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# Phase stability and elastic properties of Cr–V alloys

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#### Abstract

V is the only element in the periodic table that forms a complete solid solution with Cr and thus is particularly important in alloying strategy to ductilize Cr. This study combines first-principles density functional theory calculations and experiments to investigate the phase stability and elastic properties of Cr–V binary alloys. The cluster expansion study reveals the formation of various ordered compounds at low temperatures that were not previously known. These compounds become unstable due to the configurational entropy of bcc solid solution as the temperature is increased. The elastic constants of ordered and disordered compounds are calculated at both T = 0 K and finite temperatures. The overall trends in elastic properties are in agreement with measurements using the resonant ultrasound spectroscopy method. The calculations predict that addition of V to Cr decreases both the bulk modulus and the shear modulus, and enhances the Poisson's ratio, in agreement with experiments. Decrease in the bulk modulus is correlated to decrease in the valence electron density and increase in the lattice constant. An enhanced Poisson's ratio for bcc Cr-V alloys (compared to pure Cr) is associated with an increased density of states at the Fermi level. Furthermore, the difference charge density in the bonding region in the (110) slip plane is highest for pure Cr and decreases gradually as V is added. The present calculation also predicts a negative Cauchy pressure for pure Cr, and it becomes positive upon alloying with V. The intrinsic ductilizing effect from V may contribute, at least partially, to the experimentally observed ductilizing phenomenon in the literature.

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Ductilizing brittle Cr through alloying strategy requires that alloying elements are soluble in Cr which has a body-centered cubic (bcc) crystal structure. One known difficulty in developing ductile Cr alloys [1-3] that also have strong creep and oxidation resistance for ultra-high temperature applications (>1200 °C) is that there are only a few elements in the periodic table, including V, Mn, Re, Ru and Os, that exhibit reasonably large solubility in binary Cr systems at low temperatures [4]. Most other elements are insoluble

(e.g. group 1–4, 11, 12) in Cr [4]. Some elements such as Ti, Fe, Mo, and W exhibit large solubility in Cr only at very high temperatures [4]. As the temperature is lowered, either topologically close-packed (TCP) phases (e.g. in Cr–Ti, Cr–Fe) or a very broad miscibility gap (e.g. in Cr–Mo, Cr–W) may form, which ultimately results in very small terminal solubility in Cr at low temperatures [4]. The only element that forms complete solid solution with Cr over the whole composition range without formation of compound or miscibility gap is V according to the report by Smith which is collected in the binary alloy phase diagram handbook [4] at  $T > 1750 \,^{\circ}\text{C}$ . Note that there are no experimental reports on temperatures below  $1750 \,^{\circ}\text{C}$ .

In fact, Matsumoto et al [1] examined the alloying effect of Ti, V, Mn, Fe, Co and Ni, where they found that V has the most pronounced ductilizing effect on Cr. They argued that the ductilizing effect of V was due to a scavenging effect; impurity atoms such as oxygen and nitrogen are trapped by vanadium atoms because of the strong affinity between them [1]. Utilizing mechanical alloying and hot isostatic pressing, Kurishita et al [5] fabricated a Cr-44.2V-1.8Y (wt%) alloy that achieved a yield strength of 610-740 MPa and a total elongation of 10-19% at room temperature. They attributed the success to: (1) removing the gaseous impurities of O and N at the powder surface, thereby reducing greatly impurity precipitation at grain boundaries; (2) absorbing residual O using Y in Cr by forming Y<sub>2</sub>O<sub>3</sub> dispersoids; and (3) creating relatively small grain sizes, i.e., 1.6–4.7  $\mu$ m depending on the annealing temperatures. Certainly a low concentration of the impurities of O and N and small grain sizes will improve Cr ductility extrinsically, however, the intrinsic effect due to Cr-V alloying has not been addressed in the open literature. More importantly, the complete solid solution of Cr-V binary alloys will provide a much wider array of alloying options since V also forms complete binary solid solution with Ti, Nb, Mo and W [4]. This further motivates the present study.

Previous first-principles electronic density functional theory (DFT) calculations on a series of hypothetical Cr<sub>15</sub>X<sub>1</sub> alloys showed that several transition metals including Ti, Hf, Ta, V, Zr and Nb enhance the Poisson's ratio of Cr more noticeably than others [3]. In this report, phase stability of the Cr-V binary system is first examined using DFT calculations. The cluster expansion method as implemented in ATAT developed by van der Walle and co-workers [6, 7] was used to search for stable structures at the ground state. Various Cr-V substitutional bcc compositions and hypothetical Cr-V compounds whose structures are taken from analogous binary phase diagrams associated with Cr are also considered. Providing the values of enthalpy of formation of these hypothetical compounds is very important in developing thermodynamic database using the CALPHAD (acronym of CALculation of PHAse Diagrams) method as practiced in other reports [8–10]. To mimic disordered Cr–V solid solution, the special quasi-random structure (SQS) method [11, 12] was used. Then the elastic properties of ordered and disordered bcc structures are calculated. To calculate temperature-dependent elastic constants of Cr-V alloys, an assumption was made that the dependence is mainly from volume change due to thermal expansion. Finally experiments are carried out to measure the elastic properties of single crystal and polycrystalline samples.

#### 2. Computational method

The first-principles package of VASP (Vienna *ab initio* simulation package) [13, 14] was used in this study which solves for the electronic band structure using

electronic density functional theory. Projector augmentedwave potentials [15] were used as supplied with VASP. The Perdew–Burke–Ernzerhof [16] gradient approximation to the exchange–correlation functional was used. Brillouin-zone integrations were performed using the Monkhorst–Pack k-point meshes [17] for most structures except hexagonal structures for which  $\Gamma$ -centered grids were used. A smearing parameter of 0.2 eV was chosen for the Methfessel–Paxton [18] technique.

Reciprocal space (k-point) meshes are increased to achieve convergence to a precision of better than 1 meV/at. All structures are fully relaxed (both lattice parameters and atomic coordinates) until energies converge to a precision of 1 meV/at. A 'high precision' setting is used except the cluster expansion search. The plane-wave energy cutoff is held constant at 500 eV which is about 2.5 times the default value for Cr or V (the default was used for the cluster expansion search). The semi-core 3p electrons of V and Cr are explicitly treated as valence. Electronic spin polarization with collinear magnetization or antiferromagnetism is considered in all calculations. It is experimentally known that element Cr has an unusual ground-state magnetic structure of an antiferromagnetic spin-density wave (SDW) (for reviews see [19] for Cr and [20] for Cr alloys). Various DFT methods have been used to study the magnetic structure of pure Cr (to list a few [21-23]). For simplicity, only antiferromagnetism of pure Cr is considered in this study.

To search ground-state structures at T = 0 K, the cluster expansion method as implemented in ATAT was used. The searching was done with a 'medium' precision and no magnetism was considered for fast calculations. The as-determined ground structures were then rerun in its unit cell that was constructed from the primitive cell with the 'high' precision aforementioned and an energy cutoff of 500 eV, and magnetism was considered.

