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Theoretical investigation of cubic B1-like and corundum $(Cr_{1-x}Al_x)_2O_3$ solid solutions

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First-principles calculations are employed to investigate the stability and properties of cubic rock-salt like $(Cr_{1-x}Al_x)_2O_3$ solid solutions, stabilized by metal site vacancies as recently reported experimentally. It is demonstrated that the metal site vacancies can indeed be ordered in a way that gives rise to a suitable fourfold coordination of all O atoms in the lattice. B1-like structures with ordered and disordered metal site vacancies are studied for $(Cr_{0.5}Al_{0.5})_2O_3$ and found to have a cubic lattice spacing close to the values reported experimentally, in contrast to fluorite-like and perovskite structures. The obtained B1-like structures are higher in energy than corundum solid solutions for all compositions, but with an energy offset per atom similar to other metastable systems possible to synthesize with physical vapor deposition techniques. The obtained electronic structures show that the B1-like systems are semiconducting although with smaller band gaps than the corundum structure.

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I. INTRODUCTION

Hard oxide thin films are of high interest for cutting tool applications as well as for other processes where hardness and oxidation resistance are crucial. Coatings based on alloys of alumina, Al_2O_3, and chromia, Cr_2O_3 have recently attracted considerable interest for this purpose.[1–6]

Recently, we discovered that in addition to the well known corundum structure α-$(Al,Cr)_2O_3$ solid solutions, thin films of a novel face-centered cubic (fcc) structure could be obtained by reactive magnetron sputtering.[7,8] These results have also been confirmed in the works by Najafi et al[9,10] using cathodic arc evaporation. There is also a patent by Kurapov claiming an unspecified cubic phase[11]. Based on experimental analysis of the obtained films using x-ray diffraction, transmission electron microscopy, and compositional determination using elastic recoil detection analysis, a rock-salt B1 structure was suggested with an oxygen fcc sublattice and Al and Cr atoms distributed on the octahedrally coordinated sites leaving one third of the metal sites vacant.[7] Using Rietveld refinement of their diffraction pattern, Najafi *et al.* arrived at a very similar conclusion.[10] Previously, the different observed structures of pure Al_2O_3 has been discussed in terms of hexagonal close-packed (hcp) or fcc-lattices for oxygen together with various cation ordering patterns on the tetrahedral and octahedral sites. In particular, the thermodynamically stable corundum phase can be viewed as an hcp oxygen lattice with two thirds of the octahedral sites occupied by Al.[12]

Even though experimental investigations have revealed many of the properties of the cubic $(Al,Cr)_2O_3$ phase, several questions remain open. In particular, if it should be based on the rock-salt lattice, with a nominal metal-to-nonmetal ratio of 1:1, one third of the metal sites need to be vacancies. This is a considerable fraction and their distribution, whether disordered or with an ordering tendency, is not known. The configuration of the Cr and Al atoms is also unknown although a disordered solid solution is likely in this case. For the vacancies, a strong short-range tendency towards ordering should be considered although no experimental evidence for this is yet present. Furthermore, the measured electronic structure of this phase reported in Ref.[10] deserves further analysis. These questions, regarding its stability and electronic structure, motivate theoretical studies based on first-principles of the structure and properties of B1-like $(Cr_{1-x}Al_x)_2O_3$ solid solutions.

Theoretical studies of disordered solid solutions in related meta-stable B1 systems, such

as $Cr_{1-x}Al_xN$[13,14] have previously provided valuable information and explanations for experimental observations. However, the present oxide case posseses further complexity with corresponding challenges for a detailed theoretical study: First, the suggestion of a B1-like phase should be considered and tested against other possible cubic structures present in other M_2O_3 systems, such as fluorite structures with oxygen vacancies and the perovskite structure. Second, the metal site vacancy distributions need careful considerations. For instance, if the vacancies were completely randomly distributed, a few percent of the oxygen ions would have only one or none metal nearest neighbors. This seems unphysical and puts focus on ordering of the vacancies, at least in a short-range manner. Third, the configuration of Cr and Al atoms should be investigated on top of the vacancy configurational considerations. Fourth, the Cr ions are typically magnetic, most likely in a disorder manner at the elevated temperatures of relevance for thin film growth. Fifth, transition metal oxides belong to the type of materials usually presenting strong electron correlations where standard density functional calculations are problematic. In view of this complexity, it is clear that the theoretical approach needs to be performed in steps focusing first on the most crucial aspects of the problem. In this letter we focus on the first two issues by comparing the stability and electronic structure of cubic B1-like $(Cr_{1-x}Al_x)_2O_3$ solid solutions with disordered and ordered metal site vacancies with each other and with other crystal structures, including the corundum phase.

