

**LARGE SCALE SIMULATIONS OF THE MECHANICAL PROPERTIES OF  
LAYERED TRANSITION METAL TERNARY COMPOUNDS FOR FOSSIL ENERGY  
POWER SYSTEM APPLICATIONS**

**Wai-Yim Ching, Paul Rulis, Sitaram Aryal, and Yuxiang Mo**

**Department of Physics, University of Missouri-Kansas City, Kansas City, MO 64110  
(Contact information: 816-235-2503; chingw@umkc.edu)**

**Lizhi Ouyang,**

**Department of Mathematics and Physics, Tennessee State University, Nashville, TN 37209  
(Contact information: 615-963-7764; Louyang@Tnstate.edu)**

**ABSTRACT**

This paper reports the initiation of a new project in Advanced Materials under DOE-NETL support. The main objective of the project is to develop advanced materials for applications in fossil energy conversion technology under extreme conditions such as high temperature, high pressure, and corrosive environments using a computational approach. Investigation of a new class of materials called MAX phases, or  $M_{n+1}AX_n$  ( $M$  = a transition metal,  $A$  = Al,  $X$  = C or N) is proposed. The MAX phases are layered transition metal carbides or nitrides with some very outstanding properties due to their unique structural arrangements and directional bonding. Several crystals of the MAX phase compounds are targeted for initial study using two highly accurate *ab initio* methods. The Orthogonalized Linear Combination of Atomic Orbitals (OLCAO) method is used for the electronic structure and bonding studies; and the Vienna *Ab initio* Simulation Package (VASP) is used for the mechanical and vibrational properties. In this paper, we report results on two of these alloys,  $Ti_3AlC_2$  and  $Cr_2AlC$ .

## INTRODUCTION

Advanced materials with applications under extreme conditions such as high temperature, high pressure, and corrosive environments will play a critical role in the development of new technologies to significantly improve the performance of different types of power plants [1]. Materials that are currently employed in fossil energy conversion systems are typically the Ni-based alloys and stainless steels that have already reached their ultimate performance limits. Any incremental improvements are unlikely to meet the more stringent requirements aimed at increased efficiency and reduce risks while addressing environmental concerns and keeping costs low. Computational studies can lead the way in the search for novel materials or for significant improvements in existing materials that can meet those requirements. With sufficient predictive power such studies can provide the atomistic level understanding of the key ingredients that lead to desirable properties.

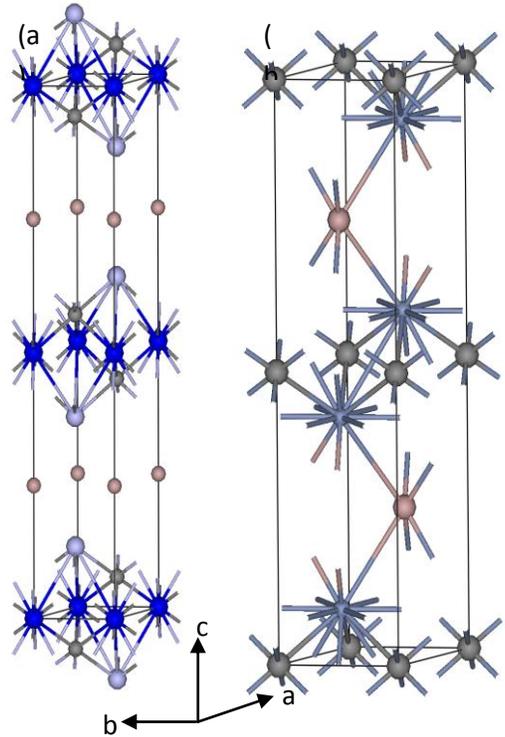
This project focuses on the computational development of a new class of materials called MAX phases, or  $M_{n+1}AX_n$  ( $M$  = a transition metal,  $A$  = Al,  $X$  = C or N) [2]. The MAX phases are layered transition metal carbides or nitrides with the rare combination of metallic and ceramic properties. Due to their unique structural arrangements and special types of bonding, these thermodynamically stable alloys possess some of the most outstanding properties such as damage-resistance, oxidation resistance, excellent thermal and electric conductivity, machinability, and fully reversible dislocation-based deformation [3-5]. These properties can be explored in the search for new phases and composites that can meet performance goals for applications in the next generation of fossil energy power systems.