In addition, 18 hypothetical compounds are selected whose structures are reported in Cr-TM (TM = transition metal) binary systems [4] (see tables 1 and 2), including AB<sub>2</sub> Laves phases Cu<sub>2</sub>Mg·cF24 (Strukturbericht designation C15), MgZn<sub>2</sub>·hP12 (C14) and MgNi<sub>2</sub>·hP24 (C36). Some bcc and fcc superstructures summarized by Sluiter [24] are also examined at the composition of 50 at.% V, e.g. CdTe·oP2, LiZn·cF16, GeLi·tI24. The structure notation in this report is {prototype or chemical formula}.{Pearson symbol}. The prototype is the name of some commonly known isostructural compound, and the Pearson symbol gives point symmetry, translational symmetry and number of sites per unit cell. To obtain enthalpy of formation values  $\Delta H_{\rm f}$ , a composition-weighted average of the pure elemental cohesive energies is subtracted from the cohesive energy of a given composition. The resulting energy is an 'enthalpy' because its volume is relaxed at zero pressure. The phase stability at 0 K is evaluated by a convex hull plot (see figure 1). Vertices of the convex hull of a scatter plot of  $\Delta H_{\rm f}$  versus composition identify stable structures.

To examine the effect of V substitution on the elastic properties of Cr, a  $2 \times 2 \times 2$  bcc supercell of Cr is built, and then individual Cr atoms are substituted by V atoms. The initial atomic positions for the solute atoms are listed below:

					Lattice parameter						
Phase symbol	V (at.%)	Prototype	Space group	$\Delta H_{\rm f}~({\rm meV/at})$	a (Å)	b (Å)	<i>c</i> (Å)	$\beta$ (degrees)			
	Stable structures (see figure 1(b))										
Cr <sub>4</sub> V·tI10	20		139	-48.5	2.873		14.410				
Cr <sub>3</sub> V·tP16	25		123	-59.4	2.878		23.125				
$Cr_2V \cdot tI6$	33.3		139	-76.9	2.888		8.707				
AuCu·oI40	50	AuCu	74	-76.4	2.914	4.118	41.292				
Cr <sub>3</sub> V <sub>4</sub> ·hR7	57.1		166	-72.2	4.133		17.794				
$Cr_2V_3 \cdot hR5$	60		166	-68.5	4.094		13.021				
CrV <sub>3</sub> ·mC16	75		12	-45.9	9.413	2.945	8.346	$\beta = 116.61$			
$(Cr_3V \cdot tP8)^a$	25		129	-59.0	2.878		11.563				
$(Cr_3V_2 \cdot oC20)^a$	40		63	-76.6	2.899	20.522	4.107				
$(Cr_1V_1 \cdot cP2)^a$	50		221	-75.4	2.915	(2.9435 [	<mark>66</mark> ])				
$(Cr_5V_5 \cdot oC20)^a$	50		65	-76.4	20.628	2.914	4.123				
		Unstable str	ructures (stable if ig	noring magnetism, se	e figure 1(a	a))					
$Cr_8V_1 \cdot mC18$	11.1		8	-22.9	12.155	2.864	6.403	$\beta = 108.44$			
$Cr_5V_1 \cdot mC12$	16.7		8	-38.8	9.082	2.870	5.743	$\beta = 108.44$			
$Cr_7V_2 \cdot tI18$	22.2		107	-51.2	2.876		25.956	P			
$Cr_8V_3 \cdot mC22$	27.3		8	-62.7	11.903	4.074	6.299	$\beta = 120.15$			
		Hypoth	etical structures tak	en from analogous pr	ototypes						
Cu <sub>3</sub> Pd·tP28	25	Cu <sub>3</sub> Pd	99	-56.8	4.075		20.163				
Cr <sub>4</sub> Pt·cP8	25	Cr <sub>3</sub> Si	223	87.6	4.606						
Co <sub>3</sub> Ta·cP4	25	AuCu <sub>3</sub>	221	383.4	3.673						
Cr <sub>2</sub> Ru <sub>2</sub> tP30 <sup>b</sup>	30	Cr <sub>2</sub> R <sub>11</sub>	136	98.1	4 666	8 906	8 930	$\alpha = 89.93$			
	50	01 <sub>2</sub> itu	150	2011	1.000	0.900	0.750	$\beta = 90.10$ $\gamma = 89.90$			
Cr <sub>2</sub> Zr·hP24	33.3	MøNia	194	58.2	4,753		15.485	/ 0/1/0			
Cr <sub>2</sub> Ti <sub>2</sub> h hl 21 Cr <sub>2</sub> Ti <sub>2</sub> hP12	33.3	MgZn <sub>2</sub>	194	70.6	4 740		7 790				
CraTicF24	33.3		227	54.6	6 714		1.170				
Cr.Nb.cE96	33.3	NiTi.	227	346.5	7 570						
NbD fIS	50	NbD	141	118.3	3 302		8 802				
LiZn.cE16	50	NoTI	227	_10.5	5 830		0.002				
GeL i.tI2/	50	GeLi	141	_48.2	4 121		17 /05				
CuTi.tP/	50	CuTi	120	-54.8	2 006		5 870				
CuDt bD6	50	CuPt	129	-5 <del>4</del> .0	2.900		11 333				
$C_{r}$ Db. bD2	50	Ma	100	201.4	2.191		11.555				
$C_1 2 K_{113} \cdot H_{117} 2$	50	CdTa	194	555.2 627.0	2.330	4 617	4.008				
	50		23	51.0	2.501	4.017	2.420	00.00			
$Cr_2 rc_3 \cdot tP30^{-1}$	30.7	CrFe	130	51.9	4.722	9.047	9.036	$\alpha = 90.09$			
								p = 90.11			
CrPt <sub>3</sub> ·cP4	75	AuCu <sub>3</sub>	221	298.5	3.770			$\gamma = 90.11$			
	Ordered	structures based	on $2 \times 2 \times 2$ bcc su	percell and disordere	d structure	s using bcc S	SQS				
Cr <sub>15</sub> V <sub>1</sub> ·cP16	6.25		221	-9.9	5.737						
$Cr_{14}V_2 \cdot cI16$	12.5		229	-26.4	5.731						
$Cr_{12}V_4 \cdot cP16$	25		221	-56.8	5.763						
$Cr_{12}V_4$ ·SOS·mC32	25		8	-46.8	12.231	4.078	8.145	$\beta = 109.44$			
$Cr_{10}V_6 \cdot cI16$	37.5		229	-71.3	5.795			1			
Cr <sub>8</sub> V <sub>8</sub> ·SOS·ap16	50		2	-49.2	4.848	5.049	8.607	$\alpha = 106.98$			
			_	.,				$\beta = 87.33$			
								$\nu = 99.79$			
Cr <sub>6</sub> V <sub>10</sub> ·cI16	62.5		229	-48.6	5.870			1 22.12			
$Cr_4V_{12}$ , cP16	75		221	-33.3	5 912						
$Cr_4 V_{12} Cr_{10} Cr_{10}$	75		8	-28.0	12 518	4 183	8 365	$\beta = 109.26$			
$Cr_{2}V_{12}$ $OQS$ $mC32$	87 5		229	_117	5 052	T.105	0.505	p = 109.20			
$Cr_1 V_{14} \cdot CP16$	100		221	_72	5.95Z						
C11 + 15 C1 10	100		<i>~~</i> 1	1.2	5.774						

Table 1.	Ab initio	calculated	energies of	of stable and	l hypothetica	l compounds	s in Cr–V s	ystem
----------	-----------	------------	-------------	---------------	---------------	-------------	-------------	-------

<sup>a</sup> These structures have energies that lie above the convex hull by ≤1 meV/at, which are well within the uncertainty of this calculation. Future study involving phonon calculations are required.
 <sup>b</sup> The structure relaxes into aP30 structure, space group No. 1.



