High-temperature neutron diffraction and first-principles study of temperature-dependent crystal structures and atomic vibrations in Ti$_3$AlC$_2$, Ti$_2$AlC, and Ti$_5$Al$_2$C$_3$

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Herein we report on the thermal expansions and temperature-dependent crystal structures of select ternary carbide MAX phases in the Ti–Al–C phase diagram in the 100–1000°C temperature range. A bulk sample containing 38(±1) wt.% Ti$_5$Al$_2$C$_3$ (“523”), 32(±1) wt.% Ti$_2$AlC (“211”), 18(±1) wt.% Ti$_3$AlC$_2$ (“312”), and 12(±1) wt.% (Ti$_{0.5}$Al$_{0.5}$)Al is studied by Rietveld analysis of high-temperature neutron diffraction data. We also report on the same for a single-phase sample of Ti$_5$Al$_2$C$_3$ for comparison. The thermal expansions of all the MAX phases studied are higher in the $c$ direction than in the $a$ direction. The bulk expansion coefficients $-9.3(±0.1) \times 10^{-6}$ K$^{-1}$ for Ti$_5$Al$_2$C$_3$, 9.2(±0.1) $\times 10^{-6}$ K$^{-1}$ for Ti$_2$AlC, and 9.0(±0.1) $\times 10^{-6}$ K$^{-1}$ for Ti$_3$AlC$_2$ are comparable within one standard deviation of each other. In Ti$_5$Al$_2$C$_3$, the dimensions of the Ti–C octahedra for the 211-like and 312-like regions are comparable to the Ti–C octahedra in Ti$_2$AlC and Ti$_3$AlC$_2$, respectively. The isotropic mean-squared atomic displacement parameters are highest for the Al atoms in all three phases, and the values predicted from first-principles phonon calculations agree well with those measured.

I. INTRODUCTION

Titanium carbide is one the hardest transition metal binary carbides known, which renders it resistant to wear and makes it a favorable material for applications such as drill bits and cutting tools. With a melting point of over 3000°C, it is thermally quite stable. However, transition metal binary carbides are brittle, difficult to machine, and highly susceptible to thermal shock. The ternary carbides known as $M_{n+1}AX_n$ (MAX) phases [1] (where $n = 1, 2, 3$ and $M$ is a transition metal, $A$ is a group A element mostly from groups 13 and 14, and $X$ is either C or N) often overcome some of these shortcomings, while still being heat tolerant. As a class, the MAX phases have unusual – yet attractive and often useful – combinations of properties that bring together some of the best attributes of ceramics and metals [2–4]. Like metals, they are excellent electric and thermal conductors, with exceptional thermal shock resistance and damage tolerance [2, 3, 5]. In some cases, they are creep [6–9], oxidation [10, 11], and fatigue [12] resistant. Furthermore, they are elastically quite stiff, yet readily machinable [13].

In this work we are interested in the MAX phases in the Ti–Al–C system. Both Ti$_2$AlC [Fig. 1(a)] and Ti$_3$AlC$_2$ [Fig. 1(b)] have been relatively well studied. The crystal structure of Ti$_3$AlC$_2$ was first solved in the 1960s [14]; Ti$_3$AlC$_2$ was discovered several decades later in 1994 [15]. Of the > 60 MAX phases known to date, Ti$_2$AlC and Ti$_3$AlC$_2$ are particularly attractive in terms of high temperature applications. They are two of the most lightweight and oxidation resistant MAX phases [16, 17], and the accessibility and relative low cost of their raw materials render them the most promising for up-scaling and industrialization.

In addition to Ti$_3$AlC, henceforth referred to as 211, and Ti$_5$Al$_2$C$_3$, henceforth referred to as 312, there is also a Ti$_5$Al$_2$C$_3$– or 523 – phase, which is in a category of higher-order MAX phases. The latter were first reported in 2004 in the Ti–Si–C system (i.e. Ti$_5$Si$_2$C$_3$ and Ti$_7$Si$_2$C$_5$) by Palmquist et al. [18]. Wilhelmsson et al. [19] reported the existence of Ti$_5$Al$_2$C$_3$ in 2006. In both cases, these phases were only observed in local stacking sequences in transmission electron microscopy, TEM, micrographs.

More recently, the stacking sequence of Ti$_5$Al$_2$C$_3$ was characterized using X-ray diffraction, XRD, in two studies [20, 21]. In our study [21], the characterized sample contained 43(±2) wt.% Ti$_5$Al$_2$C$_3$. In another study [20], only a small amount of Ti$_5$Al$_2$C$_3$ was observed and neither weight nor volume fractions were reported. We note in passing that the first structure proposed by Wang et al. in Ref. [20] is totally wrong and unsubstantiated by the results shown in that paper (see Ref. [22]). It is also crucial to note that our paper was submitted a few weeks before that of Ref. [20]. Interestingly, Ref. [20] was submitted, reviewed, and accepted in exactly one week and published soon thereafter. It was only after our paper was published that the same group, working with a composition that was only 19.7 wt% Ti$_5$Al$_2$C$_3$, made the case that the space group was P33m [23].