In this project, we use accurate and robust computational techniques to address materials issues in the Advanced Research Program at the National Energy Technology Laboratory focusing on the MAX phases. Initially, we will investigate the alloys of  $Ti_3AlC_2$ ,  $Ti_2AlC$ ,  $Ti_3SiC_2$ ,  $Ti_2AlN$ , and  $Cr_2AlC$  crystals. Later on, other compounds such as Hf (Zr)-Al (Si)-C and Nb-based MAX phases may also be investigated based on the outcome of the initial phase of study. These compounds are chosen for their exceptional structural properties and demonstrated promise of high strength, high toughness, and ability to resist corrosion and oxidation at elevated temperatures. Since the focus is mainly on the mechanical properties, an important part of the research will be on carefully designed large-scale multi-axial simulations on supercomputers. At a later stage, investigation on the effects of microstructures such as grain boundaries, surfaces, and interphase boundaries with and without impurity segregations in the MAX phase compounds will be conducted. A prerequisite for such studies is knowledge of the fundamental electronic structure and lattice dynamics based on first principles calculations. In this paper, we report some preliminary results that have been obtained on two MAX phase compounds,  $Ti_3AlC_2$  and  $Cr_2AlC_2$ .

## COMPUTATIONAL PROCEDURES

There are more than 70 phases of MAX compounds [4]. In the initial phase of investigation, we start with two of the most important crystals,  $\text{Ti}_3\text{AlC}_2$  and  $\text{Cr}_2\text{AlC}$ . The crystal structures of these two crystals are sketched in Fig. 1 and their lattice parameters are listed in Table I. Both have layered structures of Ti (Cr), Al, and C atoms in a hexagonal lattice. In  $\text{Ti}_3\text{AlC}_2$ , there are two Ti sites (Ti1 and Ti2) whereas in  $\text{Cr}_2\text{AlC}$  there is only one Cr site. Thus the key difference between them is the additional metal-carbon layer in  $\text{Ti}_3\text{AlC}_2$  and the number of  $d$  electrons in Ti and Cr.

Two well established computational methods based on density functional theory are used for this study: The Orthogonalized Linear Combination of Atomic Orbitals (OLCAO) method [6] and the Vienna *Ab initio* Simulation Package (VASP) [7]. These two methods have different strengths and are used for different purposes. The combination of the two has proven to be extremely effective for studying the properties of many complex materials. The OLCAO method was developed at the University of Missouri-Kansas City and is used for studying the underlying electronic structure and bonding of the MAX phase compounds. The use of atomic orbitals in the basis expansion makes it easy to obtain effective charge and bond order values using the Mulliken scheme [8]. VASP is a plane-wave based method using pseudopotentials and is most effective for force calculation and geometry optimization [9]. It is mainly used for the mechanical properties and phonon spectral calculations in conjunction with other available methods. With additional methods to be developed and incorporated, we can meet the ambitious goals set for this project.



**Fig. 1: Crystal structure of (a)  $\text{Ti}_3\text{AlC}_2$  with dark blue = Ti1, light blue = Ti2; (b)  $\text{Cr}_2\text{AlC}$  with purple = Cr. For both (a) and (b) Pink = Al and grey = C and the same axial orientation can be used.**

## RESULTS

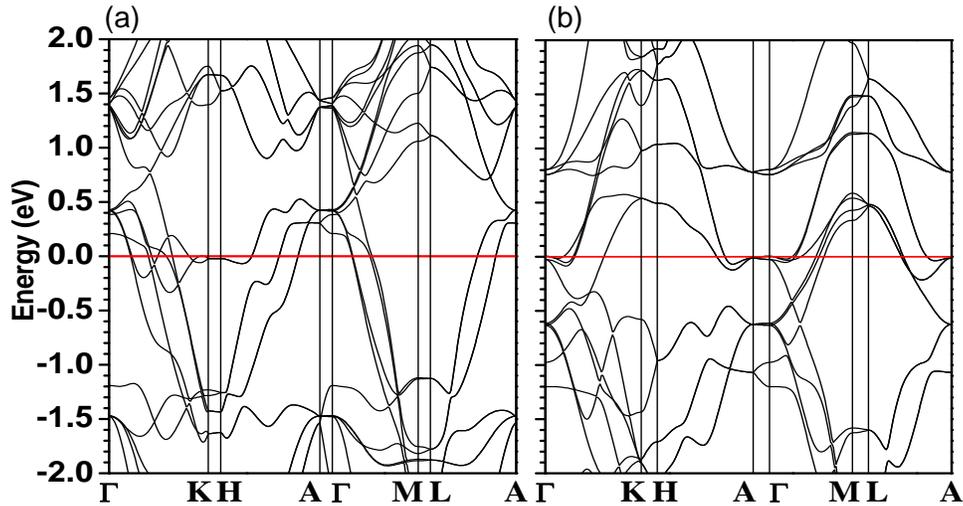
### (1) Electronic structure and bonding in $\text{Ti}_3\text{AlC}_2$ and $\text{Cr}_2\text{AlC}$