**Figure 1.** (a) Convex hull plot of Cr–V binary using cluster expansion method. (b) Convex hull plot that includes the ground structures identified from (a) and other hypothetical structures. Unstable structures that have a positive enthalpy of formation are not shown in the plot.

 $\begin{array}{lll} Cr_{15}V_1/Cr_1V_{15} & [0,0,0] \\ Cr_{14}V_2/Cr_2V_{14} & [0,0,0], [-0.5,-0.5,-0.5] \\ Cr_{12}V_4/Cr_4V_{12} & [0,0,0], [0,0,-0.5], \\ & [0,-0.5,0], [-0.5,0,0] \\ Cr_{10}V_6/Cr_6V_{10} & [0,0,-0.5], [0,-0.5,0], \\ & [0,-0.5,-0.5], [-0.5,0,0], \\ & [-0.5,0,-0.5], [-0.5,-0.5,0]. \\ \end{array}$ 

After full relaxation, the structures maintain cubic symmetries:  $Pm\bar{3}m$ , space group #221, Pearson symbol cP16; or  $Im\bar{3}m$ , space group #229, Pearson symbol

cI16. For certain compositions studied, there are several different atomic configurations depending on which positions the solute atoms are assigned to. In order to examine the effect of atomic configurations, several different configurations are chosen for compositions of  $Cr_{14}V_2$ ,  $Cr_6V_{10}$ ,  $Cr_4V_{12}$ , and  $Cr_2V_{14}$ , and the calculations show that elastic constants and Poisson's ratio are relatively insensitive to the chosen configurations (see section 4).

To calculate the single crystal elastic constants, two approaches are used. One is the stress-strain approach as

Table 2. Atomic position of the predicted stable structures and selected unstable structures at T = 0 K. The lattice parameters are listed in table 1.

	Atom	Site	x	у	Z			
		Cr <sub>4</sub> V·tI10						
••••	Cr1	4e	0	0	0.3003			
••••	Cr2	4e	0	0	0.1030			
	V	2b	0	0	0.5000			
<b>9999</b>			Cr <sub>3</sub> V·tP1	6				
••	Cr1	2g	0	0	0.9359			
•• ••	Cr2	2h	0.5	0.5	0.8756			
	Cr3	2g	0	0	0.8130			
	Cr4	2h	0.5	0.5	0.7528			
	Cr5	2h	0.5	0.5	0.6244			
	Cr6	2g	0	0	0.5643			
	V1	2g	0	0	0.6887			
	V2	1d	0.5	0.5	0.5			
	V3	1c	0.5	0.5	0			
			Cr <sub>2</sub> V·tI6	Ď				
	Cr1	4e	0	0	0.1703			
	Cr2	4e	0	0	0.5			
			AuCu∙oI4	0				
•	Cr1	4e	0.5	0.25	0.4750			
•	Cr2	4e	0	0.75	0.0749			
•	Cr3	4e	0.5	0.25	0.3752			
•	Cr4	4e	0	0.75	0.1749			
•	Cr5	4e	0.5	0.25	0.2741			
•	V1	4e	0.5	0.25	0.9750			
•	V2	4e	0.5	0.25	0.0750			
	V3	4e	0.5	0.25	0.8749			
•	V4	4e	0.5	0.25	0.1749			
<b>\$ •</b>	V5	4e	0.5	0.25	0.7760			

documented in [25] and [26] as implemented in MedeA [27]. The other is the total energy method proposed by Mehl [28]. According to [25], the corresponding stress components  $\sigma_i$  (i = 1-6) after applying a small strain  $\varepsilon_j$  (j = 1-6) are:

$$\sigma_i = \sum_{j=1}^6 C_{ij} \varepsilon_j \tag{1}$$

Table 2. (Co	ntinued.)								
	Atom	Site	x	у	z				
	$Cr_3V_4 \cdot hR7$								
	Cr1	3a	0	0	0.0000				
	Cr2	6c	0	0	0.4307				
	V1	6c	0	0	0.7126				
	V2	6c	0	0	0.8608				
			Cr <sub>2</sub> V <sub>3</sub> ·hR	.5					
• •	Cr	6c	0	0	0.4025				
	V1	6c	0	0	0.7947				
	V2	3a	0	0	0				
•	CrV <sub>3</sub> ·mC16								
	Cr	4i	0.8740	0.5	0.8110				
	V1	4i	0.6205	0.5	0.9410				
	V2	4i	0.3789	0.5	0.5716				
$\checkmark$	V3	4i	0.1336	0.5	0.6911				
	$Cr_7V_2$ ·tI18								
	Cr1	2a	0	0	1/3				
	Cr2	2a	0	0	0.1112				
	Cr3	2a	0	0	0.0018				
•••	Cr4	2a	0	0	0.8879				
	Cr5	2a	0	0	0.7788				
	Cr6	2a	0	0	0.6649				
	Cr7	2a	0	0	0.5554				
•••	V1	2a	0	0	0.4445				
	V2	2a	0	0	0.2222				
			$Cr_3V \cdot tP8$	3					
	Cr1	2c	0.25	0.25	0.0626				
	Cr2	2c	0.25	0.25	0.8169				
	Cr3	2c	0.25	0.25	0.5601				
+-1	V	2c	0.75	0.75	0.6888				

where  $C_{ij}$  are the elastic constants. To apply a small strain, the new lattice vectors  $a'_i$  are related to the original ones  $a_j$  by  $a'_i = D_{ij}a_j$  where  $D_{ij}$  is a distortion matrix defined as:

$$D_{ij} = \begin{pmatrix} 1 + e_1 & e_6/2 & e_5/2 \\ e_6/2 & 1 + e_2 & e_4/2 \\ e_5/2 & e_4/2 & 1 + e_3 \end{pmatrix}.$$
 (2)

Table 2. (Continued.)

	Atom	Site	x	у	Z				
		$Cr_{12}V_8 \cdot oC20$							
	Cr1	4c	0.5	0.2484	0.75				
	Cr2	4c	0.5	0.3472	0.25				
	Cr3	4c	0.5	0.4493	0.75				
	V1	4c	0.5	0.9497	0.25				
• •	V2	4c	0.5	0.1506	0.25				
<b>9399</b>			Cr <sub>5</sub> V <sub>5</sub> ·oC	20					
• • •	Cr1	4h	0.7981	0	0.5				
• • •	Cr2	4g	0.9000	0	0				
• • •	Cr3	2d	0	0	0.5				
	V1	4h	0.4003	0	0.5				
	V2	2b	0.5000	0	0				
4	V3	4g	0.3020	0	0				
			CrV·cP2						
	Cr	1a	0	0	0				
	V1	1b	0.5	0.5	0.5				

For cubic crystals, only two distortion matrices are used: (1)  $e_1 = \delta$ ,  $e_{2-6} = 0$ ; (2)  $e_1 = \delta$ ,  $e_2 = -\delta$ ,  $e_{3-6} = 0$ . After full relaxation of each composition, a series of small strain at  $\delta = \pm 0.005$ ,  $\pm 0.01$ ,  $\pm 0.015$ ,  $\pm 0.02$ ,  $\pm 0.025$  is applied to the relaxed structure. The elastic constants are then extracted from a linear least-square fit of the first-principles Hellmann–Feynman stresses calculated at those applied strains.

