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HIGHLIGHTS
- Unexpected electron doping effect in $M_3\text{Al}_2\text{C}$ system with the removal of electron donor
- Superconductivity originates from the M-C phonon modes
- The peculiar charge state greatly influences both its structure and superconductivity

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Anomalous Charge State Evolution and Its Control of Superconductivity in $M_3Al_2C$ ($M = Mo, W$)

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SUMMARY
The charge states of elements dictate the behavior of electrons and phonons in a lattice, either directly or indirectly. Here, we report the discovery of an anomalous charge state evolution in the superconducting $M_3Al_2C$ ($M = Mo, W$) system, where electron doping can be achieved through “oxidation.” Specifically, with the continuous removal of electron donor (Al) from the structure, we found an electron doping effect in the negatively charged transition metals. Over a certain threshold, the charge state of transition metals goes through a sudden reversion from negative to positive, which leads to a subsequent structure collapse. Concomitantly, the previous robust superconducting transition temperatures ($T_c$s) can be flexibly modulated. Detailed analysis reveals the origin of the superconductivity and the intimate relationship between the charge state and the electron-phonon coupling constant. The peculiar charge state in $M_3Al_2C$ plays an important role in both its structure and superconductivity.

INTRODUCTION
The charge state of atomic constituents in a solid is controlled by the chemical bonding strength and the surrounding structural environment (Pauling, 1960; Repp et al., 2004). It is taken for granted that continuously increasing or removing carrier donors from a system will monotonically shift the charge state of the remaining atoms, if keeping the anions intact. Take LiCoO$_2$ and LiFePO$_4$, for example, the oxidation reaction at the anode (extraction of Li) elevates the charge state of the transition metals to a higher value. Such a behavior has been widely accepted with seldom violations. Deliberate modulation of the charge state through physical or chemical routes could bring about rich phenomena, like structural transition and superconductivity.

$Mo_3Al_2C$ attracts considerable attention owing to the relatively high superconducting transition temperature ($T_c$) and its noncentrosymmetric structure, which holds the promise of spin-triplet pairing superconductivity (Bauer et al., 2010; Koyama et al., 2011; Koyama et al., 2013; Kuo et al., 2012; Karki et al., 2010; Bonalde et al., 2011; Bauer et al., 2014). Meanwhile, there is accumulated evidence for a conventional s-wave pairing; it remains indecisive which phonon mode is responsible for the formation of Cooper pairs (Karki et al., 2010; Bonalde et al., 2011). Furthermore, only one $T_c$ (= 9 K) is observed, despite the variation of nominal composition and synthesis conditions (Bauer et al., 2010; Bauer et al., 2014). This robustness is rooted in its structure. As shown in Figure 1A, the well-established structure of $Mo_3Al_2C$ (P4$_1$32) can be viewed as four $Mo_3C$ octahedra interconnected with each other by corner sharing to form a framework while leaving Al atoms to fill the interstices. Theoretical calculation shows only carbon vacancies could exist, and the Mo and Al sites tend to be fully occupied (Reith et al., 2012). The C content is suggested to be controlled by the synthesis temperature and will influence the superconductivity (Reith et al., 2012). However, samples prepared at different temperatures show quite similar $T_c$s, indicating the high stability of the C confined inside of the Mo cage. On the other hand, the substitution of Nb with poor 4$d$ electrons (hole doping) or Ru with rich 4$d$ electrons (electron doping) at the Mo site slightly lowers the $T_c$, but dramatically reduces the superconducting volume fraction (Ramachandran et al., 2016). This deterioration of superconductivity cannot be simply ascribed to a carrier doping effect, but is more suitable to a phase separation phenomenon.

