 40 GPa.

For covalent and ionic compounds, the relationships between bulk (B) and shear (G) moduli are $G \approx 1.1B$ and $G \approx 0.6B$, respectively. For FM $\text{Cr}_2\text{TiAlC}_2$ the simulated values of G/B are 0.8643 at 0 GPa, 0.4576 at 100 GPa, and 0.2977 at 500 GPa, respectively, indicating that the mixed bonding is suitable for FM $\text{Cr}_2\text{TiAlC}_2$ at 0 GPa and the degree of ionicity increases with pressure. All of these values are larger than their counterparts in NM $\text{Mo}_2\text{TiAlC}_2$, corresponding to 0.715 at 0 GPa and 0.403 at 100 GPa, respectively⁹. However, the comparable values of 0.5146 in NM $\text{Mo}_2\text{TiAlC}_2$ ⁹ and 0.5187 in FM $\text{Cr}_2\text{TiAlC}_2$ at 50 GPa mean that the pressure could effectively tune the chemical bonds of magnetic materials.

Pugh *et al.* use the B/G ratio⁴¹ to estimate crystal ductility (<0.57) or brittleness (<1.75). The FM $\text{Cr}_2\text{TiAlC}_2$ is brittle ($G/B = 0.8643$) at 0 GPa, and the degree of brittleness increases with pressure, such as the values are 0.4576 at 100 GPa and 0.2977 at 500 GPa, respectively. However those values are 0.715 at 0 GPa and 0.4031 at 100 GPa in NM $\text{Mo}_2\text{TiAlC}_2$ ⁹, demonstrating that the FM $\text{Cr}_2\text{TiAlC}_2$ is more brittleness owing to the appearance of the magnetic moment. Moreover, the current B/C_{44} is 1.2068, which is also slightly smaller than that of 1.44⁹ of NM $\text{Mo}_2\text{TiAlC}_2$ but just within the range (1.2–1.7) of $\text{M}_{n+1}\text{AX}_n$ phases.

The Poisson's ratios are 0.1634 (0 GPa), 0.3015 (100 GPa), and 0.3646 (500 GPa) in FM $\text{Cr}_2\text{TiAlC}_2$, respectively, far smaller⁹ than those of 0.2667 (0 GPa) and 0.3423 (100 GPa) in NM $\text{Mo}_2\text{TiAlC}_2$, meaning that the FM $\text{Cr}_2\text{TiAlC}_2$ is covalent and ionic materials at 0 GPa, and a mixed bonding with partial metallic and certain ionic participation combination could be assumed at higher pressure. The Poisson's ratios of NM/FM $\text{Cr}_2\text{TiAlC}_2$ present similar variations with the only exception of lower counterparts within 10–40 GPa as there is an obvious reduction in FM one, which could be attributed to the influence of magnetic moment.

Thermodynamical properties. Several thermodynamical properties are studied for FM $\text{Cr}_2\text{TiAlC}_2$ by the quasi-harmonic Debye model, the calculation details⁴² could be obtained elsewhere. Grüneisen parameter γ characterizes the anharmonicity of lattice, the calculated γ are shown in Figures S11 and 12, in which the γ of FM $\text{Cr}_2\text{TiAlC}_2$ is far larger than that of NM $\text{Mo}_2\text{TiAlC}_2$, particularly at low pressure, such difference is obviously decreased with pressure. In Figure S11, the inserted small figure means the values of FM $\text{Cr}_2\text{TiAlC}_2$ and NM $\text{Mo}_2\text{TiAlC}_2$ at 0 GPa within 0–1500 K, the significantly larger value of Cr-containing compound represents the stronger phonon-phonon interaction originating probably from the effect of magnetism at low temperature, whereas the value of γ approaches its maximum limit at about 600–700 K and then decreases gradually with temperature in FM $\text{Cr}_2\text{TiAlC}_2$, such inverse variation indicates probably the opposite strength response of the phonon-phonon interaction with the volume change. Previous calculations for Ti_2SC ⁴³ also detected such decreasing trend at 0 GPa within 0–2000 K. The general variation trends of γ in FM $\text{Cr}_2\text{TiAlC}_2$ are similar with those⁹ of NM $\text{Mo}_2\text{TiAlC}_2$ and thus we here neglect the detailed discussions. Generally, the values of γ are within 1.5–2⁴⁴, previous calculations⁴⁴ for several MAX phases found that Cr_2GeC presents largest γ with a value of 2.38, which is still smaller than the present FM $\text{Cr}_2\text{TiAlC}_2$ which is 2.63 at 0 GPa and 0 K, meaning that the present compound behaves the largest γ among all known MAX phases till now, to the author's knowledge.