The isotropic polycrystalline bulk modulus (*B*) and shear modulus (*G*) are taken from the average of theoretical lower and upper bounds of *B* and *G* respectively given by Reuss (assuming uniform stress throughout polycrystalline solid) and Voigt (assuming uniform strain) [25], i.e.  $B = (B_{\rm R} + B_{\rm V})/2$ ;  $G = (G_{\rm R} + G_{\rm V})/2$ . The values of  $B_{\rm R}$ ,  $B_{\rm V}$ ,  $G_{\rm R}$  and  $G_{\rm V}$  can be computed as follows:

$$B_{\rm V} = B_{\rm R} = \frac{C_{11} + 2C_{12}}{3} \tag{3}$$

$$G_{\rm V} = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{4}$$

$$G_{\rm R} = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$$
(5)

$$\nu = \frac{3B - 2G}{6B + 2G}.\tag{6}$$

A 16 atom cell of SQS [29] was used to generate three compositions, namely  $Cr_{12}V_4$ ,  $Cr_8V_8$ , and  $Cr_4V_{12}$ .

Calculations using 32 atom cell of SQS [30] resulted in a well converged energy of 1-2 meV/at for these 3 composition with respect to the 16 atom cell. The SQS structure does not have the bcc symmetry; rather it has P1 or Cm symmetry. In order to get elastic constants of bcc disordered structure, the following averaging was performed:

$$C_{11}(bcc) = \frac{C_{11} + C_{22} + C_{33}}{3} \bigg|_{SOS}$$
(7)

$$C_{12}(bcc) = \frac{C_{12} + C_{23} + C_{13}}{3}$$
(8)

$$C_{44}(bcc) = \frac{C_{44} + C_{55} + C_{66}}{3}$$
(9)

and neglecting  $C_{15}$ ,  $C_{25}$ ,  $C_{35}$ ,  $C_{46}$ . This is equivalent to calculate the elastic constants from bulk and shear modulus, as well as (if required to beyond isotropy) Zener's anisotropy ratio  $A = \frac{c_{11}-c_{22}}{2c_{44}}$ . This procedure works for Voigt, Reuss and Hill conditions. To calculate the temperature dependent elastic constants, it was assumed that the volume change is solely due to thermal expansion.

#### **3. Experimental procedure**

Five polycrystalline Cr-V alloys (approximately 400 g each) containing nominally 0, 25, 50, 75 and 100 at.% V were synthesized on a water-cooled copper hearth in a vacuum arc furnace back filled with high-purity argon (99.999%). The alloys were remelted three times to ensure macroscopic homogeneity. Elemental Cr (99.95 wt% purity) and V (99.7 wt% purity) were used as charge materials. Chemical compositions of the alloys were analyzed using x-ray fluorescence (XRF) and a gas analysis technique. They are given in table 3. Yttrium was added to tie oxygen and other interstitials. A significant amount of B was also detected. The reason for B detection is unknown. A heat treatment was performed to further homogenize on a micron scale the distribution of elements that segregated during solidification. The heat treatment was done in a vacuum furnace back filled with high-purity argon at 1200 °C for 8 h. In addition to the polycrystalline alloys, four single crystal Cr alloys were fabricated using arc-zone melting at Ames Laboratory. The single crystal Cr alloys contained nominally 0, 25, 50, and 75 at.% V.

Resonant ultrasound spectroscopy (RUS) [31–33] was employed to measure the elastic properties of the Cr–V alloys at ambient temperature. Broadband transducers make weak contact to the rectangular parallelepiped specimens whose lengths range from 2 to 5 mm. The frequency was swept typically from 0.3 to 1.5 MHz. The inverse calculation (RUS fit) [34] was performed using measured resonant frequencies to obtain the longitudinal modulus,  $C_{\rm L}$  the shear modulus, G, and the bulk modulus, B (as calculated by  $B = C_{\rm L} - 3G/4$ ), for polycrystalline samples, and cubic elastic moduli,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for single crystal samples with the cubic symmetry. Errors arise principally from errors in sample

**Table 3.** Chemical composition (wt%) of the polycrystalline alloys investigated. C, S, O, and N were determined using Leco gas analysis technique. The other elements were determined by XRF.

Alloy         Cr         V         Y         N         O         S         C         B         Al         Si         Fe         Mo           0V         98.98         —         0.12         0.0003         0.003         0.0015         0.08         0.68         0.023         0.014         0.048         0.054           25V         74.14         24.72         0.23         0.002         0.003         0.0010         0.07         0.66         0.030         0.017         0.040         0.094           50V         49.69         49.14         0.31         0.004         0.009         0.06         0.63         0.023         0.052         0.067           75V         25.03         73.70         0.42         0.003         0.005         0.0010         0.05         0.64         0.035         0.034         0.049         0.030													
OV         98.98         —         0.12         0.0003         0.003         0.0015         0.08         0.68         0.023         0.014         0.048         0.054           25V         74.14         24.72         0.23         0.002         0.003         0.0010         0.07         0.66         0.030         0.017         0.040         0.094           50V         49.69         49.14         0.31         0.004         0.009         0.06         0.63         0.023         0.023         0.052         0.067           75V         25.03         73.70         0.42         0.003         0.005         0.0010         0.05         0.64         0.035         0.034         0.049         0.030	Alloy	Cr	V	Y	Ν	0	S	С	В	Al	Si	Fe	Mo
	0V 25V 50V 75V	98.98 74.14 49.69 25.03	 24.72 49.14 73.70	0.12 0.23 0.31 0.42	0.0003 0.002 0.004 0.003	0.003 0.003 0.004 0.005	0.0015 0.0010 0.0009 0.0010	0.08 0.07 0.06 0.05	0.68 0.66 0.63 0.64	0.023 0.030 0.023 0.035	0.014 0.017 0.023 0.034	0.048 0.040 0.052 0.049	0.054 0.094 0.067 0.030

geometry and the measurement of dimensions, as well as, the sample quality. The recorded resonances have Q as high as ~1.5 × 10<sup>4</sup>. There were no unexplained resonances and the average of 35 resonances used for the RUS fit produced rms errors in the calculated frequencies as low as 0.1%. The estimated inaccuracies for these measurements are 0.5% for  $C_{11}$ , 1.7% for  $C_{12}$  and 0.07% for  $C_{44}$  for single crystal samples. X-ray diffraction (XRD) analysis was performed at room temperature using a Rigaku Ultima III instrument utilizing Cu K $\alpha$  radiation.