Table I summarizes the lattice parameters, the calculated effective charges  $Q^*$  in each atom, the bond order (BO) values between atomic pairs and the corresponding bond lengths (BLs), and the density of states (DOS)  $N(E_f)$  at the Fermi level in the two crystals. The BO values provide information on the strength of particular bonds and the DOS at the Fermi level  $N(E_f)$  is related to the stability and the conductivity of the crystal. It can be further broken down into s, p, and d orbital components.

**Table 1.** Lattice parameters and calculated  $Q^*$ , BO, and  $N(E_F)$  in  $Ti_3AlC_2$  and  $Cr_2AlC$ .

Crystal	$Ti_3AlC_2$	$Cr_2AlC$
Lattice type:	Hexagonal	Hexagonal
Lattice vector a,b:	3.0753 Å	2.858 Å
Lattice vector c:	18.578 Å	12.818 Å
Effective Charge ( $Q^*$ ) (electrons):		
	Ti1 3.39	Cr 5.91
	Ti2 3.66	-
	Al 2.97	2.67
	C 4.66	4.52
Bond Order (BO) (electrons) and Bond Length (BL) (Å):		
	Ti1-C 0.205 (2.137 Å)	Cr-Cr 0.026 (2.754 Å)
	Ti2-Ti2 0.136 (3.075 Å)	Cr-Cr 0.098 (2.858 Å)
	Ti2-Al 0.153 (2.878 Å)	Cr-Al 0.147 (2.672 Å)
	Ti2-C 0.221 (2.137 Å)	Cr-C 0.199 (1.984 Å)
	Al-Al 0.122 (3.075 Å)	Al-Al 0.143 (2.858 Å)
Density of States at the Fermi Level $N(E_F)$ (states/eV-cell):		
	Ti-1 (s,p,d) 0.001, 0.004, 0.554	
	Ti-2 (s,p,d) 0.006, 0.107, 2.288	
	Cr (s,p,d)	0.000, 0.041, 5.930
	Al (s,p,d) 0.029, 0.292, 0.351	0.009, 0.222, 0.398
	C (s,p) 0.006, 0.179	0.004, 0.060
Total:	3.817	6.652

The calculated band structures for  $Ti_3AlC_2$  and  $Cr_2AlC$  are shown in Fig. 2. These band structures are typical of many metals, but these two systems do have some different features nonetheless. The greatest concentration of states at the Fermi level in  $Ti_3AlC_2$  is along the K-H line while for  $Cr_2AlC$  it is along the A- $\Gamma$  line. Both of these lines are oriented in the same direction in  $k$ -space, but they are in different regions of the first Brillouin zone. The K-H line is on the edge while the A- $\Gamma$  line is in the center.

**Fig. 2:** Band structure near the Fermi level (red line at zero eV) for (a)  $Ti_3AlC_2$ , and (b)

The calculated DOS and partial DOS (PDOS) of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Cr}_2\text{AlC}$  are in Fig. 3 and Fig. 4 respectively. They are quite different. The total DOS for  $\text{Ti}_3\text{AlC}_2$  at the Fermi level is at a minimum while for  $\text{Cr}_2\text{AlC}$ , it is a peak. This property is often used as a guide to the relative stability of the system and thus we can say that  $\text{Ti}_3\text{AlC}_2$  is more stable than  $\text{Cr}_2\text{AlC}$ . The question of where this peak in  $\text{Cr}_2\text{AlC}$  comes from is apparent from the  $e_g$  and  $t_{2g}$  resolved PDOS of the Cr atom shown in Fig. 4 (c). In  $\text{Ti}_3\text{AlC}_2$ , the  $e_g$  and  $t_{2g}$  state from the Ti 3d electrons are at higher energies. These issues will be further discussed in the next section.