Like most other MAX phases, Ti$_2$AlC and Ti$_5$Al$_2$C$_3$ both have layered hexagonal structures [Figs. 1(a) and 1(b), respectively] belonging to space group P6$_3$/mmc (No. 194). In both structures, Ti–C layers (Ti$_2$C for Ti$_2$AlC and Ti$_5$C$_2$ for Ti$_5$Al$_2$C$_3$) are interleaved between layers of Al. The Ti$_5$Al$_2$C$_3$ phase, on the other hand [Fig.
The original aim of this work was to determine the crystal structure parameters of phase-pure Ti$_2$AlC. However, for reasons that are not fully understood, during processing, Ti$_2$AlC decomposed to yield Ti$_5$Al$_2$C$_3$ and some Ti$_3$AlC$_2$ [21]. And while obtaining the relevant crystal structure parameters on such a multiphase sample is not ideal we decided to proceed with this HTND study nevertheless for the following reasons:

(a) To date, neither we nor others have been able to synthesize phase-pure Ti$_2$Al$_2$C$_3$, and the results obtained here are better than no results;

(b) Given the very similar crystal structures, elastic properties, and TECs among the three phases (see below), the deviations from phase-pure behavior due to the presence of other phases should be small;

(c) Careful Rietveld analysis can deconvolute the contributions from each phase.

These comments notwithstanding, to estimate the error in the various parameters as a function of temperature, we compare the results obtained on the multiphase sample with a predominantly single-phase sample of Ti$_3$AlC$_2$ and show that the differences, for the most part, are equal to (or less than) the experimental uncertainty.

Herein we use HTND on a sample consisting of 38(±1) wt.% Ti$_5$Al$_2$C$_3$ (“523”), 32(±1) wt.% Ti$_2$AlC (“211”), 18(±1) wt.% Ti$_3$AlC$_2$ (“312”), and 12(±1) wt.% of an additional intermetallic TiAl phase to determine the temperature-dependent crystal structures of all three Ti–Al–C carbide phases. We report on the temperature evolution of the lattice parameters, isotropic thermal atomic displacement parameters, ADPs, and bond lengths during both heating and cooling for Ti$_2$AlC and Ti$_3$AlC$_2$. We verify our results by comparing the room temperature lattice parameters and lattice expansions to previous studies of predominantly single-phase Ti$_2$AlC and Ti$_3$AlC$_2$ samples [15, 27-30]. We also present HTND results for a predominantly single-phase Ti$_3$AlC$_2$ sample for comparison.

II. EXPERIMENTAL DETAILS

A. Sample synthesis

The sample used herein was prepared using pre-reacted Ti$_2$AlC powders that were commercially obtained (Kanthal, Hallstahammar, Sweden). The powders were cold isostatic pressed, CIPed, at 200MPa and heated at a rate of 300°C h$^{-1}$ to 1500°C, then sintered for 2 h under a hydrogen atmosphere.

The Ti$_3$AlC$_2$ sample was prepared by hot pressing, HPing, pre-reacted Ti$_2$AlC (Kanthal, Hallstahammar, Sweden) and titanium carbide (Alfa Aesar, Ward Hill, MA) in a 1:1 ratio to make 3:1:2 stoichiometry of Ti:Al:C. Powders were ball milled for 24 h, placed in a graphite
die, and heated in a graphite-heated hot press under a vacuum of $10^{-1}$ Torr at a rate of 500°C h$^{-1}$ to 1400°C. It was held for 4 h under a pressure of $\sim$ 40 MPa before cooling.

In both cases, bulk samples 9 mm in diameter and 3 cm high were used for the HTND experiments.

**B. High-temperature neutron diffraction**

The HTND experiments were conducted on the High-Pressure Preferred Orientation (HIPPO) neutron diffractometer [31–33] at the Lujan Neutron Scattering Center, Los Alamos National Laboratory. For both the multiphase Ti–Al–C sample and Ti$_3$AlC$_2$, bulk samples were placed in a vanadium, V, holder (9 mm diameter, 0.15 mm wall thickness), mounted in an ILL-type high-temperature vacuum furnace with a V setup, and heated at a rate of 20°C min$^{-1}$. Data were collected every 100°C during heating from 100°C to 1000°C. For the multiphase sample only, data were collected every 200°C upon cooling as well. At each measurement, the temperature was held constant during data collection and neutrons were detected with 42 panels of $^3$He detector tubes arranged on five rings with nominal diffraction angles of 39°, 60°, 90°, 120°, and 144°. To allow texture analysis, the sample was measured at rotation angles of 0°, 22°, and 45° around the vertical axis for each temperature, with a count time of 15 min per orientation for a total count time of 45 min per temperature.

**C. Structure refinement**

A texture analysis using the Material Analysis Using Diffraction, MAUD, code [32, 34] showed a mild fiber texture for all temperature points. As the texture was weak, the data from the three rotations and the detector rings were integrated, resulting in one histogram per detector bank. Due to the large detector coverage of HIPPO, this procedure is similar to spinning the sample to randomize the preferred orientation. The neutron time-of-flight data were analyzed as texture-free powders with the Rietveld method using the General Structure Analysis System, GSAS [35]. Only the higher resolution data from the 90°, 120°, and 144° banks were used in the analysis. The MAUD refinements, which incorporated preferred orientation, gave parameters that were within error bars of those determined without including texture by Rietveld refinement with GSAS. Therefore, all results reported herein are from the GSAS refinements assuming random texture.