#### 4. Results

The convex hull plot from the cluster expansion search is shown in figure 1(a). The as-identified ground structures are Cr<sub>7</sub>V<sub>2</sub>·tI18, Cr<sub>3</sub>V<sub>2</sub>·oC20, Cr<sub>3</sub>V<sub>4</sub>·hR7, Cr<sub>2</sub>V<sub>3</sub>·hR5, CrV<sub>3</sub>·mC16, Cr<sub>8</sub>V<sub>1</sub>·mC18, Cr<sub>5</sub>V<sub>1</sub>·mC12, Cr<sub>4</sub>V<sub>1</sub>·tI10, Cr<sub>8</sub>V<sub>3</sub>· mC22, and  $Cr_2V_1$  tI6. Figure 1(b) shows the final convex hull plot predicted considering magnetism and those hypothetical structures are also included. Clearly including magnetism of Cr has a large impact on the predicted ground-state structures especially on the Cr-rich side. The calculated atomic magnetic spin moment is  $\pm 1.21$  Bohr magnetons for pure Cr. The antiferromagnetism weakens very rapidly as V is added. Cr<sub>15</sub>V<sub>1</sub> largely maintains a weak antiferromagnetic structure with the calculated average atomic magnetic spin moment is about  $\pm 0.85$  Bohr magnetons for Cr atoms and 0.49 for V atoms. Most alloys of higher V contents in the bcc structure and all hypothetical compounds examined prefer a nonmagnetic structure at the ground state. For a clear presentation, those structures that have energies larger than +40 meV/at are not shown in the plot. At T = 0 K, the true ground-state structures are Cr<sub>4</sub>V·tI10, Cr<sub>3</sub>V·tP16 (or Cr<sub>3</sub>V·tP8), Cr<sub>2</sub>V·tI6, (and Cr<sub>3</sub>V<sub>2</sub>·oC20), AuCu·oI40  $(Cr_5V_5 \cdot oC20 \text{ or } Cr_1V_1 \cdot cP2), Cr_3V_4 \cdot hR7, Cr_2V_3 \cdot hR5, and$  $CrV_3 \cdot mC16$ . Note that  $Cr_5V_5 \cdot oC20$  and  $Cr_1V_1 \cdot cP2$  have energies higher than AuCu·oI40 by +0.1 and 1.0 meV/at respectively, which are well within the accuracy of this calculation. Similarly, Cr<sub>3</sub>V<sub>2</sub>·oC20 has an energy above the convex hull by  $+0.1 \text{ meV/at. } Cr_3V \cdot tP8$  and  $Cr_3V \cdot tP16$  have a very similar crystal structure with slightly different stacking sequence in the c axis direction, and thus their energies are nearly equal within the computational error. In order to further study the phase stability among Cr<sub>3</sub>V·tP16/Cr<sub>3</sub>V·tP8, Cr<sub>3</sub>V<sub>2</sub>·oC20, and AuCu·oI40/Cr<sub>5</sub>V<sub>5</sub>·oC20/Cr<sub>1</sub>V<sub>1</sub>·cP2, lattice phonon vibration needs to be conducted for all these structures as well as Cr<sub>2</sub>V·tI6 since the composition of Cr<sub>3</sub>V<sub>2</sub>·oC20 lies between Cr<sub>2</sub>V·tI6 and AuCu·oI40 for future studies.



**Figure 2.** Calculated and experimental lattice parameters for the Cr–V alloys.

The calculated lattice parameters and enthalpy of formation of all the structures examined are listed in table 1, and the atomic positions of the stable and selected unstable structures are presented in table 2. The results show that many hypothetical Cr-V compounds studied have positive enthalpies of formation while the energies are negative for all ordered and disordered bcc structures. Nine ordered bcc substitutional alloys all have a negative enthalpy of formation at T = 0 K, suggesting the attractive interaction between Cr and V in the bcc structure. None of them are stable at T = 0 K, but their energies are merely above the convex hull within 20 meV/at (figure 1(b)). The three SQS compositions (25%, 50% and 75% V) all have a higher energy than their ordered bcc counterpart, and they lie above the convex hull plot by 12.6, 27.3 and 17.9 meV/at respectively. The Laves phases  $Cu_2Mg \cdot cF24$  and  $MgZn_2 \cdot hP12$  are stable in Cr-X (X = Ti, Zr, Hf, Nb, Ta) systems, but they are unstable in Cr–V system [4]. The present study predicts their enthalpy of formation is +54.7 and +70.6 meV/at in Cr-V system respectively.

The calculated lattice constants of ordered bcc Cr–V alloys are also plotted in figure 2. The current experimental results agree well with the earlier results found in the literature [35-37]. On the other hand, the *ab initio* results for the lattice parameters were 0.4–1.4% lower than the experimental values for the entire compositional range of the Cr–V binary system. In the compositional range from below 12.5 at.% V to pure V the calculated lattice parameters show a linear increase parallel to the experimental data. However, the calculated results are persistently about 1.4% lower than

Table 4. Calculated and measured lattice spacing values Å for the Cr–V system.

	Ab initio cal	Experimental data		
V content (at.%)	Uncompensated	CTE compensated	This study	Literature
0	2.870	2.881 <sup>a</sup>	2.881	2.885 [35]
				2.884 [36] 2.883 [37]
6.25	2.869	2.886 <sup>b</sup>		[]
10				2.893 [35]
12.5	2.866			
20				2.906 [35]
25	2.882		2.912	
30				2.920 [35]
37.5	2.898			
41				2.932 [ <mark>35</mark> ]
50	2.915		2.957	2.948 [35]
61				2.966 [35]
62.5	2.936			
70			• • • • •	2.978 [35]
75	2.956		2.999	
80	0.074			2.998 [35]
87.5	2.976			2 015 [25]
90	2 0 9 7			3.015 [35]
95.75	2.98/	2 0205	2.024	2 025 1251
1	2.997	3.039	3.024	3.035 [35]
				<b>3.027</b> [ <b>39</b> ]

<sup>a</sup>  $a_{0 \text{ K}} [1 + \int_{0 \text{ K}}^{298 \text{ K}} (-32 \times 10^{-10} T + 2 \times 10^{-12} T^3)] dT [38].$ <sup>b</sup>  $a_{0 \text{ K}} [1 + \int_{0 \text{ K}}^{298 \text{ K}} (11 \times 10^{-10} T + 3 \times 10^{-12} T^3)] dT [38].$ <sup>c</sup>  $a_{0 \text{ K}} [1 + \int_{0 \text{ K}}^{298 \text{ K}} (39 \times 10^{-10} T + 7 \times 10^{-12} T^3)] dT [39].$ 

the experimental data. The alloys near pure Cr (namely 0 and 6.25% V) break away from the linear behavior and exhibit somewhat larger lattice parameters. This break away behavior is thought to be due to exhibition of antiferromagnetism of Cr at low vanadium contents. Compensating for the thermal expansion from 0 K to room temperature brings the calculated values to the proximity of the experimental data as shown in figure 2 and table 4. This compensation was applied by using the available coefficient of thermal expansion (CTE) data at low temperatures for three compositions: Cr [38], Cr-5 at.% V [38], and V [39]. To calculate the CTE compensated lattice parameter of the Cr-6.25%V alloy, CTE for the Cr-5%V was used.

The calculated and experimental elastic properties are listed in table 5. The calculated results out of two ab initio methods are fairly close to each other, indicating their equivalency. The elastic constants of five polycrystalline and four single crystal Cr-V alloys were measured using the resonant ultrasound spectroscopy in this study. In addition, Lenkkeri and Lahteenkorva [40] previously measured the elastic constants of six polycrystalline Cr-V alloys, single crystal Cr and V using the pulse echo method.