Very recently, we reported the discovery of an isostructural phase of $W_3Al_2C$ with $T_c$ = 7.6 K (Ying et al., 2019). The replacement of Mo 4$d$ to W 5$d$ orbitals gives rise to a larger specific-heat jump and
superconducting gap energy. Different from its Mo-counterpart, W3Al2C shows a significant deficiency at the Al site according to the composition analysis (Ying et al., 2019). This observation gives us a clue to understand the rigid $T_c$ and the origin of the superconductivity in both Mo3Al2C and W3Al2C. From a structural point of view, the interconnected W6C and Mo6C subunits may be viewed as nanoporous structures, whereas Al ions are weakly connected to the surrounding metals. Considering the amphoteric properties of aluminum toward both acids and bases, it may provide an ideal tuning knob to control the properties of this family. Similar strategies have been applied to the preparation of several MXene materials (Naguib et al., 2011; Li et al., 2018; Alhabeb et al., 2017; Xuan et al., 2016).

Here, by applying a chemical etching method, we successfully extract Al from $M_3Al_2C$ ($M$ = Mo, W). Most prominently, the combination of theoretical calculations, heat capacity, and X-ray photoelectron spectroscopy (XPS) measurements reveals an anomalous electron doping effect by extracting electron donors (Al), which is in sharp contrast to the preconceived knowledge. Further extraction leads to a sudden reversion of the charge state in the transition metals and concomitantly collapses the crystal structure from corner sharing to edge and face sharing. As a consequence, the previous rigid $T_c$ can be continuously shifted while keeping a full superconducting volume fraction. Based on the Debye-Einstein analysis of the high temperature heat capacity and phonon calculations of the samples with different Al contents, we suggest the superconductivity in the $M_3Al_2C$ system originates from the charge state of $M$, which leads to the hardening of the $M$-$M$ and $M$-$C$ vibrations.

RESULTS AND DISCUSSION
Intrinsic Aluminum Vacancy

We first investigate the influence of Al vacancy toward the dynamical stability of the structure. According to Figure 2, the phonon dispersions of fully occupied $W_3Al_2C$ show imaginary optical modes all over the first Brillouin zone. In $Mo_4Al_2C$, part of the reciprocal space (e.g., the R point) is free from imaginary frequencies (Reith et al., 2012) and its absolute values are also smaller than that of $W_3Al_2C$, indicating vacancies should appear in $W_3Al_2C$ to stabilize the $P4_132$ cubic structure. Generally, the inclusion of vacancies at all three sites (Al: Figure 2B, W and C: Figure S1) can eliminate the imaginary modes. A scrutiny of the relaxed structures reveals an opposite effect of Al and C vacancies toward the W6C subunit. The inclusion of one C vacancy increased the average W-C bond length by 1.0% and the corresponding W6C octahedral volume by 2.0%, agreeing well with that of $Mo_3Al_2C$ (1.4% and 3.6%) (Reith et al., 2012). However, Al vacancy shrank the W-C bond length and octahedral size by −0.3% and −2.6%, respectively. This contradiction implies the existence of charge redistribution and will be discussed later.

Previous calculation showed that only C vacancies are allowed in the $Mo_3Al_2C$ (Reith et al., 2012). It is thus interesting to observe appreciable Al deficiencies in $W_3Al_2C$ judging from its chemical composition (Ying et al., 2019). This observation gives us a clue to understand the rigid $T_c$ and the origin of the superconductivity in both Mo3Al2C and W3Al2C. From a structural point of view, the interconnected W6C and Mo6C subunits may be viewed as nanoporous structures, whereas Al ions are weakly connected to the surrounding metals. Considering the amphoteric properties of aluminum toward both acids and bases, it may provide an ideal tuning knob to control the properties of this family. Similar strategies have been applied to the preparation of several MXene materials (Naguib et al., 2011; Li et al., 2018; Alhabeb et al., 2017; Xuan et al., 2016).