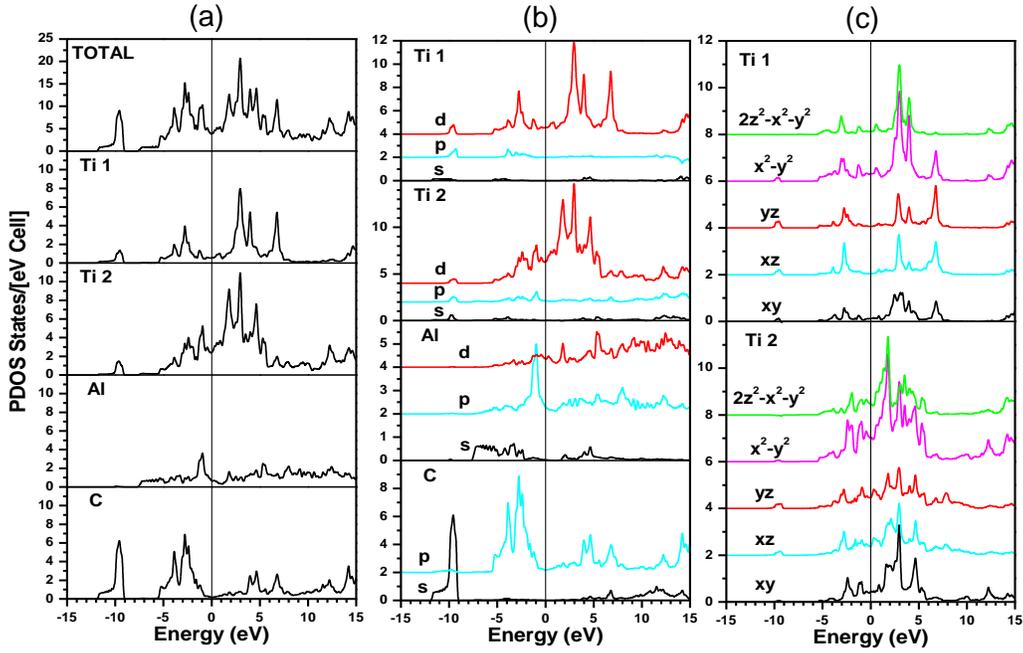


Fig. 3: DOS and PDOS of  $\text{Ti}_3\text{AlC}_2$ . (a) Total DOS and atomic type resolved PDOS; (b) Orbital resolved PDOS of each atomic type; (c)  $e_g$  and  $t_{2g}$  resolved d orbitals of Ti1 and Ti2.

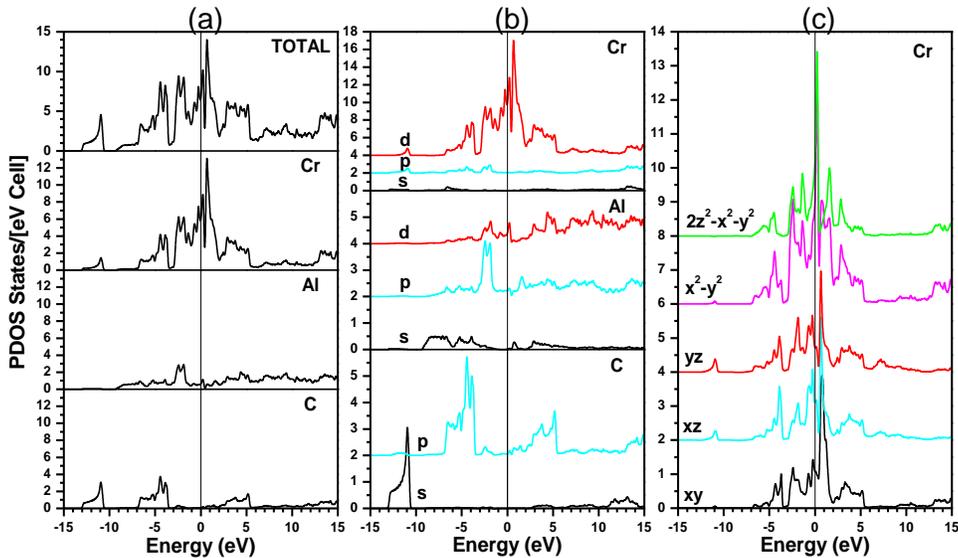


Fig. 4: DOS and PDOS of  $\text{Cr}_2\text{AlC}$ . (a) Total DOS and atomic type resolved PDOS; (b) Orbital resolved PDOS of each atomic type; (c)  $e_g$  and  $t_{2g}$  resolved d orbitals of Cr.