The ab initio calculated values are plotted against the present experiments and the literature data [40] for Poisson's ratio, Young's modulus and Cauchy pressure in figures 3, 4 and 5 respectively. The experimental data from this study are in close agreement with the literature data as shown in figures 4 and 5. The calculated (Poisson's ratio, Young's modulus, and Cauchy pressure) values are largely acceptable for Cr-rich compositions, but deviate from the experimental



Figure 3. Calculated and experimental Poisson's ratio of Cr-V alloys.

data greatly on the V-rich compositions although the overall trends are consistent. The calculated Poisson's ratio increases with increasing V up to 75 at.% V, and then decreases gradually as V content is further increased. Similar trend is observed for Cauchy pressure. Conversely, Young's modulus decreases quickly as increasing V contents and gradually levels off over 60% V. The alternative atomic configurations have small impact on the elastic properties of  $Cr_{14}V_2$ ,  $Cr_6V_{10}$ ,  $Cr_4V_{12}$ , and  $Cr_2V_{14}$  alloys as is evident in figure 3.

In order to examine the possibility of forming metastable structures in Cr-V system, the lattice instabilities along

**Table 5.** *Ab initio* calculated elastic properties for bcc Cr–V alloys in comparison with experimental data generated in this study and found in literature. (Note: RUS = resonant ultrasound spectroscopy at room temperature (this work); SC = single crystal; PC = polycrystalline;  $\nu$  = Poisson's ratio; *B* = bulk modulus; *G* = shear modulus; *C<sub>ij</sub>* = elastic constants. Data from [40] was obtained at 300 K, data from [48] at 77 K, data from [47, 49] at 4.2 K.)

			Cauchy pressure	Young's modulus			Elastic	constant	s (GPa)
Alloy	Method	ν	(GPa)	(GPa)	B (GPa)	G (GPa)	$C_{11}$	<i>C</i> <sub>12</sub>	C <sub>44</sub>
Cr·cI2	Ab initio <sup>a</sup>	0.215	-39	302	179	124	426	56	95
	Ab initio <sup>b</sup>	0.249	-14	290	192	116	433	73	87
	Ab initio <sup>c</sup>	0.22	-37	308	184	126	434	59	96
	RUS-SC	0.21	-33	281	161	116	347	67	100
	RUS-PC	0.21		266	152	110			
	Literature	0.21 [54]	-33	279.8	161 [ <mark>40</mark> ]	116 [ <mark>40</mark> ]	351 [ <mark>40</mark> ]	66 [ <mark>40</mark> ]	100 [ <mark>40</mark> ]
			-13		191 [ <mark>48</mark> ]		391 [ <mark>48</mark> ]	90 [ <mark>48</mark> ]	103 [48]
$Cr_{15}V_1 \cdot cP16$	Ab initio <sup>a</sup>	0.207	-32	289	174	118	403	59	91
	Ab initio <sup>b</sup>	0.260	1	294	204	117	431	92	91
$Cr_{14}V_2 \cdot cI16$	Ab initio <sup>a</sup>	0.300	49	302	251	116	476	138	89
	Ab initio <sup>b</sup>	0.284	28	298	230	116	455	118	90
Cr12V4·cP16	Ab initio <sup>a</sup>	0.311	22	273	241	104	452	136	78
	Ab initio <sup>b</sup>	0.322	72	270	252	102	458	149	77
	SQS <sup>c</sup>	0.31	57	272	239	104	382	168	111
	SQS@500 K <sup>c</sup>	0.31	55	267	235	102	375	165	110
	RUS-SC	0.29	35	247	194	96	358	112	77
	RUS-PC	0.28		233	175	91			
Cr10V6.cI16	Ab initio <sup>a</sup>	0.335	73	230	233	86	423	137	61
	Ab initio <sup>b</sup>	0.341	87	231	242	86	431	149	62
$Cr_1V_1 \cdot cP2$	Ab initio <sup>a</sup>	0.390	117	145	220	52	367	147	30
	Ab initio <sup>b</sup>	0.386	118	157	230	57	386	152	34
	SQS <sup>c</sup>	0.38	111	165	225	60	300	189	77
	SQS@500 K <sup>c</sup>	0.38	104	165	216	60	289	180	76
	RUS-SC	0.34	65	168	171	63	287	113	48
	RUS-PC	0.35	87	156	172	58			
$Cr_6V_{10}$ ·cI16	Ab initio <sup>a</sup>	0.428	138	91	209	32	324	152	14
	Ab initio <sup>b</sup>	0.436	146	85	219	30	339	160	13
$Cr_4V_{12} \cdot cP16$	Ab initio <sup>a</sup>	0.439	139	72	200	25	301	149	10
	Ab initio <sup>b</sup>	0.447	149	67	209	23	310	159	10
	SQS <sup>c</sup>	0.42	134	94	204	33	258	177	43
	SQS@500 K <sup>c</sup>	0.42	127	94	196	33	250	169	42
	RUS-SC	0.36	79	146	170	54	264	123	44
~	RUS-PC	0.36	149	129	171	47	• • •		10
$Cr_2V_{14}$ ·cl16	Ab initio <sup>a</sup>	0.419	126	94	192	33	287	144	18
	Ab initio <sup>b</sup>	0.423	135	92	199	32	290	155	19
$Cr_1V_{15} \cdot cP16$	Ab initio <sup>a</sup>	0.420	125	91	188	32	277	143	18
	Ab initio <sup>b</sup>	0.424	136	90	197	32	282	155	19
V·cI2	Ab initio <sup>a</sup>	0.411	119	99	184	35	270	142	23
	Ab initio <sup>b</sup>	0.416	128	97	191	34	273	150	23
	Ab initio <sup>c</sup>	0.40	120	107	183	38	270	140	19
	Ab initio@500 K <sup>c</sup>	0.41	114	90	175	32	258	133	19
		0.37		129	163	47			
		0.37 [40]	83 [40]	130.4 [40]	162.9 [ <mark>40</mark> ]	47.7 [ <mark>40</mark> ]	236 [40]	127 [40]	44 [ <mark>40</mark> ]
	RUS-PC	0.37 [ <mark>48</mark> ]	73 [47]		1 (0 [ (0]		232 [47]	119 [47]	46 [47]
	Literature		/4 [ <mark>49</mark> ]		160 [49]		237 [49]	121 [49]	47 [49]

DFT values are at T = 0 K except:.

<sup>a</sup>  $C_{ij}$  calculations are done using the method described in [25] (equation (1) and (2)).

<sup>b</sup>  $C_{ij}$  calculations were done using the method by Mehl *et al* [28].

<sup>c</sup>  $C_{ij}$  calculations were done using the method by Le Page and Saxe [26].

the tetragonal/bain transformation path are investigated and the results are shown in figure 6. The procedure is to recalculate the total energy of each structure with various c/a ratios holding volume and shape fixed while relaxing atomic positions. Both Cr and V have a simple bcc structure, and the energy of the bcc structure is the minimum (c/a = 1) while the energy of the fcc structure (c/a = 1.414) is a local maximum with respect to the Bain deformation. The energy difference between these two structures,  $E_{fcc}-E_{bcc}$ , increases with increasing V up to 37.5 at.% V and then decreases with further increases in V up to pure V. The curvature of energy with respect to c/a in the vicinity of c/a = 1 is governed by the shear modulus. As the V content increases the curvature diminishes, consistently with the calculated reduction in shear modulus.