The $gsaslanguage$ refinement script [36] was used to ensure that identical refinement strategies were employed for all temperatures. The instrument alignment (DIFC parameter in GSAS) was fixed for the backscattered (144°)
detector bank, which has the highest resolution, and refined for the 90° and 120° banks for the lowest temperature run at 100°C. For subsequent runs, DIFC was fixed for all three banks. Refined parameters were 16 background parameters of GSAS background function #1, lattice parameters of all phases, phase fractions, σ₁ profile parameter for peak width, atomic positions, and isotropic thermal motion parameters. The atomic positions in Ti₂AlC [z coordinate of Ti; see Fig. 1(a)] and in Ti₃AlC₂ [z coordinates of Ti₁ and C; see Fig. 1(b)] were both refined in the P6₃/mmc space group.

For Ti₅Al₃C₅, there are six unique atomic sites: Ti₁, Ti₂, and C₁ with 312-like stacking, Ti₃ and C₂ with 211-like stacking, and one Al site between 211- and 312-stacked octahedra throughout the cell [see Fig. 1(c)]. The best space group to represent these positions was found to be R3m; therefore, the z coordinates of Ti₁, Ti₃, Al, and C₁ were refined according to the constraints induced by the trigonal R3m space group.

In addition to the three MAX phase carbidies, peaks corresponding to an intermetallic that crystallizes like γ-TiAl, with tetragonal space group P₄/mmm [37], were found. Refinement of the site occupancy factor on the Ti site led to 50% Ti and 50% Al antisite defects, yielding a stoichiometry of (Ti₀.₅Al₀.₅)Al. Given the nearly null scattering intensity of the mixed site, and the low phase fraction of this phase, the isotropic thermal motion parameters were constrained together to reduce the number of variables.

D. First-principles calculations

First-principles phonon calculations were used to calculate the anisotropic mean-squared atomic displacements.

The DFT calculations were performed using the projector-augmented wave (PAW) method [38], as implemented in the Vienna Ab initio Simulation Package (VASP) code [39–41]. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used [42] with a cutoff of 500 eV. The total energy was converged to 10⁻⁸ eV, with a k-point grid of 12 × 12 × 4 for Ti₂AlC and Ti₃AlC₂ and 12 × 12 × 2 for Ti₅Al₃C₅.

The real-space force constants were calculated using density functional perturbation theory (DFPT) [43] implemented in the VASP code. The phonon frequencies were calculated from the force constants with Phonopy [44], and the ADPs were calculated from the frequencies and eigenvectors of the force constant matrix. Further details on the ADP calculations can be found in Ref. [45].
III. RESULTS

As noted above, texture analysis (Fig. 2) showed a mild (000I) fiber texture for all three MAX phases. Not surprisingly, the texture did not change during heating or cooling [compare Figs. 2(a), (b), (c) to Figs. 2(d), (e), (f), respectively]. The Rietveld fits for the neutron time-of-flight data – integrated for the full detector rings and the three measured orientations – are shown for the lowest temperature run at 100°C for the 90° [Fig. 3(a)] and the 144° detector banks [Fig. 3(b)]. The calculated fit (solid green lines) and measured data (red plus signs) are compared, with the difference curve plotted at the bottom (solid purple line). The markers above the difference curve show the peak positions for the phases: from top to bottom, (Ti0.5Al0.5)Al (green), 323 (blue), 312 (red), and 211 (black). The higher-d-spacing peaks resulting from diffraction by the basal planes are labeled for the (0 0 0 6) peak of Ti3AlC2, the (0 0 0 4) peak of Ti2AlC, and the (0 0 0 15) and (0 0 0 12) peaks of Ti5Al2C3. The latter two peaks unambiguously identify Ti5Al2C3 as the dominant phase, as they cannot be accounted for by any other known phase in the Ti–Al–C system.

The profile agreement factors for the Rietveld fits are listed in Table I at select temperatures, giving the weighted profile $R$ index, $wR_p$, the goodness of fit, $\chi^2$, and the expected $R$ factor, $R_{\text{exp}}$ [46]. Good agreement is observed between the calculated and observed profiles, with one unidentified peak at 2.09 Å whose origin remains unclear. A broad peak at 3.80 Å is present only in the 90° bank [Fig. 3(a)], which is likely due to background interference.

The composition determined from Rietveld analysis is 38(±1) wt. % Ti5Al2C3, 32(±1) wt.% Ti2AlC, 18(±1) wt. % Ti3AlC2, and 12(±1) wt.% (Ti0.5Al0.5)Al. The temperature dependencies of the fractions of each phase are plotted in Fig. 4, where the dashed lines indicate the ±1 wt.% limits. The compositions generally stay within 1 wt.% of the average value during heating and cooling, lending credibility to our data analysis and the resulting uncertainties for the compositions.

