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Coulomb-potential-dependent decohesion of Magnéli phases

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Abstract

Transition metal oxide Magnéli phases are traditionally described as crystallographic shear structures. Some of these phases feature a layered crystal structure based on deformed metal–oxygen octahedra. Here, we describe the correlation between structure, decohesion energies and elastic properties of WO3, ReO3, MoO3, VO2, V2O5 and TiO2 using ab initio calculations. Decohesion energies and elastic constants $C_{44}$ are inversely proportional to the original distance between the cleaved layers and correspond to the screened Coulomb potential. This can be understood based on the electronic structure. The bond strength decreases rapidly as the distance is increased, resulting in weak coupling between the layers, which in turn causes the formation of easily plastically deformable structures.

(Some figures in this article are in colour only in the electronic version)
Figure 1. Decohesion energy $G$ (filled circles) and elastic constant $C_{44}$ (open circles) as a function of the original distance $d$ between the cleaved layers. Data was fitted with $a*1/d*\exp(-b*d)$ (screened Coulomb potential, with $a$ and $b$ as fitting parameters). Values for VO$_2$ and V$_2$O$_5$ were taken from [32].

a mesh of $7 \times 7 \times 7$ irreducible $k$-points (unless otherwise noted). Initial structural data for the \textit{ab initio} calculations were taken from the literature for five phases WO$_3$, namely WO$_3$ ($P4/nccZ$ structure) [37], WO$_3$ ($P4/nmmZ$) [38], WO$_3$ ($P\bar{4}2_1m$) [39], WO$_3$ ($Pcnb$) [37] and WO$_3$ ($Pmnb$) [40]. In addition, a WO$_3$ parent structure ReO$_3$ [41] was calculated as well as a VO$_2$ prototype TiO$_2$ (rutile) [42] and the isostructural MoO$_2$. Data of VO$_2$ and V$_2$O$_5$ were taken from our previous work [32]. Due to large structural anisotropy for some phases, calculations were carried out with full structural relaxations at every volume [32, 43, 44]. To study cleavage in the phases calculated, the decohesion energies for cleavage were calculated as the energy required for the separation of the cleaved crystal layers. As the original distance between the cleaved crystal layers is increased from 1.1 to 2.8 Å, the decohesion energy decreases from 5.83 to 0.05 J m$^{-2}$. The data points were fitted with $a*1/d*\exp(-b*d)$ (screened Coulomb potential, with $a$ and $b$ as fitting parameters). Good agreement between the calculated decohesion energy and the fitting curve is observed. Our data suggest that the bonding distance between the cleaved layers is one of the key factors determining the decohesion energy for the phases studied here. It is reasonable to assume that these easy cleaving planes in WO$_3$ and V$_2$O$_5$ are therefore responsible for the lubricating properties observed experimentally [29, 47]. This assumption is supported by the dependence of the elastic constant $C_{44}$ on the distance between the cleaved layers ($d$), see figure 1. As $d$ is increased from 1.4 to 2.8 Å, $C_{44}$ decreases from 139 to 25 GPa. It is evident that the decohesion energy and $C_{44}$ can be estimated based on the layer distance only. This behaviour can be described by the screened Coulomb potential. Based on these results of the oxide phases calculated here, we propose that these correlations can be applied to other Magnéli phase oxides with a similar building principle of metal–oxygen octahedra.

As the decohesion energy and $C_{44}$ are shown to depend primarily on the interlayer distance, we can see that this is
not the case for the bulk modulus \( B \). The bulk modulus was obtained by fitting the energy–volume curves to the Birch–Murnaghan equation of states \([48]\). For the \( \text{WO}_3 \) phases, \( B \) is in the range from 78 to 159 GPa; thus in part close to \( B \) to for \( \text{V}_2\text{O}_5 \) (87 GPa) but much lower than for the rutile structures (e.g. \( \text{MoO}_2 \) with 255 GPa). Since (at least) 11 different structures with composition \( \text{WO}_3 \) exist \([14]\), these values may differ to a considerable degree due to very narrow stability regions within the phase diagram. The bulk modulus as well as the calculated lattice parameters, the number of formula units per unit cell \( Z \), the elastic constant \( C_{44} \) and the decohesion energy in the plane with the longest interlayer bonding for \( \text{VO}_2 \) \([32]\), \( \text{V}_2\text{O}_5 \) \([32]\), \( \text{MoO}_2 \) and the five \( \text{WO}_3 \) phases are given in table 1.