Figure 4. Calculated Young's modulus in comparison with experimental data.



Figure 5. Calculated Cauchy pressure in comparison with experimental data.

#### 5. Discussion

The present phase stability study reveals several important features pertaining to the Cr-V system that are not known previously. For the first time it is predicted that there exist various stable ordered compounds at T = 0 K using the cluster expansion method (see figure 1(b)). It is expected that they will become unstable compared to bcc solid solution phase at elevated temperatures, presumably due to configurational entropy of solid solution. Future experimental study to verify the existence of these ordered compounds at low temperatures will be important. What is equally important is to study the vibrational and configurational free energy of ordered compounds and bcc solid solution to estimate the phase transition temperature as future work. As an approximation, the solid solution can be modeled by SQS method. The present theoretical study reveals that the three SQS structures are not stable at T = 0 K as expected. Ignoring the vibrational free energy and short-range ordering in the solid solution, the critical temperature over which bcc solid solution becomes stable can be estimated as  $T_{\rm c} = \frac{\Delta E}{-k_{\rm B} \sum x \ln x}$  as a very crude



**Figure 6.** Total energy  $(E - E_{bcc})$  along the tetragonal transformation path for Cr, V and their binary alloys. c/a ratio of 1.0 refers to bcc structure and 1.414 refers to fcc structure.

approximation, where  $\triangle E$  is the energy of SQS structures above the convex hull, and  $k_{\rm B}$  is the Boltzmann constant. Plugging in  $\triangle E = 12.6$ , 27.3 and 17.9 meV/at reveals a transition temperature of 150, 320, and 210 K for 25%, 50% and 75% V respectively with a possible uncertainty of a few hundred.

It is worth noting that the nine ordered substitution bcc structures all have a negative enthalpy of formation, and their energies are fairly close to the convex hull. For example,  $Cr_{15}V_1$ ,  $Cr_{14}V_2$ ,  $Cr_{12}V_4$ ,  $Cr_{10}V_6$ ,  $Cr_1V_1$ ,  $Cr_6V_{10}$ ,  $Cr_4V_{12}$ ,  $Cr_2V_{14}$ ,  $Cr_1V_{15}$ , lies above the convex hull plot by merely 5.3, 4.0, 2.6, 5.5, 1.0, 16.1, 12.8, 11.3, and 4.3 meV/at respectively. Conversely, previous study [3] showed positive enthalpies of formation of other transition metal elements (except V) in bcc Cr at the  $Cr_{15}X_1$  composition. This hints that bcc Cr–V structure would behave differently than other transition metals in bcc Cr. The authors believe that the drastic difference in the solubility of transition metals in Cr as shown in the handbook [4] is closely correlated to their enthalpy of formation in bcc Cr, which in turn can be used to guide alloying design to improve ductility and strength of Cr.

The present study predicts a very large positive enthalpy of formation of Laves phases in Cr-V system, and thus Laves phases are not stable in the Cr-V system. This is in contrast to Cr-Ti (Zr, Hf, Nb, Ta) systems. Although the ideal atomic radius ratio for AB<sub>2</sub> type Laves phases is 1.225 assuming a close packing of hard spheres, experimental observations show the ratio actually varies between 1.05 and 1.7 [41]. Using the metallic atomic radii of Cr = 1.28 Å, V =1.34 Å and Ti = 1.47 Å and assuming a coordinate number of 12 [42], the ratio is 1.15 for Ti/Cr, and 1.05 for V/Cr. That means the atomic sizes of Cr and V are too close to satisfy formation criterion of Cr2V type Laves phase. On the other hand, the total and partial electronic density of states (DOS) plots using the G(P, T) package [43, 44] reveal a significant difference in the DOS at the Fermi level for both the C14 and C15 phases, as shown in figure 7. There exists a pseudo-gap for both Laves phases in the Cr-V and Cr-Ti systems where the DOS is relatively low. The Fermi level sits within the



**Figure 7.** (a) Total and partial DOS plot of (a)  $Cr_2V \cdot F_{24}$  versus  $Cr_2Ti \cdot cF_{24}$  and (b) density of states plot of  $Cr_2V \cdot hP12$  versus  $Cr_2Ti \cdot hP12$ . The vertical dashed line indicates the Fermi level.

pseudo-gap for Cr–Ti Laves compounds, however, the Fermi level shifts to the right edge of the gap causing a significantly higher DOS for Cr–V Laves phases due to contributions from the additional valence electron in V relative to Ti. Placement of the Fermi level within the pseudo-gap is one mechanism to enhance structural stability by reducing the band structure energy.

Except pure Cr, bulk modulus decreases with increasing V content (see table 5). Monotonic decrease in B is correlated with decreasing valence electron density. Cohen [45] observed that B is inversely proportional to the third power of lattice constant in various zinc-blend solids. Such an inverse

relation between *B* and *a* is also observed in Cr–V alloys. The predicted overall trend in *B* agrees with experimental measurements [40, 46–49] although the calculated values are consistently larger than the experimental data especially for the Cr-rich compositions. The abrupt drop in bulk modulus at  $Cr_{14}V_2$  is thought to be due to the Néel point anomaly [38, 40]. The shear modulus decreases monotonically with increasing V content up to 52.5 at.% V, and remains roughly constant thereafter.

Published experimental data on the ductility of crystalline metals have demonstrated that they tend to be ductile under the roughly similar processing condition (e.g. recrystallized grains to lower the dislocation density as much as possible) if they have a high Poisson's ratio (e.g. larger than 0.33) at low homologous temperatures [3, 50, 51]. Similar observation was also reported in amorphous metals [52, 53]. At room temperature, V is very ductile with a Poisson's ratio of 0.37 [54], and its ductile to brittle transition (DBTT) is  $-196 \,^{\circ}\text{C}$  [55]. On the other hand, Cr is very brittle at room temperature with a Poisson's ratio of 0.21 [54] and its DBTT is about 150 °C. The present DFT calculations predict that the addition of V increases the Poison's ratio of Cr, suggesting an intrinsic ductilizing effect of V. The total and partial DOS plots of selected compositions are shown in figure 8. The electronic structure appears similar for all the compositions presented in figure 8; the DOS is dominated by the contribution from the d-orbital of Cr and V. For Cr, the Fermi level sits in the pseudo-gap, and thus it shifts to the left edge of the pseudo-gap of higher energy states upon alloying with V, which provides one less valence electron. As a result, the DOS at the Fermi level increases. Pure V has the highest Fermi level DOS among this group of compositions. Since a higher Fermi level DOS is often associated with good ductility [52, 53, 56], V addition can bring a ductilizing effect to Cr at least intrinsically although extrinsic effects (e.g. impurity [1, 5, 57], grain size distribution [5, 58], interface/grain boundary segregation [57], etc) also impact ductility significantly. The same trend in DOS is also observed for the three SQS structures, namely, DOS at the Fermi level increases with increasing V contents in the alloy.