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et al., 2019). We tackle this issue by analyzing the vacancy formation energies in $W_3Al_2C$. As we know, standard DFT calculations are only valid at $T = 0K$, and the formation energy is defined as

$$D = \frac{E(W_3Al_2C) - E(X)}{2} + \frac{E(X)}{2} - E(W_3Al_2C).$$

Here, $X$ denotes the extracted element and there are four chemical formula $W_3Al_2C$ in a unit cell. To describe the synthesis condition, we included the temperature-dependent vibrational free energy $F_{\text{phonon}}$ and thermal electronic contribution $F_{\text{electron}}$ in the calculations, and thus, the formation energy can be written as

$$D = D + D_{\text{phonon}} + D_{\text{electron}}.$$ 

Details of the calculation can be found in the Methods section and the definition of $D_{\text{phonon}}$ and $D_{\text{electron}}$ are similar to that of $D$. As shown in Figure 2C, the vacancy formation energy of W, Al, and C are all negative above certain temperatures, which means the spontaneous vacancy formation are favored at the synthesis temperature. This is in sharp contrast to that of $Mo_3Al_2C$, where only the formation of C vacancies are possible (Reith et al., 2012). We note that the previous calculation did not consider the $F_{\text{electron}}$. Thus, the vacancy formation energy of Al in $Mo_3Al_2C$ including $F_{\text{electron}}$ was superimposed in Figure 2C for comparison. We will not consider the W vacancies as its formation energy is relatively large compared with that of Al and C vacancies. Prominently, the vacancy formation energy of Al of $W_3Al_2C$ is even smaller than that of C over the whole temperature range. Considering structural rigidity of M and C as mentioned in the introduction, we investigated the role of Al vacancies in $M_3Al_2C$.

Because of the amphoteric property of Al and its weak connection with the surrounding transition metals, it is possible to tune the content of Al through a soft chemical method. Here, NaOH was used as an etching agent. The XRD refinements of the raw and etched $W_3Al_2C_{0.8}$ are shown in Figure S2. Composition analyses show that the Al content decreases from 1.75 to 1.4 in $W_3Al_1.4C_{0.8}$ and 2.0 to 1.52 in $Mo_3Al_1.52C_{0.85}$. The $M_6C$ building blocks are found to be quite rigid, and their lattice parameters only shrank 0.2% and 0.25% for $W_3Al_1.4C_{0.8}$ and $Mo_3Al_1.52C_{0.85}$, respectively. The shrinkage of the W-C bond (~0.6%) and octahedron volume (~1.6%) after etching is consistent with the calculation results.

Considering no peak splitting at both low and high diffraction angles of the Al-extracted sample (Figure S3A) and the continuous peak evolution (Figure S3B), the extraction of aluminum can be viewed as homogeneous without phase separation. As no superstructure peaks can be identified from the XRD diffraction, the remaining Al should be randomly distributed. It is thus not clear why only about one-quarter of Al can be extracted from the porous interstices for both Mo and W cases. Further reaction at a moderate temperature (below 140°C) did not increase the content of Al vacancies. However, a slight increase of the reaction temperature to above 150°C completely collapses the structure from $M_3Al_2C$ to $WC$ or $Mo_2C$ with a sudden loss of all the structural aluminum. To understand all these phenomena, it is necessary to trace the evolution of the charge state during the reaction (Figure 1B).

**Anomalous Charge State Evolution**

Bader analysis of the charge transfer could give us a deeper insight. To our surprise, the charge state of W after the extraction becomes more negative from $[W]^{0.37}$ in Figure 1B to $[W]^{-0.43}$ in Figure 3C. At the same time, the carbon also becomes more negatively charged from $[C]^{-1.42}$ to $[C]^{-1.47}$. To balance the charge state, the average electron donation of Al raises from $[Al]^{1.08}$ to $[Al]^{1.37}$, which is to say, the loss of
electrons from one Al vacancy is overcompensated by other Al atoms. The same conclusion is applied for the charge state evolution in Mo$_3$Al$_2$C. Because the valence of Mo and W in the binary carbides must be positive, one could expect the sudden reversion of the charge state in the transition metals from negative to positive at further extraction. This observation well explains the existence of a lower limit of Al in M$_3$Al$_2/C_0$$_x$C$_{0.8}$ and agrees well with the sudden phase transition from the corner-sharing P4$_1$32 structure to an edge/face-sharing WC or edge/corner-sharing Mo$_2$C.