The temperature-dependent expansions of the lattice parameters and interatomic distances in Ti5Al2C3, Ti3AlC2, and Ti2AlC are shown in Figs. 6(a), (b), and (c), respectively. In Fig. 6(b), the parameters for the predominantly single-phase Ti3AlC2 sample are also plotted as open symbols. The anisotropic TEC values are listed in Table II, along with those from previous studies on Ti2AlC [28] and Ti3AlC2 [26, 29, 30].

To further compare the thermal expansions of the three phases, the temperature dependencies of $(\Delta V/V_o)^{1/3}$ – where $AV$ is the change in unit cell at temperature $T$ as compared to that at the reference temperature, 25°C (extrapolated), $V_o$ – are plotted in Fig 6(d). The results for (Ti0.5Al0.5)Al are also shown. The slope of these lines yields the average thermal expansion $\alpha_{av}$. From these results we find that for Ti2AlC, $\alpha_{av} = 9.2(\pm0.1) \times 10^{-6} K^{-1}$; for Ti3AlC2, $\alpha_{av} = 9.0(\pm0.1) \times 10^{-6} K^{-1}$; for Ti5Al2C3 $\alpha_{av} = 9.3(\pm0.1) \times 10^{-6} K^{-1}$. It is thus clear from Fig. 6(d) that the TECs of the three MAX phases are almost identical within the error bars. The absolute values of the $c$ and $a$ lattice parameters [Figs. 5(a) and (b), Table III] are also comparable, but it is apparent that Ti3AlC2 has the highest $a$ lattice parameter and Ti2AlC has the lowest, with that of Ti5Al2C3 falling in between. The same is true of the $c$ lattice parameters, after normalizing it by three to account for the three formula units in Ti5Al2C3 [Fig. 5(b)].

The temperature dependences of the absolute values of the Ti–C and Al–Ti bonds are shown in Figs. 5(c) and (d), respectively. The bonds in 211, 312, and 523 are shown in black, red, and blue, respectively. Note that the absolute range for the scale is the same for the graphs shown in Figs. 5(c) and 5(d). The extrapolated room temperature values for all bonds are also listed in Table IV, along with their expansion rates.

Due to the overlap of peaks in our data set we were unable to determine the anisotropic displacements as was done in our previous HTND studies [45, 49–52]. Instead, we examine the isotropic ADPs, $U_{iso}$, which represent the mean-squared displacements of the atoms from their equilibrium positions. Figures 7(a), (b), and (c) show the temperature dependences of $U_{iso}$ for the unique Ti (red), Al (blue), and C (black) atoms in Ti5Al2C3, Ti3AlC2, and Ti2AlC, respectively. In Fig. 7(b) the values for predominantly single-phase Ti3AlC2 are shown for comparison’s sake.

The values calculated with first-principles phonon calculations are shown as lines. In both experimental and calculated results, the Al atom shows the highest amplitude. Figure 8 compares the experimental and calculated values of $U_{iso}$ for the Al atoms in all three phases

![Graph showing compositions (wt.%) of each phase in the Ti–Al–C sample as a function of temperature upon heating and cooling. Dashed lines indicate limits for ±1% range.](image-url)
FIG. 5. Temperature dependence of (a) $a$ and (b) $c$ lattice parameters, and (c) Ti–C and (d) Ti–Al interatomic distances in Ti$_5$Al$_2$C$_3$ (blue), Ti$_3$AlC$_2$ (red) and Ti$_2$AlC (black). Refer to Fig. 1 for notations of Ti and C atoms. Errors are typically smaller than symbol size.

Ti$_5$Al$_2$C$_3$, Ti$_3$AlC$_2$ and Ti$_2$AlC in the multiphase sample, along with $U_{\text{iso}}$ for pure Ti$_3$AlC$_2$. Also shown are the experimental $U_{\text{eq}}$ values for the Al-containing phases Ti$_2$AlN and Ti$_4$AlN$_3$, determined from previous HTND studies [50, 52], along with calculated values for those phases from Ref. [45]. The $U_{\text{iso}}$ values for Al in the three Ti–Al–C phases are similar to each other, and slightly higher than $U_{\text{eq}}$ of for Al in the Ti–Al–N phases, which is consistent with the values determined from first-principles calculations. Note that the calculated $U_{\text{iso}}$ curves for Al in Ti$_5$Al$_2$C$_3$, Ti$_2$AlC, and Ti$_3$AlC$_2$ in Fig. 7 lie essentially on top of one another, and those for Al in Ti$_2$AlN and Ti$_4$AlN$_3$ are similar as well, but smaller than those of the carbide phases.