II. MODELLING

We use a density functional theory approach within the local spin density approximation[15] combined with a Hubbard Coulomb term (LDA+U)[16,17] with the value of effective (U-J) $U^{eff} = 3$ eV applied to the Cr 3*d*-orbitals. This approach corrects for the over-delocalisation of Cr 3*d* electrons by the LDA and was found to be suitable for cubic B1 CrN[18] and also applied for CrAlN[14] and is very close to the the value of U^{eff} used for pure Cr_2O_3[19]. Our calculations were performed using the projector augmented wave (PAW) method[20] as implemented in the Vienna Ab-initio Simulation Package (VASP)[21]. Monkhorst-Pack grids of $3 \times 3 \times 3$, $5 \times 5 \times 5$, $13 \times 13 \times 13$, and $21 \times 21 \times 21$ k-points were used for structures with 120, 80 and 60, 10, and 5 atoms, respectively. Convergency tests were performed ensuring that further increase in k-point density did not induce any considerable change in energies.

We used an energy cut-off of 400 eV for the plane-wave basis set. The magnetic state is approximated with a ferromagnetic ordering of Cr spins, leaving the investigation of the details of the spin degree of freedom of the problem to future works.

III. RESULTS AND DISCUSSION

The first step in our investigation is to search for an energetically favorable distribution of metal site vacancies. The starting point for this search is a Connolly-Williams cluster expansion[22,23] of the configuration energy associated with different vacancy distributions. As an input the energies of 9 different ordered structures with ad-hoc chosen vacancy, Al, and Cr distributions on the metal sublattice were calculated by first-principles. The lattice parameter was chosen as $a_0 = 4.05$Å inspired by the experimental findings[7]. Using a least square fit, these energies were subsequently mapped onto concentration dependent pair cluster interactions between vacancy and metal atoms (Al or Cr) on the first 3 fcc-coordination shells. As expected the interactions on the first two shells were found to be strong and positive, 0.45 and 0.53 eV, respectively, indicating a tendency where metal vacancies avoids each other on these shells. The third interaction potential was weaker and negative, -0.20 eV. Using these interactions in a Monte-Carlo simulated annealing procedure, we obtain a ground state vacancy ordering with the short-range order (SRO) parameters α_i of -0.125, -0.5, and 0.125 for $i = 1, 2$, and 3, respectively. This vacancy ordering can be obtained with a supercell of 32 metal, 16 metal-vacancies and 48 oxygen sites, based on a $4 \times 3 \times 2$ repetion of the tetragonal $L1_0$ fcc structure with an additional octahedral O sublattice. This structure fulfills the optimal coordination criteria where all oxygen atoms are coordinated by four metal atoms, and thus two vacancies. We use this structure as a model for an ordered distribution of vacancies for all the compositions considered in this work, although noting that there could exist also other structures with the same SRO-parameters on the first three coordination shells. In order to simultaneously consider an Al and Cr solid solution on the remaining 32 metal sites, five different distributions were derived by means of random number generation for each of the compositions $x = 0.25, 0.50$, and 0.75. The average of the energies of the five samples, taken at their average equilibrium volume, was used to represent that of the ordered vacancy structure as a function of composition. The energy differences between the considered Cr and Al distributions were of the order of 0.01 eV per

formula unit (f.u.). This is much smaller than the energy differences between the considered vacancy orderings that were one to two orders of magnitude larger.