We substantiate the results of calculation by XPS. As shown in Figure 3D, a systematic shift of the W4f$_{5/2}$ and 4f$_{7/2}$ peaks of W$_3$Al$_1.4$C$_{0.8}$, W$_3$Al$_1.75$C$_{0.8}$, pure W metal, and WO$_3$. The peak position was calibrated by using the absorbed C1s as shown in Figure S4, where the signals of absorbed carbon and the lattice carbon can be clearly distinguished. The positively charged W in WO$_3$ shifted oppositely to a higher binding energy. The extra two peaks of W$_3$Al$_1.4$C$_{0.8}$ in (D) come from the oxidation state of WO$_2$.+

This anomalous charge state evolution, to our knowledge, has not been reported before. The negative valences and the anomalous charge state evolution of Mo$_3$Al$_2$C are shown Figure S5. Although proved theoretically and experimentally for M$_3$Al$_2$C$_{0.8}$, a clear understanding of this peculiar behavior is still lacking. The choice of elements with proper electron affinity should be crucial, but whether the structure is an important ingredient is unknown. The MXene material can be an independent arbitrator. However, species like -O or -OH are always present after the NaOH treatment to compensate the dangling bonds in MXenes, which complicate further analyses.

**Tunable Superconductivity**

As shown in Figure 4A, the $T_c$ of etched W$_3$Al$_2$.C$_{0.8}$ shifts from 7.5 to 6.4 K. For Mo$_3$Al$_2$.C$_{0.8}$, a much significant decrease of $T_c$ from 9.1 to 5 K is achieved. It is possible to finely control the $T_c$ by varying the reaction time, as illustrated in Figure 4B. A prominent feature of the etched W$_3$Al$_2$.C$_{0.8}$ and Mo$_3$Al$_2$.C$_{0.8}$ is that their diamagnetization signal reach $\chi = -1$ at low temperature. Although the etched W$_3$Al$_1$.C$_{0.8}$ shows a nearly full diamagnetism, we note that a core-shell structure with a non-superconducting bulk embedded inside a superconducting shell sometimes may give a similar signal. It is thus important to exclude this possibility by using a bulk sensitive method such as heat capacity. A shown in Figure S6, a full gap opening...
toward 0 K is reached, confirming the bulk superconductivity in the Al-etched sample. Thus the superconducting volume of W3Al2/C0 remains almost the same before and after etching. This is quite different from the previous report of Nb- and Ru-doped Mo3Al2C where the change of Tc is barely observable but the superconductivity is quickly quenched by doping (Ramachandran et al., 2016). A plausible explanation is given in the discussion.

To determine whether the decline of Tc is related to carrier doping, we measured the low temperature heat capacity of the raw and etched W3Al2/C0 before and after etching. The measurements were carried out under a magnetic field of H = 9 T to suppress the Tc to a lower temperature.

Figure 4. Tunable Superconductivity

(A and B) The magnetization of W3Al2/C0.8 and Mo3Al2/C0.85 before and after etching. The susceptibilities were calibrated using Pb as a reference. The kink at ~3 K in (B) comes from the residual Mo2C during arc melting, where the evaporation of Al is inevitable.

(C) Heat capacity of W3Al2/C0 before and after etching. The measurements were performed under an external field of 9 T to suppress the Tc to a lower temperature.

(D) Density of states (DOS) for W3Al1.75C0.75 and W3Al1.5C0.75. The electrons at the Ef remain to be the same before and after etching.

Vibration Modes

The tunable Tc provides us an opportunity to clarify the origin of superconductivity in the Mo3Al2C system. From Figure 4C, the Debye temperature can be extracted from the slope of the heat capacity, which is 259
and 274 K for raw and etched W$_3$Al$_2$C$_0.8$, respectively. We temporarily use the McMillan expression (McMillan, 1968) to estimate the electron-phonon coupling constant ($\lambda$):

$$T_c = \frac{\bar{\mu}}{1.20} \exp \left[ \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62)} \right]$$

(Equation 1)

where $\bar{\mu}$ is the Debye vibration frequency. The residual screened Coulomb repulsive interaction $\mu^*$ can be viewed as a constant for a certain system with a typical value ranging from 0.1 to 0.16. Intuitively, the $T_c$ should be positively correlated with the Debye frequency. The opposite tendency of the $T_c$ evolution with the Debye temperature implies the decline of $\lambda$ after Al extraction. By using $\mu^* = 0.13$ and their respective Debye temperatures, we got the $\lambda = 0.77$ for W$_3$Al$_1.75$C$_0.75$ and 0.71 for W$_3$Al$_2$C$_0.8$. The decrease of $\lambda$ drives us to further investigate the phonon vibration modes in the present system.