IV. DISCUSSION

A. Lattice parameters, expansions, and anisotropies

Not surprising, the measured $a$- and scaled $c$-parameters of the 523 phase are in between those of the 211 and 312 phases [Fig. 5(b)]. This is also consistent with the val-
TABLE II. Thermal expansions from HTND for Ti–Al–C phases in the sample studied in this work, along with those from other studies \cite{26, 28–30, 47, 48} determined through HTXRD and dilatometry. Numbers in parentheses are estimated standard deviations in the last significant digit of the refined parameters.

| Phase       | $\alpha_a$ (10^{-6} K^{-1}) | $\alpha_c$ (10^{-6} K^{-1}) | $\alpha_{av}$ (10^{-6} K^{-1}) | Anisotropy Ref. | Ref.     |
|-------------|-------------------|-------------------|-------------------|----------------|---------|
| Ti$_5$Al$_2$C$_3$ | 9.1(1)$^\dagger$ | 9.8(1)$^\dagger$ | 9.3(1)$^\dagger$ | 1.08(3)$^\dagger$ | This work |
| Ti$_2$AlC   | 9.0(1)$^\dagger$ | 9.6(1)$^\dagger$ | 9.2(1)$^\dagger$ | 1.07(3)$^\dagger$ | This work |
| Ti$_3$AlC$_2$ | 7.1(3)$^a$   | 10.0(5)$^a$   | 8.1(5)$^{a,b}$, 8.2(2)$^c$ | 1.41(4)         | Ref. [28] |
| Ti$_3$AlC$_2$ | 8.6(1)$^\dagger$ | 9.7(1)$^\dagger$ | 9.0(1)$^\dagger$ | 1.13(3)$^\dagger$ | This work |
| Ti$_3$AlC$_2$ | 7.6(1)       | 9.0(1)       | 8.1(1)       | 1.18(3)       | This work |
| Ti$_3$AlC$_2$ | 8.3(1)$^a$   | 11.1(1)$^a$   | 9.2(1)$^{a,b}$, 7.9(5)$^c$ | 1.33(1)$^a$ | Ref. [29] |
| Ti$_3$AlC$_2$ | -             | -             | 9.0(2)$^c$   | -              | Ref. [30] |
| Ti$_3$AlC$_2$ | 8.5           | 10.2          | 9.2$^b$      | 1.2            | Ref. [26] |
| Ti$_3$AlC$_2$ | 10.7(1)$^\dagger$ | 11.5(1)$^\dagger$ | 11.0(1)$^\dagger$ | 1.074(3)$^\dagger$ | This work |
| Ti$_3$AlC$_2$ | 9.77          | 9.26          | -             | -              | Ref. [47] |

$^\dagger$ Multiphase sample.

$^a$ High-temperature XRD.

$^b$ Assuming $\alpha_{av} = (2/3\alpha_a + 1/3\alpha_c) = V_0^{-1/3}dV^{1/3}/dT$.

$^c$ Dilatometry.

uses from our first-principles calculations (Table III). Our lattice parameters are in good agreement with literature values for Ti$_2$AlC \cite{21, 27, 28}, Ti$_5$Al$_2$C$_3$ \cite{21}, and Ti$_3$AlC$_2$ \cite{15, 21}. Their order of increase is likely due to intricacies in charge transfer involved in bonding. The fact that the $a$ lattice parameter scales with the number of Ti–C bonds is consistent with first principles calculations \cite{21}.

The overall expansions of the three MAX phases in the multiphase sample are, within their error bars, nearly equivalent (Table II). The $a$ and $c$ lattice expansions are qualitatively comparable, with the $a$ lattice parameters and their thermal expansions all within 1% of each other [Fig. 5(a)]. Consistent with previous studies, the expansion in the $c$ direction is greater than along the $a$. However, for reasons discussed below, in the present study the degree of anisotropy is lower than in Refs. [28–30] (Table II). We now consider each of the phases separately.

**Ti$_2$AlC:** The TECs along the $a$- and $c$-direction for the Ti$_2$AlC sample measured herein – 9.6(±0.1) × 10^{-6} K^{-1} and 8.9(±0.1) × 10^{-6} K^{-1} respectively [Fig. 6(c)] – fall in between those reported previously for Ti$_2$AlC (Ref. [28]). The reason(s) for the discrepancy is unknown at this time but could very well reflect differences in chemistry. Recent work in the literature suggests that Ti$_3$AlC exists over a range of stoichiometries. For example, Bai et al. recently reported the existence of a Ti$_3$AlC$_x$ phase where $x$ was as low as 0.69 \cite{53, 54}. Herein, it is more likely than not that the Ti$_2$AlC is Al-deficient since it is believed that the loss of Al is what triggers the transformation to the 523 and possibly the 312 phase.

**Ti$_3$AlC$_2$:** The TEC values measured herein for the 312 phase depended on sample. The predominantly single-phase Ti$_3$AlC$_2$ sample has a lower expansion in both directions, resulting in a statistically significant lower $\alpha_{av}$ of 8.1(±0.1) × 10^{-6} K^{-1} (Fig. 6). At 9.0(±0.1) × 10^{-6} K^{-1}, $\alpha_{av}$ for the 312 phase in the multiphase sample is about 10% higher than in the single phase one.

**Ti$_5$Al$_2$C$_3$:** Since this is the first report on the effect of temperature on the lattice parameters of the 523 phase, there are no previous results to compare them with. However, the fact that $\alpha_{av}$ of this phase is very comparable to the 211 and 312 phases is not surprising and is consistent with the fact that the former is comprised of the same building blocks as the latter.

Lastly, a few remarks on the expansions. The ability to measure phase sensitive TECs is an advantage of HTND, as compared to other methods such as dilatometry, that require pure phases to measure their volume TECs. However, it is important to appreciate that the TEC values measured herein per force are less anisotropic than those one would measure in loose powders. In the latter case, the solid is free to expand, whereas when the measurement is made on bulk solids, residual stresses can accrue and reduce the values of the thermal expansions in various directions. The effect is best appreciated when the TECs in the $a$ and $c$ directions are compared with those measured on powder Ti$_2$AlC samples [29].