The differing decohesion energies and \( C_{44} \) values of these oxides may be understood based on the electronic structure. Electron density distributions (EDDs) obtained by \textit{ab initio} calculations were evaluated using VESTA \([49]\). EDDs are presented for ReO3 in figure 2(a), the \( \text{WO}_3 \) phase \( P4/ncc \)Z in figure 2(b) and \( \text{V}_2\text{O}_5 \) in figure 2(c). The \( \text{WO}_3 \) phase \( P4/ncc \)Z was chosen since it bears the largest bonding length difference within the \( \text{WO}_6 \) polyhedron (1.79–2.17 Å). In general, these oxides are predominantly characterized by ionic bonding, due to the charge transfer from the metal to oxygen. To some extent, there is charge shared between these elements, giving rise to a smaller covalent contribution. In particular for the \( \text{V}_2\text{O}_5 \) vanadyl bond, covalent character is apparent, while it is not for the interlayer bonding. It is important to note that these EDDs never exhibit regions without charge (0 eV/Å\(^3\)), which may indicate that some minor metallic contributions are present. However, striking differences between these phases can be observed. In ReO3 (figure 2(a)), \( Pm5m \), the perfect octahedral coordination causes identical bonding for all six Re–O bonds. The bond length is 1.89 Å. In \( \text{WO}_3 \) (figure 2(b)), \( P4/ncc \)Z, the \( \text{WO}_6 \) octahedron is distorted and the W cation is shifted from the centre. Thus, three different W–O bonds are formed: four identical bonds with a length of 1.92 Å parallel to the (1\( \text{T}_0 \)) layer, a short 1.79 Å ‘intralayer’ bond and a long 2.17 Å ‘interlayer’ bond. Hence, in the shorter interaction there is more charge shared and a higher covalent contribution compared to the non-covalent longer interaction with less charge shared. This causes the formation of distinct layers within this crystal structure and thus a lower decohesion energy between these layers. In \( \text{V}_2\text{O}_5 \) (figure 2(c)), \( Pmmm \), the \( \text{VO}_6 \) octahedron is largely distorted. The actual coordination can be described as a square pyramid with an interlayer bond length of 2.79 Å. The short bond opposed is only 1.61 Å. This strong vanadyl bond is mainly of covalent character. The other bonds are characterized with bond lengths between 1.78 and 2.03 Å. Since the bonding differences are much larger than those in \( \text{WO}_3 \), clearly visible layers are formed, causing the extremely low decohesion energy between these layers.

It is evident that distorted metal–oxyg en octahedra result in large layer distances and hence lower \( C_{44} \) values as compared to undistorted octahedra. Decohesion energy and \( C_{44} \) are inversely proportional to the distance between the cleaved crystal layers, and accordingly to the screened Coulomb potential, and thus the bond strength decreases rapidly as the distance is increased. This results in weak coupling between the layers which then causes the formation of easily plastically deformable structures, for instance \( \text{WO}_3 \) or \( \text{V}_2\text{O}_5 \). This behaviour can be understood based on changes in the crystal and electronic structure as displayed for ReO3, \( \text{WO}_3 \) and \( \text{V}_2\text{O}_5 \). This relationship previously established for vanadium oxides \([32]\) applies to other Magnéli phases. The fact that structures such as \( \text{WO}_3 \) can also be described by the above-presented correlations provides the basis for quantum mechanical guided design of Magnéli phase structured solid lubricants, based on tailoring the layer distance by varying the chemical composition.

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### References

1. Magnéli A 1953 Acta Crystallogr. 6 495–500

### Table 1. Calculated lattice parameters, number of formula units per unit cell (\( Z \)), bulk modulus \( B \), elastic constant \( C_{44} \) and decohesion energy \( G \) for \( \text{VO}_2 \), \( \text{V}_2\text{O}_5 \), \( \text{MoO}_2 \) and five \( \text{WO}_3 \) phases.

<table>
<thead>
<tr>
<th>Structure Space group</th>
<th>( \text{VO}_2 ) ( P4/m/mnm )</th>
<th>( \text{V}_2\text{O}_5 ) ( Pmmn )</th>
<th>( \text{MoO}_2 ) ( P4_1/m/mnm )</th>
<th>( \text{WO}_3 ) ( P4/ncc )</th>
<th>( \text{WO}_3 ) ( P4/nmm )</th>
<th>( \text{WO}_3 ) ( P4_2/m )</th>
<th>( \text{WO}_3 ) ( Pnmb )</th>
<th>( \text{WO}_3 ) ( Pmnb )</th>
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<td>( a (\text{Å}) )</td>
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<td>7.389</td>
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<td>( b (\text{Å}) )</td>
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<td>4.014</td>
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<td>2.000</td>
<td>2.000</td>
<td>4.002</td>
<td>4.002</td>
<td>4.002</td>
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<tr>
<td>( Z )</td>
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<td>1.000</td>
<td>1.000</td>
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<td>1.000</td>
<td>1.000</td>
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<tr>
<td>( B ) (GPa)</td>
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<td>86.6</td>
<td>254.9</td>
<td>103.4</td>
<td>159.4</td>
<td>147.4</td>
<td>78.1</td>
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<td>55.6</td>
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<td>(002)</td>
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<td>(002)</td>
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<tr>
<td>( G (\text{J m}^{-2}) )</td>
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