To clarify the decisive phonon mode for the superconductivity, we investigate the high-temperature heat capacity and phonon DOS. In Figure 5A, the heat capacity of W$_3$Al$_1.75$C$_0.75$ was measured from 7.5 to 200 K and fitted by using the hybrid Debye-Einstein model:

$$C_v(T) = \gamma T + 9RN_D \left( \frac{T}{\Theta_D} \right)^3 \int_0^\infty x^4 e^{x^4} \left( e^{x^4} - 1 \right) dx + 3R \sum_{E} N_E \left( \frac{\Theta_E}{k_B T} \right)^2 \frac{\ln \left( \frac{k_B T}{\Theta_E} \right)}{e^{\Theta_E/k_B T} - 1}$$

(Equation 2)

where the subscripts D and E denote the Debye and Einstein modes, respectively, and $R$ is the gas constant. $N_E$ means $N_E$ states at an energy $\Theta_E$. For example, in W$_3$Al$_1.4$C$_0.8$, there are 5.2 atoms per formula unit and 15.6 phonon modes in total. Three acoustic phonons were averaged as one Debye mode, whereas the rest of the optical phonons were described as two Einstein modes ($i = 2$). The sum of $(N_D + N_E)$ equals the number of atoms in the formula unit.

The fitting of W$_3$Al$_1.75$C$_0.75$ can be found in Figure S7, and the fitted parameters are summarized in Table 1. Comparing with the low-temperature fitting, the Debye temperatures fitted from high temperature have lower values. This is caused by the inclusion of two Einstein modes to describe the optical vibrations. By inspecting the phonon contribution, the Debye mode and the second Einstein mode are dominant, whereas the first Einstein mode can be neglected. All the three temperatures ($\Theta_D$, $\Theta_{E1}$, and $\Theta_{E2}$) shifted toward higher values, indicating the growing stiffness of the lattice.

The phonon DOS before and after Al extraction are shown in Figures 5B and 5C. In accord with the atomic weight, the phonon contribution of W, Al, and C are roughly located at three different regions of the spectra. Since Al is detached from C, the overlap of the spectra between Al and C is negligible. Although Al is located in the large interstices and weakly attached to the surrounding W, the overlap between Al and W is significant, extending from 2 to 13 THz. This means the filling rate of Al will significantly influence the wobbling frequency of W. As a result, the W-Al spectra shifted to a lower frequency in the etched sample, as indicated by blue arrows. Concomitantly, the W-W and W-C phonon peaks at around 1 THz (red arrow, W component dominated) and W-C peaks above 14 THz (dark gray arrow, C component dominated) shifted to around 2.5 and above 16 THz,
The Einstein mode can be viewed as a combination of both W-Al and W-C optical modes. Considering the enhancement of both $Q_{E1}$ and $Q_{E2}$, the increase of W-C frequency should outweigh the decrease of W-Al component. Based on the discussion above, we conclude the W-W and W-C optical modes to be responsible for the superconductivity. This conclusion is reasonable when considering the Al-free WC and Mo$_2$C are also superconductors, but various Al-Mo and Al-W binary compounds do not superconduct (except AlMo$_3$ with a $T_c$ of 0.58 K). From this point of view, we could also understand the previous reported Nb and Ru substitution at Mo site, which impairs the connection of the Mo-Mo and Mo-C bonding, can effectively quench the volume fraction of the superconductivity (Ramachandran et al., 2016).