**B. Bond lengths**

While the overall expansions and anisotropies in the three MAX-like phases are comparable, the most interesting aspect of this work is the relationship between bond length evolution and the stacking of the octahedra.
FIG. 6. Temperature dependences of the thermal strains of the lattice parameters and interatomic distances in (a) Ti₅Al₂C₃, (b) Ti₃AlC₂, and (c) Ti₂AlC for the multiphase sample. In (b), the results for predominantly single-phase Ti₃AlC₂ are also shown. (d) Volume expansion of Ti₅Al₂C₃ (blue circles), Ti₃AlC₂ (red solid squares), Ti₂AlC (black diamonds), and (Ti₀.₅Al₀.₅)Al (green triangles) in the multiphase sample, and pure Ti₃AlC₂ (open red squares). Room temperature (25°C) values were extrapolated to use for $L_0$ and $V_0$. Errors for volume expansions in (d) are typically smaller than symbol size.

among the three phases. In the literature, it is fairly well established, both experimentally and theoretically, that the $M$–$C$ bonds adjacent to the $A$ layers (i.e. Ti₁–C in Fig. 1) are shorter than those in the stoichiometric binary $MX$, while the ones that are not, (viz. Ti₂I–C, in Fig. 1) are longer. Figure 5(c) and the Ti–C lengths in Table IV are fully consistent with this general conclusion. Not surprisingly, the Ti–C bond lengths in the 211 slab in the 523 phase are almost identical to those of the 211 phase [Fig. 5(c)]. Similarly, the Ti–C bond lengths in the 312 phase are very similar to those of the 312 slabs in the 523 phase [Fig. 5(c)]. This applies not only to the absolute Ti–C bond lengths values but also to their thermal expansions, which are quite comparable as well [Fig. 1(c)]. It should be noted that the longest bonds in the 312-stacked octahedra in Ti₅Al₂C₃ are slightly shorter than $r_{Ti_{II}–C}$ in Ti₃AlC₂, while the Ti–C bonds in the 211-stacked octahedra in Ti₅Al₂C₃ are slightly longer than those in Ti₂AlC [Fig. 5(c)]. This suggests that the structure is slightly more uniform than the individual 211- and 312-stacked phases due to the interleaved nature of the stacking sequences. These comments notwithstanding, it is clear from Fig. 5(c) that the same structural units behave similarly. These results are gratifying because they indirectly validate our Rietveld analysis.

The situation for the Ti-Al bonds is not as clear. Since
the difference between the 211 and 312 phases is the number of Ti–C octahedra between Al layers, it is expected that only the Ti–C bonds would be significantly affected by the change in Ti–C stacking while the Al–Ti bonds should be similar among the three phases. However, we find that the Al–Ti bonds are clearly affected by stoichiometry [Fig. 5(d)]; $r_{\text{Ti} \text{– Ti}}$ is significantly longer in the 211 phase [black diamonds in Fig. 5(d)] than in the 312 phase [red crosses in Fig. 5(d)], while the opposite is true of those bonds in the 523 phase; i.e., $r_{\text{Al} \text{– Ti}} > r_{\text{Al} \text{– Ti}}$ in Ti$_5$Al$_2$C$_3$ [compare blue circles and blue squares in 5(d)]. The reasons for this state of affairs are not fully understood, but are likely related to the following observations:

(i) The Ti–C bonds are relatively stiff building blocks of the individual 312 and 211 units, as evidenced by the fact that they stay relatively the same size as in the original Ti$_3$AlC$_2$ and Ti$_2$AlC phases when the stacking sequences are interleaved. The dimension within the crystal that thus has the most flexibility is the Al–Ti bond. Therefore, it is likely that the Al–Ti bond plays a role as an effective “compensating spring” in the structure to minimize the crystal energy. Furthermore, this role would be different – and most probably more dominant – in the more complex Ti$_5$Al$_2$C$_3$ higher-order phase.

(ii) Among the possible factors that could be compensated for in the flexible Al–Ti bond discussed above are those related to constraints on the lattice parameters – especially on the c-lattice parameter, which essentially determines the Al–Ti bond length, given that the Ti–C octahedra are rigid blocks. In a sample with multiple competing phases, it is likely that these effects are prominent and manifest themselves in the Al–Ti bond.

(iii) The Al atoms in Ti$_2$AlC and Ti$_3$AlC$_2$ lie in a mirror plane within the structures, while Al is not constrained to mirror symmetry between the Ti–C atoms in the Ti$_5$Al$_2$C$_3$ phase (see Fig. 1). Therefore, the changes in the Al–Ti distances in the 211-stacked and 312-stacked structures that occur when they are interleaved to form 523 may be a consequence of the symmetry break.