## (2) Elastic and mechanical properties in $\text{Ti}_3\text{AlC}_2$ and $\text{Cr}_2\text{AlC}$

The study of the mechanical properties of the MAX phase compounds starts with the calculation of the elastic constants for the crystal based on the stress vs. strain relationship. From the elastic constants, bulk mechanical properties in the form of the bulk modulus (K), shear modulus (G), Young's modulus (E), and the Poisson ratio ( $\eta$ ) can be obtained using the Voigt-Reuss-Hill approximation [10]. Table 2 below lists the calculated elastic tensors and the mechanical properties for  $\text{Ti}_3\text{AlC}_2$  and  $\text{Cr}_2\text{AlC}$  which are in agreement with the published values. It is noted that  $\text{Cr}_2\text{AlC}$  has larger moduli than  $\text{Ti}_3\text{AlC}_2$  and is therefore presumably a stronger material. It will be interesting to see if this improvement in the mechanical properties is due to the crystal structure of the MAX phase (312 vs. 211), or if it is due to the presence of Cr which has a larger  $3d$  electron number than Ti. Multiaxial tensile experiments on both crystals can reveal more details about its mechanical properties.

<b>Table 2</b> Calculated elastic constants $C_{ij}$ and bulk parameters in $\text{Ti}_3\text{AlC}_2$ and $\text{Cr}_2\text{AlC}$ in GPa.										
	$C_{11}$	$C_{33}$	$C_{13}$	$C_{12}$	$C_{44}$	$C_{66}$	K	G	E	$\eta$
$\text{Ti}_3\text{AlC}_2$	354.3	295.4	76.3	82.0	122.3	136.1	163.0	127.1	302.7	0.191
$\text{Cr}_2\text{AlC}$	351.3	371.2	121.9	73.8	134.2	138.8	189.1	131.3	319.9	0.218

## (3) Phonon spectra of $\text{Ti}_3\text{AlC}_2$ and $\text{Cr}_2\text{AlC}$

The investigation of the temperature dependent properties of a crystal starts with lattice dynamics in the quasi harmonic approximation (QHA) [11]. We have calculated the *ab initio* phonon spectra and phonon DOS for  $\text{Ti}_3\text{AlC}_2$  and  $\text{Cr}_2\text{AlC}$  which are shown in Fig. 5. The phonon DOS can be divided into two regions separate by a gap of about  $160\text{ cm}^{-1}$  and  $220\text{ cm}^{-1}$  respectively for the two crystals. The vibrational modes in the upper region are associated with the lighter C atoms, and those in the lower segment come from the heavier Al and Ti (Cr) atoms. The upper portion of the phonon DOS in  $\text{Cr}_2\text{AlC}$  are at a slightly higher frequency indicating