### Charge State Controlled Structure and Superconductivity

The structure collapse caused by the charge state reversion is easy to understand. We explain the change of the $M_6C$ subunit from a charge point of view. We know that the Al vacancies shrink the M-C bond length and the volume of $M_6C$, whereas the inclusion of C vacancies expand them. This contradiction can be qualitatively explained by the competition between Coulomb force and charge redistribution. The extraction of Al decreases the number of W-Al bonds (reduce the attraction force) but moderately increases the valence of W by 16% and Al by 27% (enhance the attraction force). Judging from the results, the reducing effect dominates the shrinkage. However, the removal of one C from the lattice doubled the valence of W, as shown in Figures 3A and 3B. It is the strong Coulomb repulsion of the W-W bonds caused by charge redistribution that expands the subunits.

The relationship between the superconductivity and the charge state is straightforward. As discussed above, the combined effect of $M_6C$ shrinkage and the enhancement of the negative charge states in both M and C will enhance the Coulomb repulsion and further the frequency of the M-M and M-C vibrations. The electron-phonon coupling constant is negatively correlated to the phonon frequency according to Migdal (1958); Eliashberg, (1960):

$$\lambda = \frac{1}{\pi N_f} \sum \bar{\Omega},$$  

(Equation 3)

where $\bar{\Omega}$, $N_f$, and $\omega$ are the imaginary part of phonon self-energy, DOS of the normal metal, and phonon frequency, respectively. This well explains the observed decline of $\lambda$ and $T_c$.

### Conclusion

To start with, we found the intrinsic Al vacancy is dynamically favored in W$_2$Al$_2$C but not in Mo$_2$Al$_2$C. A soft chemical etching method was applied, and the content of Al could be feasibly controlled. An interesting discovery is the non-monotonic evolution of the charge state in the transition metals. This observation may provide new insights into the design of functional materials where electron doping can be achieved by the extraction of electron donors. The subsequent collapse of the crystal structure can be well explained by the abrupt reversion of the charge state in the transition metals. This anomaly may be related to the moderate electron negativity of Al and its surrounding chemical environment, which is worth further investigations. Apart from the tunable $T_c$, the controllable Al also provides us an ideal opportunity to compare the heat capacity and phonon contribution in different samples, which clarifies the origin of the

|                | Raw   | Etched | Raw   | Etched |
|----------------|-------|--------|-------|--------|
| $T_c$(K)       | 7.5   | 6.4    |       |        |
| $\Theta_0$(K)  | 204   | 229    |       |        |
| $\Theta_{E1}$(K) | 58    | 74     |       |        |
| $\Theta_{E2}$(K) | 384   | 423    |       |        |
| $V_{E1}$(%)    | 37.6  | 48.7   | 0.6   | 1.3    |
| $V_{E2}$(%)    | 61    | 50     | 0.77  | 0.71   |

Table 1. Physical Parameters of W$_3$Al$_{2-x}$C$_{0.8}$

respectively. The Einstein mode can be viewed as a combination of both W-Al and W-C optical modes. Considering the enhancement of both $\Theta_{E1}$ and $\Theta_{E2}$, the increase of W-C frequency should outweigh the decrease of W-Al component. Based on the discussion above, we conclude the W-W and W-C optical modes to be responsible for the superconductivity. This conclusion is reasonable when considering the Al-free WC and Mo$_2$C are also superconductors, but various Al-Mo and Al-W binary compounds do not superconduct (except AlMo$_3$ with a $T_c$ of 0.58 K). From this point of view, we could also understand the previous reported Nb and Ru substitution at Mo site, which impairs the connection of the Mo-Mo and Mo-C bonding, can effectively quench the volume fraction of the superconductivity (Ramachandran et al., 2016).
superconductivity in the $M_6Al_2C$ system. Detailed analysis shows the negatively charged transition metal and the charge redistribution change the $M_6C$ subunits are responsible for the observed phonon hardening. The existence of an intrinsic Al deficiency in the as-prepared $W_3Al_{1.75}C_{0.8}$ implies that a further enhancement of $T_c$ can be expected through non-equilibrium processes such as electrochemical intercalation at room temperature. According to Figure 2C, the Al sites tend to be fully occupied at low temperature. It is thus also possible to backfill the vacancies thermodynamically through the reaction of the $W_3Al_{1.75}C_{0.8}$ in the bath of certain metals with low melting points. The proposed etching method should be applicable to other superconductors containing Al and Zn.