These comments notwithstanding, it is important to note that the average Ti–Al bond length in 523 (2.863 Å) is equal the average of the Al–Ti bond lengths in 312 and 211 (also 2.863 Å). The average expansions of those bonds are also similar (see below). While more work is needed to fully understand the Al–Ti bond length behavior, it can be reasonably concluded that the dimensions of the Ti–C units are consistent for a given stacking, regardless of whether they are interleaved in a higher-order phase or in a conventional MAX phase. Based on this fact and the inconsistency of the Al–Ti bonds, it is further speculated that the Al–Ti bonds serve to compensate other energy minimization factors for the crystal, especially those related to symmetry and lattice constraints.

C. Bond expansions

In Ti$_2$AlC and Ti$_3$AlC$_2$, the Al–Ti bonds show the highest expansion [see Table II and Figs. 6(b) and 6(c)]. To our knowledge, there are no previous reports of temperature-dependent bond lengths in any of the Ti–Al–C MAX phases to which to compare our results. However, in a previous HTND study of the nitride Ti$_2$AlN, the Al–Ti bond also showed a higher expansion rate than the
TABLE III. Temperature-dependent $a$ and $c$ lattice parameters from Rietveld refinement of neutron diffraction data collected during heating and cooling. Numbers in parentheses are estimated standard deviations in the last significant figure of the refined parameters. Room temperature values are extrapolated to 25°C from linear interpolation.

| Temp. (°C) | $a$ (Å) | $c$ (Å) | $a$ (Å) | $c$ (Å) | $a$ (Å) | $c$ (Å) |
|-----------|---------|---------|---------|---------|---------|---------|
| RT (Ref. [15]) | - | - | - | - | 3.0753 | 18.578 |
| RT (Ref. [27]) | - | - | 3.065(4) | 13.71(3) | - | - |
| RT (Ref. [28]) | - | - | 3.051 | 13.637 | - | - |
| RT (Ref. [21]) | 3.064(2) | 48.23(2) | 3.063 | 13.645 | 3.060 | 18.66 |
| RT (Ref. [21]) | 3.068 | 48.186 | 3.067 | 13.75 | 3.083 | 18.661 |
| RT<sup>a</sup> | 3.05678 | 48.189 | 3.05405 | 13.6422 | 3.06186 | 18.4994 |
| 100 | 3.05926(6) | 48.237(1) | 3.05656(7) | 13.6551(5) | 3.06424(8) | 18.5172(8) |
| 200 | 3.06184(6) | 48.280(1) | 3.05912(7) | 13.6609(4) | 3.06667(8) | 18.5331(8) |
| 300 | 3.06419(6) | 48.317(1) | 3.06141(7) | 13.6777(5) | 3.06887(8) | 18.5483(8) |
| 400 | 3.06642(6) | 48.354(1) | 3.06353(7) | 13.6945(4) | 3.07108(8) | 18.5617(8) |
| 500 | 3.06911(6) | 48.400(1) | 3.06566(7) | 13.7120(5) | 3.07359(8) | 18.5803(8) |
| 600 | 3.07208(6) | 48.449(1) | 3.06920(7) | 13.7145(4) | 3.07635(8) | 18.5991(8) |
| 700 | 3.07501(6) | 48.497(1) | 3.07206(7) | 13.7280(4) | 3.07908(8) | 18.6184(8) |
| 800 | 3.07814(6) | 48.554(1) | 3.07510(7) | 13.7431(5) | 3.08213(8) | 18.6380(8) |
| 900 | 3.08141(6) | 48.608(2) | 3.07825(7) | 13.7581(5) | 3.08519(8) | 18.6587(9) |
| 1000 | 3.08460(6) | 48.667(2) | 3.08126(7) | 13.7743(5) | 3.08818(8) | 18.6811(9) |
| 800<sup>c</sup> | 3.08786(6) | 48.559(2) | 3.07552(7) | 13.7453(5) | 3.08264(9) | 18.6404(9) |
| 600<sup>c</sup> | 3.07301(6) | 48.459(2) | 3.06978(7) | 13.7180(5) | 3.07730(9) | 18.6025(9) |
| 400<sup>c</sup> | 3.06770(6) | 48.368(2) | 3.06753(7) | 13.6922(5) | 3.07200(9) | 18.5684(9) |
| 200<sup>c</sup> | 3.06239(6) | 48.279(2) | 3.05928(7) | 13.6672(5) | 3.06712(9) | 18.5337(9) |

<sup>a</sup> DFT calculations.
<sup>b</sup> Extrapolated value.
<sup>c</sup> Data collected during cooling.

Ti–N bond [50]. Similarly, a higher expansion rate was observed for the A–M bonds than the M–C bonds in Ti$_2$SiC$_2$ [49] and Cr$_2$GeC [50]. This result is also consistent with a high-pressure XRD study of Ti$_3$AlC$_2$, where the Al–Ti bond was the most compressible, while the Ti–C and Ti$_3$–C bonds were more rigid [55].