The variation trend of the thermal expansion coefficient α with temperature and pressure of FM $\text{Cr}_2\text{TiAlC}_2$ is generally the same with that⁹ of NM $\text{Mo}_2\text{TiAlC}_2$, as are shown in Figures S13 and 14. The α approaches its upper limit at about 1200 K in FM $\text{Cr}_2\text{TiAlC}_2$, with a value of $3.5343 \times 10^{-5} \times \text{K}^{-1}$, which is far larger than those of counterparts⁹ of NM $\text{Mo}_2\text{TiAlC}_2$, with a maximum value of $2.064 \times 10^{-5} \times \text{K}^{-1}$ at 1500 K. Such larger α can also be found in other Cr-containing MAX compounds, such as Cr_2GaC and Cr_2AlC ⁴⁵, with respective values are $2.9885 \times 10^{-5} \times \text{K}^{-1}$ and $2.4312 \times 10^{-5} \times \text{K}^{-1}$ at 1500 K. Moreover, previous calculations for Ti_2SC ⁴³ still found a peak in such evolution curve, with a maximum value of $1.8909 \times 10^{-5} \times \text{K}^{-1}$ K at 900 K, and it decreases to $1.8007 \times 10^{-5} \times \text{K}^{-1}$ at 1500 K. The detailed summary of α and other coefficients could be found in a recent review⁴⁶. The present α probably is the largest value among all the MAX phases.

The isothermal (B_T) and adiabatic (B_S) bulk moduli present similar variation trends with those⁹ of NM $\text{Mo}_2\text{TiAlC}_2$ with the only exception of 0 GPa, as is shown in Figure S15 and the inserted figure. Usually, B_T and B_S exist small difference owing to the small α and γ , $B_S = B_T(1 + \alpha\gamma T)$, where T means temperature. Variations of the discrepancy in ($\text{Mo}_2\text{TiAlC}_2$ - $\text{Cr}_2\text{TiAlC}_2$) for B_T and B_S present just opposite variation trends between 0 GPa and higher pressures because the novel variation trends of FM $\text{Cr}_2\text{TiAlC}_2$ (inserted the small figure), which approaches the minimum value 130.63 GPa at about 1400 K in B_T and 144.08 GPa at 800 K in B_S . Such nonlinear variation is closely related to the variations of α and γ . Previous calculations for Ti_2SC ⁴³ also observed such phenomenon in B_T and B_S .

Conclusion

The magnetic moment collapse induced axial alternative compressibility in FM $\text{Cr}_2\text{TiAlC}_2$ at 420 GPa is observed for the first time in this family of compounds. The correctness of this conclusion could be evidenced by the electronic and mechanical properties. The strong influence of the magnetic moment caused many excellent thermodynamic properties. The implication of the current investigation is that both the spin transition and the charge rearrangement could be adjusted by high pressure. The ferromagnetic moment collapse has crossed a series of antiferromagnetic order state and stabilized ultimately at a nonmagnetic order state.

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Author Contributions

Y.Z.-J. organized the research and wrote the paper; G.Q.-H. did the calculations; L.R.-F., X.H.-N., X.Z.-J., T.L., J.G.-Z. and G.Y.-D. analyzed the data. These authors contributed equally to this work.

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