Resource Availability
Lead Contact
Further information and requests for the samples should be directed to and will be fulfilled by the Lead Contact, Yanpeng Qi (qiyp@shanghaitech.edu.cn).

Materials Availability
All the samples used in this study are available from the Lead Contact without restriction.

Data and Code Availability
All relevant data are available from the corresponding author (qiyp@shanghaitech.edu.cn) upon reasonable request.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101196.

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AUTHOR CONTRIBUTIONS
T. Ying, Y.Q., and H.H. designed research; Y.Q., T. Ying, Y.M., S.I., P.C., Y.L., and J.L. performed experiments; T. Ying and T.K. carried out theoretical calculations; T. Ying, T. Yu, Y.Q., and H.H. analyzed data and wrote the paper.

DECLARATION OF INTERESTS
The authors declare no competing interest.

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Supplemental Information

Anomalous Charge State Evolution
and Its Control of Superconductivity
in $M_3\text{Al}_2\text{C}$ ($M = \text{Mo, W}$)

Tianping Ying, Yoshinori Muraba, Soshi Iimura, Tongxu Yu, Peihong Cheng, Toshio Kamiya, Yangfan Lu, Jiang Li, Yanpeng Qi, and Hideo Hosono
Figure 1: Phonon dispersions up to 5 THz of (a) $W_{2.75}Al_2C$ and (b) $W_3Al_2C_{0.75}$. Related to Figure 2.

Figure 2: (a) and (b) Rietveld refinements of $W_3Al_{1.75}C_{0.8}$ and $W_3Al_{1.4}C_{0.8}$. (c) and (d) The evolution of the XRD patterns of $W_3Al_{2-x}C_{0.8}$ and $Mo_3Al_{2-x}C_{0.85}$ with the extraction of Al. The '*' and ‘▽’ labelled in (d) denote $Al_8Mo_3$ and $Mo_2C$ impurities, respectively. Related to Figure 1.
Figure 3: (a) Enlargement of 210 and 420 XRD diffraction peaks of Al-extracted W\textsubscript{3}Al\textsubscript{1.4}C\textsubscript{0.8}. (b) Continuous peak shift in Mo\textsubscript{3}Al\textsubscript{2-δ}C\textsubscript{0.85} (Laue index: 221). Related to Figure 1.

Figure 4: XPS C1\textsubscript{s} peak of W\textsubscript{3}Al\textsubscript{1.4}C\textsubscript{0.8}, and W\textsubscript{3}Al\textsubscript{1.75}C\textsubscript{0.8} before and after polishing. The absorbed and structural carbon can be clearly distinguished, and the polished sample shows an enhancement of the structural carbon peak. Importantly, the structural C1\textsubscript{s} peak in the etched sample (W\textsubscript{3}Al\textsubscript{1.4}C\textsubscript{0.8}) shifts to a lower binding energy, indicating an electron doping effect and agreeing well with the theoretical prediction. Related to Figure 3.
Figure 5: XPS Mo3\textit{d}$_{5/2}$ and Mo3\textit{d}$_{3/2}$ peaks of Mo$_3$Al$_{1.52}$C$_{0.85}$, Mo$_3$Al$_2$C$_{0.85}$, pure Mo metal and MoO$_2$. Related to Figure 3.

Figure 6: Electronic heat capacity contribution of the etched W$_3$Al$_{1.4}$C$_{0.8}$ from 2 to 10 K. The Sommerfeld coefficient of the normal state is around 7.6 mJ/mol$^{-1}$K$^{-2}$, which is comparable to that of the parent material. The extrapolation of the $C_{es}/T$ to zero at 0 K indicates a complete opening of the superconducting gap and confirms the full superconducting volume fraction after etching. Related to Figure 4.
Figure 7: Heat capacity of W$_3$Al$_{1.75}$C$_{0.8}$ from 7.5 K to 200 K. The components of Debye-Einstein fitting curves are superimposed. Related to Figure 5.
Transparent Methods