In order to model a system with randomly distributed metal vacancies, the metal fcc-sublattice was obtained using a three component special quasi random structure (SQS)[24] based on $4 \times 3 \times 3$ B1 unit cells with 24 metal atoms, 12 metal vacancies and 36 oxygen atoms. In this structure the correlation functions between vacancies and Al, vacancies and Cr, as well as Al and Cr atoms are zero, that is identical to the ideal random disorder on the important first two coordination shells. The vacancy-Al and vacancy-Cr correlations functions also have a magnitude below 0.05 for the third and fourth coordination shells.

Figure 1 shows the total energy as a function of cubic lattice parameter for the B1-like structures with $x = 0.5$ and ordered and disordered metal vacancies, as compared to a $CrAlO_3$ perovskite and a fluorite-like $(Al_{0.5}Cr_{0.5})_2O_3$ created with one fourth ordered *oxygen* vacancies and a $L1_0$ type order of Al and Cr. The B1-like structures are considerably below the two other prototypes in energy and have equilibrium lattice spacings just below the experimentally observed[7], in contrast to the perovskite and flourite-like phases. This result verifies the relevance of B1-like structures to explain the experimental observations of cubic $(Cr,Al)_2O_3$ phases.[7,10]

The energy difference between the structures with ordered and disordered vacancies are 0.361 eV/f.u. The entropy associated with solving three types of species with equal probability on three sites/f.u.(disordered vacancies) is considerably higher than that of solving two types on two sites/f.u. (ordered vacancies). However, this is not enough to completely counter the energy difference and thermodynamics should favor, if not long-range ordered, at least a considerable degree of short-range ordering of vacancies at relevant temperatures.

The next step in our investigation is to compare the $(Cr_{1-x}Al_x)_2O_3$ solid solutions in the B1-like structure having ordered vacancies with the corundum solid solutions. The corundum structures are modeled as random alloys using the SQS method for $x = 0.25, 0.50,$ and 0.75 based on a 48 metal sites and 72 oxygen sites supercell. Figure 2 shows the mixing enthalpies, calculated at zero pressure, for the B1-like solid solutions with ordered metal vacancies as well as the solid solutions in the corundum structure. The values are taken with respect to the enthalpies of pure corundum Al_2O_3 and Cr_2O_3. It can be seen that the B1-like structure has a higher energy than the corundum structure for all compositions. The difference is smallest for $x = 0.5$, 0.64 eV/f.u., and largest for pure Al_2O_3, 0.73 eV/f.u. This

considerable energy offset indicates that the B1-like phases can only be metastable, and formed due to supremacy of growth kinetics over thermodynamics during physical vapor deposition (PVD) synthesis. Thus, the B1-like phase is predicted to transform into the corundum phase if sufficient thermal energy is provided, and indeed such a transformation upon annealing is found experimentally.[8]

It is illustrative to compare the enthalpy differences in Figure 2 to those for other metastable B1 systems such as $Ti_{0.5}Al_{0.5}N$, possible to grow with PVD techniques. The differences in enthalpies of the corundum and B1-like phases per B1 formula unit, which is one third of the M_2O_3 formula unit, are about 0.21 eV/B1-f.u. for the intermediate compositions. B1 $Ti_{0.5}Al_{0.5}N$ has an isostructural mixing enthalpy with respect to B1 TiN and B1 AlN of about 0.2 eV/B1-f.u. while the mixing enthalpy with respect to the stable wurtzite AlN has been calculated to be 0.37 eV/B1-f.u.[25] If the enthalpy and additional configurational entropy of the B1-like $(Cr_{0.5}Al_{0.5})_2O_3$ structure with disordered vacancies is considered at the growth temperature in Ref.[7] $500°C$, the difference in free energy to the corundum phase is about 0.29 eV/B1-f.u. Considering these energetic arguments it seems reasonable that a metastable B1-like solid solution can be formed in the $(Cr_{1-x}Al_x)_2O_3$ system during PVD synthesis as this method is known to favor high symmetry disordered and compositionally homogeneous phases with a tolerance for structural defects at the expense of phase separated as well as complex low-symmetry ordered phases.[26]