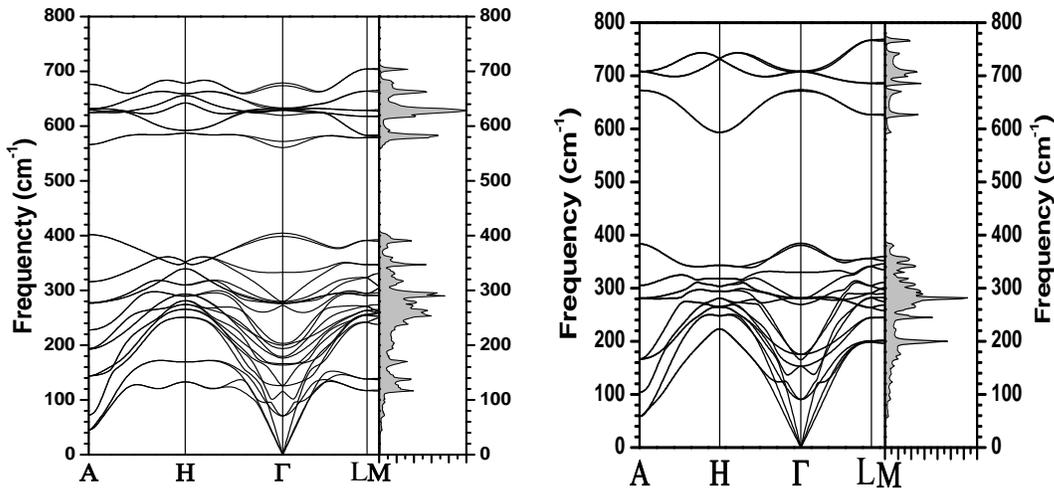


Fig. 5: Phonon dispersion and phonon DOS of  $\text{Ti}_3\text{AlC}_2$  (left) and  $\text{Cr}_2\text{AlC}$  (right).

stronger Cr-C vibrational modes. The sharp peaks in the DOS are indicative of a strong preference for particular modes that have not yet been fully identified. The phonon spectra for the two crystals are quite similar except near the H point where  $\text{Ti}_3\text{AlC}_2$  has two flat phonon branches. This could be due to the different local environments of Ti1 and Ti2 in the layered structure. The specific phonon frequencies  $\hbar\omega_j$  within the Brillouin zone and can be used to evaluate the temperature dependent properties.

## DISCUSSION

The electronic structure results shown in the previous section provide the rich details of the atomic scale bonding information in these two crystals and the role played by the local geometry as well as the number of the  $d$  electrons in the transition metal element Ti or Cr. This is most evident in the calculated effective charges of Al and C. In  $\text{Cr}_2\text{AlC}$ , Al loses more charge than in  $\text{Ti}_3\text{AlC}_2$  and the C atom in  $\text{Ti}_3\text{AlC}_2$  gains fewer electrons than in  $\text{Cr}_2\text{AlC}$ . The Ti2-C bond has a larger BO value than the Cr-C bond, even though the later has a shorter bond length. Also to be noted is the considerable contribution to the total bonding in the crystal between metallic ions which have a varying number of bonds in these two crystals. Taking the crystal as a whole,  $\text{Cr}_2\text{AlC}$  has a larger total BO in the cell than  $\text{Ti}_3\text{AlC}_2$ , a fact consistent with the stronger mechanical properties calculated. On the other hand, the Fermi level in  $\text{Ti}_3\text{AlC}_2$  resides in a valley in the DOS while it is near a very sharp peak of the  $e_g$  states in  $\text{Cr}_2\text{AlC}$ . Conventional wisdom implies that  $\text{Cr}_2\text{AlC}$  is less stable than  $\text{Ti}_3\text{AlC}_2$  and its properties could vary significantly as a function of the change in temperature and pressure.

The calculated phonon spectra at the zero temperature can provide the starting point for investigating the temperature dependent properties. One approach is to use the temperature and pressure dependent isothermal coefficient of expansion to obtain the structures at higher temperature and use a similar numerical method to calculate the mechanical properties of these structures. Such calculations will be computationally very demanding and require investment in new computational algorithms and codes. Another new and innovative idea is to develop a method to construct a failure envelop for a crystal in the stress space using multi-axial data. The construction of such an envelope enables us to describe the strength of a material in a simple picture that will facilitate the search for new materials. Such simulations are much more realistic for the deformation behavior which is expected to be nonlinear, complex, and highly anisotropic in the MAX phase compounds. This approach is currently under consideration.

## CONCLUSION

This new three-year project is divided into two phases. We are currently in the first phase which focuses on the fundamental electronic structure and mechanical properties of the five most important MAX phases. In this paper, we have reported some results for  $\text{Ti}_3\text{AlC}_2$  and  $\text{Cr}_2\text{AlC}$  while investigations on the other phases are in progress. Our rather comprehensive results demonstrate that the physical properties of these new intermetallic alloys can be explained and

are intimately related to their local atomic scale electronic structure and vibrational spectra. These calculations, which are based on fundamental quantum mechanics, will have sufficient predictive power in the search for better materials. More importantly, the techniques we develop and demonstrate will enable us to study the same materials but with the addition of defects or in conjunction with the effects of a harsh environment. These circumstances succinctly describe the goal of the entire project.

## ACKNOWLEDGEMENTS

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