Computational Details

Density functional theory (DFT) calculations were performed using the projector augmented wave (PAW) method encoded in the Vienna Ab Initio Simulation Package (VASP) (G. Kresse and Hafner, 1993; Georg Kresse and Furthmüller, 1996; G. Kresse and Furthmüller, 1996). The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE) electron exchange-correlation functional (Perdew, Burke, and Ernzerhof, 1996). The lattice constants and the internal atomic positions were relaxed on a $7 \times 7 \times 7$ Monkhorst-Pack mesh (Monkhorst and Pack, 1976) with the plane-wave cutoff energy of 500 eV, and forces are minimized to less than 0.01 eV/Å. The Brillouin-zone integration for the computation of total energy was made using the tetrahedron method with Blochl’s corrections based on a $10 \times 10 \times 10$ $k$-point mesh.

We used the code from the Henkelman group for Bader charge analysis (Tang, Sanville, and Henkelman, 2009). The phonon dispersions, phonon DOS, and thermodynamic properties were calculated within the finite displacement method based on the open-source package Phonopy (Togo and Tanaka, 2015). Phonon ($F_{\text{phonon}}$) and thermal electronic contributions ($F_{\text{electron}}$) are included to describe the vacancy formation process. The phonon contribution can be written as

$$F_{\text{phonon}} = \frac{1}{2} \sum_{q,\nu} \hbar \omega_{q,\nu} + k_B T \sum_{q,\nu} \ln[1 - e^{-\hbar \omega_{q,\nu}/k_B T}],$$  \hspace{1cm} (1)

where $q$, $\nu$, $\hbar$ and $k_B$ are the wave vector, band index, reduced Planck constant and Boltzmann constant, respectively. $\omega_{q,\nu}$ is the phonon frequency at state $q$ and $\nu$. The thermal electronic contribution is defined to be

$$F_{\text{electron}} = E_{\text{electron}} - TS_{\text{electron}},$$ \hspace{1cm} (2)

where $E_{\text{electron}}$ and $TS_{\text{electron}}$ are the thermal internal energy and entropy contribution, respectively. The thermal internal energy due to electron excitation is given by

$$E_{\text{electron}} = \int_{-\infty}^{\infty} n(\varepsilon)f\varepsilon d\varepsilon - \int_{-\infty}^{E_F(0)} n(\varepsilon)\varepsilon d\varepsilon,$$ \hspace{1cm} (3)

where $n(\varepsilon)$ is the electronic density of states and $f$ is the Fermi-Dirac distribution. The Fermi energy at $T \neq 0$ K is determined by the charge neutral condition at a given temperature through

$$S_{\text{electron}} = -k_B \int_{-\infty}^{\infty} n(\varepsilon)[f\ln f + (1 - f)\ln(1 - f)] d\varepsilon.$$ \hspace{1cm} (4)

Experimental Details

The syntheses of $\text{Mo}_3\text{Al}_2\text{C}$ and $\text{W}_3\text{Al}_2\text{C}$ can be found in (Bauer et al., 2014) and (Ying, Qi, and Hosono, 2019), respectively. The soft chemical etching process was applied by immersing finely grounded powder into aqueous solution of NaOH (2.5M) at room temperature. Magnetic stirring is needed and the Al content is controlled by the etching time ranging from 30 minutes to several hours. The collapsed samples were prepared by using an autoclave and heated to 150 °C. The powder XRD patterns were taken by using a Bruker D8 Advance diffractometer with Cu-Kα radiation. The crystal structures were visualized with the VESTA code (Momma and Izumi, 2011). Magnetic and heat capacity properties were measured by using the SQUID vibrating sample magnetometer (SVSM, Quantum Design) and Physical Property Measurement System (PPMS, Quantum Design), respectively. The chemical state of the elements was investigated by using X-ray photoelectron spectroscopy (XPS, Thermo Fisher 250Xi). The possible existence of OH$^-$ and H$^+$ was checked by TDS (ESCO, TDS1400TV). Electron-probe microanalyzer (EPMA, JEOL, Inc., model JXA-8530F) was used to measure the chemical compositions.

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