Other parameters have also been proposed in the literature to gauge ductility criterion of metals and alloys. For example, Pettifor [59] suggested that the Cauchy pressure  $P_{\rm C} = (C_{12} - C_{44})$  can be used to describe the angular character of atomic bonding in metals and compounds, which can be responsible for the brittle or ductile behavior of materials. For covalent materials with a directional character of atomic bonds, the Cauchy pressure is negative because the material resist against the shear strain  $(C_{44})$  much more strongly than that for the volume change  $(C_{12})$ . For most metals, Cauchy pressure is positive since they are relatively ductile. It is experimentally known that Cr has negative Cauchy pressure and the present DFT calculations are in agreement. A negative Cauchy pressure may be another reason why pure Cr is brittle. The present study shows that Cauchy pressure increases with increasing V content, a sign of ductilization. The  $P_c$ value becomes significant once V content is over 50 at.%, since the  $C_{44}$  value becomes extremely small, suggesting that chemically the composition is expected to be ductile.



**Figure 8.** Total and partial DOS plot of selected compositions: (a) Cr, B2 CrV, and V; (b) disordered  $Cr_3V$ , CrV, and  $CrV_3$  SQS structures. The vertical dashed line indicates the Fermi level. The DOS at Fermi level versus composition is also shown.

To further analyze the directionality of bonding, the difference charge density of Cr, ordered B2 CrV, and V in the (110) plane (which is the close-packed plane in bcc,

the preferred slip plane at low temperatures) is presented in figure 9. The difference charge density is calculated by subtracting the superposition of atomic charge densities from



Figure 9. Difference charge density of Cr, B2 CrV, and V.



Figure 10. Tension Young's modulus along (001), (011), and (111). Included data are taken from table 4 and experimental data in [40, 46].

the self-consistent valence charge density using MedeA [27]. Clearly, the charge-density contour surrounding Cr atoms in pure Cr shows irregular distribution. The charge density along  $\langle 111 \rangle$  direction is higher than  $\langle 001 \rangle$ , suggesting forming stronger bonding along  $\langle 111 \rangle$  (which is the closed-packed direction and thus the preferred slip direction). Conversely, charge-density contour surrounding V atoms in pure V is more circular and uniform, and the charge density along  $\langle 111 \rangle$  is weaker than  $\langle 001 \rangle$  direction. In the B2 CrV alloy, a direct Cr–Cr bond formation along  $\langle 111 \rangle$  is interrupted by insertion of V atoms. It is noticeable that the charge density in the bonding region is the highest for pure Cr and decreases gradually as V is added. The trend in bond analysis is consistent with the Young's modulus, bulk modulus and

shear modulus. Weakened  $\langle 111 \rangle$  bonds in the presence of V may favor dislocation movement and thus plasticity. In addition, the difference electron charge density in another slip plane (112) for Cr, B2 CrV and V was analyzed, and a similar trend in electron charge density as in the case of (110) plane was observed (results not shown).

Another important engineering parameter is the Young's modulus (also called tension modulus), which is the slope of the stress-strain curve at infinitesimal strain. Therefore, a smaller Young's modulus means larger strain at the same stress. Young's modulus was used previously to guide design Gum Metals<sup>TM</sup> [60–62], namely alloy screening was performed in searching for low Young's modulus in addition to high strength. A valence electron concentration (e/a) of 4.24 was identified for Gum Metals [60, 61]. The highest symmetry direction in Cr–V bcc lattice is (001), (011), and  $\langle 111 \rangle$ . Therefore, moduli governing tension (*E<sub>hkl</sub>*) and shear  $(G_{hkl})$  in these directions were calculated. The results are shown in figures 10 and 11 respectively. Although certain discrepancy exists between experiments and calculations, the overall trend is clear: (1) both  $E_{hkl}$  and  $G_{hkl}$  decreases monotonically as increasing V content up to  $\sim 62.5\%$ (corresponding to e/a ratio of 5.4) then levels off. (2) V-rich compositions are more isotropic than Cr-rich compositions. In contrast, the bcc Ti–Nb [60, 61] and Ti–V [62] alloys show prominent anisotropy in elasticity.

Based on the present theoretical and experimental study together with literature available, it is tempting to conclude that, as far as intrinsic ductility solely due to alloy chemistry is concerned, Cr contents need to be kept as low as 37.5 at.% in order to make the alloy ductile. Alloying with V can and probably is the only choice to start with because V is the only element in the period table that forms complete solid solution over the entire composition range above room temperature. A wide mutual solubility between V and other transition metals



**Figure 11.** Shear modulus along  $\langle 001 \rangle$  on  $\{100\}$ ,  $\langle 011 \rangle$  on  $\{011\}$ , and  $\langle 111 \rangle$  on  $\{011\}$   $\{112\}$   $\{123\}$ . Included data are taken from table 4 and experimental data in [40, 46].

such as Ti, Nb, Ta, Mo, and W will make it feasible to design ductile Cr-based multi-component alloys. Lastly it is worth mentioning that other ductility criteria based on dislocations are also important in designing ductile bcc alloys such as Rice–Thompson ratio [56, 63] and solute softening effect [64, 65], which deserves separate study as future work.

#### 6. Conclusions

In summary, *ab initio* DFT calculations and RUS experiments were performed to study the phase stability and elastic properties of Cr–V alloys. The following conclusions have been reached:

- (1) There are various stable compounds discovered at T = 0 K, namely Cr<sub>4</sub>V·tI10, Cr<sub>3</sub>V·tP16, Cr<sub>2</sub>V·tI6, AuCu·oI40, Cr<sub>3</sub>V<sub>4</sub>·hR7, Cr<sub>2</sub>V<sub>3</sub>·hR5, and CrV<sub>3</sub>·mC16. However, Cr<sub>3</sub>V·tP8, Cr<sub>3</sub>V<sub>2</sub>·oC20, Cr<sub>5</sub>V<sub>5</sub>·oC20 and Cr<sub>1</sub>V<sub>1</sub>·cP2 lie above the convex hull by  $\leq 1.0$  meV/at, which are well within the computational uncertainty of this study. Future studies on lattice phonon vibrations on these structures are required.
- (2) Nine ordered bcc substitutional structures have an energy that are close to the convex hull while many analogous compound structures are unstable such as the AB<sub>2</sub> Laves phases.
- (3) The elastic constants of ordered and disordered (using SQS method) bcc structures were calculated. Discrepancy with experiments was observed but the overall trends were consistent.
- (4) Three ductility parameters, namely Poisson's ratio, Young's modulus, and Cauchy pressure, were analyzed with respect to composition. Both Poisson's ratio and Young's modulus monotonically decreases with increasing V content up to 62.5% V and then levels off. A negative Cauchy pressure for Cr is confirmed. With

increasing V content, Cauchy pressure increases steadily up to 62.5% and then levels off.

- (5) The electronic structure appears similar for all the bcc (ordered and disordered) compositions and the DOS is dominated by the contribution from the d-orbital of Cr and V. V addition shifts the Fermi level to the left edge of the pseudo-gap of higher energy states.
- (6) The difference charge density in the bonding region is the highest for pure Cr and decreases gradually as V is added. The intrinsic ductilization effect from V addition is proposed due to increase in DOS at the Fermi level, more uniform distribution of electron charge density, and decreased bonding along (111) direction that may also favor dislocation mobility.
- (7) Experimental RUS measurements on elastic constants on single crystal and polycrystalline agree well with previous data reported in the literature.

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