In Ti$_3$AlC$_2$, the expansion rate of the Al–Ti bond – 14.6 $\times 10^{-6}$ K$^{-1}$ – is the highest of all the bonds in the sample, but the Al–Ti$_3$ bond expansion is unexpectedly low, at 5.5 $\times 10^{-6}$ K$^{-1}$ (Table IV). Nonetheless, the average bond expansion in 523 (10.5 $\times 10^{-6}$ K$^{-1}$) is still similar to the 211 and 312 average (11.3 $\times 10^{-6}$ K$^{-1}$). Also note that the error bars for the Ti–Al bond expansions in Ti$_5$Al$_2$C$_3$ are the highest of those for the bonds in all phases (see Fig. 6). This uncertainty further suggests that the Al–Ti bond behavior is flexible within the structure and indicates other crystal imperfections and/or symmetry and lattice dimension effects, as discussed above.

D. Atomic displacement parameters

The results in Fig. 7 show that, like all other MAX phases studied to date, the A atom – Al in this case – is a rattler in that it vibrates with a significantly higher amplitude than the other atoms in the structures. The high ADPs of Al, both calculated and experimental, relative to the Ti and C atomic displacement values [Figs. 7(a)-(c)] are also consistent with the relatively weaker Al bonding evidenced by the higher Al–Ti expansion rates, at least in Ti$_3$AlC and Ti$_3$AlC$_2$ (Table IV) and the flexibility of the Al–Ti interaction, as discussed above.

Previous HTND studies of Ti$_3$SiC$_2$ [49, 51], Ti$_3$GeC$_2$ [49], Ti$_2$AlN [50], Cr$_2$GeC [50], and Ti$_3$AlN$_3$ [52] have shown the same rattling phenomenon for the A-group element. A comparison of the vibrational behavior of Al with two other HTND studies of the Al-containing nitrides Ti$_2$AlN and Ti$_4$AlN$_3$ (Fig. 8) further suggests that this “rattling” effect is independent of stacking sequence.

The results shown in Figs. 7 and 8 also clearly indicate that from a theoretical point of view, the ADPs of the three MAX phases should be very comparable. Given that the Al atoms in Ti–Al–N nitrides are also predicted to behave similarly to one another – but different from the carbides – in their vibrational amplitudes (see lines for Ti$_2$AlN and Ti$_4$AlN$_3$ in Fig. 8), the DFT calculations indicate that the ADPs of Al should not be greatly influenced by stoichiometry. Interestingly, the agreement between theoretical and experimental isotropic ADPs for the Al atoms is quite good in all five compounds plotted in 8. The agreement for the other atoms is less good for reasons that are not well understood, but are typical of...
TABLE IV. Interatomic distances in Ti5AlC2, Ti2AlC, and Ti3AlC2 in the multiphase sample from Rietveld refinement of neutron diffraction data collected during heating and cooling, along with their expansions. All values are extrapolated to 25°C from linear interpolation. Numbers in parentheses are estimated standard deviations in the last significant digit of the refined parameters.

| Phase       | Bond       | Bond length (Å) | Bond expansion$^\dagger$ (10$^{-6}$ K$^{-1}$) |
|-------------|------------|-----------------|--------------------------------------------|
| Ti5Al2C3    | Al–TiI     | 2.878           | 14.6                                       |
|             | Al–TiII    | 2.848           | 5.5                                        |
|             | Ti–C1      | 2.079           | 8.8                                        |
|             | Ti–C3      | 2.180           | 8.1                                        |
|             | TiIII–CIII | 2.106           | 10.0                                       |
| Ti2AlC      | Al–TiI     | 2.873           | 10.8                                       |
|             | Ti–C       | 2.101           | 7.7                                        |
| Ti3AlC2     | Al–TiI     | 2.854           | 11.8                                       |
|             | Ti–C       | 2.087           | 6.8                                        |
|             | TiIII–CII  | 2.182           | 8.8                                        |

$^\dagger$ Bond expansion: $L^{-1} \cdot dL/dT$ from least-squares fit of $\Delta L/L_0$ vs. $T$.

the MAX phases [45].

V. SUMMARY AND CONCLUSIONS

Rietveld analysis of HTND data for a bulk sample containing Ti5Al2C3 [38(±1) wt.%], Ti2AlC [32(±1) wt. %], Ti3AlC2 [18(±1) wt. %], and (Ti0.5Al0.5)Al [12(±1) wt.%] has shown that Ti5Al2C3 exhibits similar thermal expansion and thermal motion parameters as Ti2AlC and Ti3AlC2. The thermal expansions for Ti5Al2C3 in the α- and c- directions, respectively, are $\alpha_\alpha = 9.1(±0.1) \times 10^{-6}$ K$^{-1}$ and $\alpha_c = 9.8(±0.1) \times 10^{-6}$ K$^{-1}$. In all three phases, the average expansion rates of all the Al–Ti bonds are higher than the average Ti–C bond expansions. Ti5Al2C3 consists of alternating layers of 312- and 211-like stacking, where the 312 layers are similar to Ti3AlC2 and the 211 layers are similar to Ti2AlC in dimensions and bond expansions. The Al atoms in all three phases vibrate with higher amplitudes than the Ti and C atoms. This work shows that Ti5Al2C3 exhibits similar properties to Ti3AlC2 and Ti2AlC, two of the most promising MAX phases, which indicates that phase purity can be more relaxed in processing when considering applications. In addition, this work shows that further studies on Ti5Al2C3 can lead to enhanced property optimization and engineering for ternary carbides in the Ti–Al–C system.

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