The electronic structure in terms of the spin polarized total and site projected density of states (DOS) are shown in Figure 3 for B1-like as well as corundum $(Cr_{0.5}Al_{0.5})_2O_3$ solid solutions. The energy axis is presented with respect to the Fermi level (E_F) that is placed in the middle of the bandgap. In the lower panel, the corundum solid solution DOS displays an oxygen $2s$ semi core state about 18 eV below E_F. A hybridization region between oxygen $2p$ and Al $3s$ and $3p$ as well as Cr$4s$ and Cr$3d$ orbitals is present between 8 and 3 eV below E_F. The highest occupied states are the spin up Cr$3d$ state with a small admixture of O character 1 to 3 eV below E_F. The calculated bandgap is found to be about 2.5 eV. Above E_F the spin up anti-bonding Cr$3d$-states as well as spin down non-bonding states compose the lowest unoccupied states. Further up in energy follows the spin-down anti-bonding Cr $3d$ state and at 5 eV above E_F is the Al-derived anti-bonding state.

In the middle panel the DOS for the B1-like structure with ordered vacancies is presented. The main features are very similar to the corundum case underlying the similarities of the

local environments in the two structures with octahedral coordination of metal atoms within a close-packed oxygen network. However, the calculated bandgap, about 1.5 eV, is lower than in the corundum structure. The top panel shows the DOS of the B1-like structure with disordered metal vacancies. The DOS spectrum bears the signatures of structural disorder. In particular, the SQS structure employed in these calculations includes oxygen sites coordinated with as few as two and as many as five metal atoms, not only the ideal four metal atoms. This is directly reflected in a broadening of the O 2s semicore state as well as in a smearing of the O 2p band. A distinct effect is also seen in the broadening of the Cr3d-dominated state just below E_F. The bandgap in this structure is found to be only 0.1 eV. These calculated density of states are in good agreement with the measured valence band in Ref.[10] and facilitates their interpretation. It should be noted that bandgaps are typically underestimated in standard LDA calculations. This is in line with the experimental estimation by Kim *et al.* of the d-d bandgap of Corundum $(Cr_{1-x}Al_x)_2O_3$ to be around 3.7 eV for all Cr-rich compositions[27] to be compared with our calculated value of 2.5 eV. As a further comparison, Praveen *et al.* performed hybrid functional calculations of different ordered corundum $(Fe,Cr,Al)_2O_3$ phases and found the band gap for Cr_2O_3 to be 4.30 eV.[28] An octahedral crystal field splitting between t_{2g} and e_g states can be seen in the Cr 3d states. For the corundum structure the splitting in the spin up channel is equal to the band gap of 2.5 eV and around 1 eV between the unoccupied spin down Cr 3d states in line with calculations for Cr_2O_3 in the litterature[19].

In the present case, where the band gap is determined by the separation of strongly correlated Cr 3d states, the band gaps are sensitive to the specific value of the Hubbard U in our simulations. It could also be sensitive to the chosen magnetic state where the disordered paramagnetic state is probably in a better agreement with the experimental situation than the here considered ferromagnetic approximation. Nevertheless, the qualitative differences between the three structures observed in the calculations should be trustworthy.

It is clear from the electronic band structure of disordered B1-like $(Cr_{0.5}Al_{0.5})_2O_3$, in particular the very small bandgap at E_F, that this structure is more tolerant for lattice defects in the form of deviations from the ideal 2:3 stoichiometry with additional metal ions, as reported in Ref.[10] or nitrogen substitutions for oxygen as in Refs.[9,29], as compared to its more ordered counterparts.

In conclusion, we have modeled the B1-like cubic as well as corundum $(Cr_{1-x}Al_x)_2O_3$

solid solutions with a disordered Cr and Al distribution using first principles calculations. Our results in terms of lattice parameters, energetics, and valence band spectra verify the experimental reports of metastable cubic B1-like $(Cr_{1-x}Al_x)_2O_3$ structures stabilized by about one third metal site vacancies. The cubic phase is higher in energy than the corundum solutions although with excess values similar to well known metastable B1 nitride solid solutions. The electronic DOS shows that also the B1-like $(Cr_{1-x}Al_x)_2O_3$ structure is a semiconductor at the ideal 2:3 metal-to-oxygen ratio, although with smaller band gaps than for the corundum phase.

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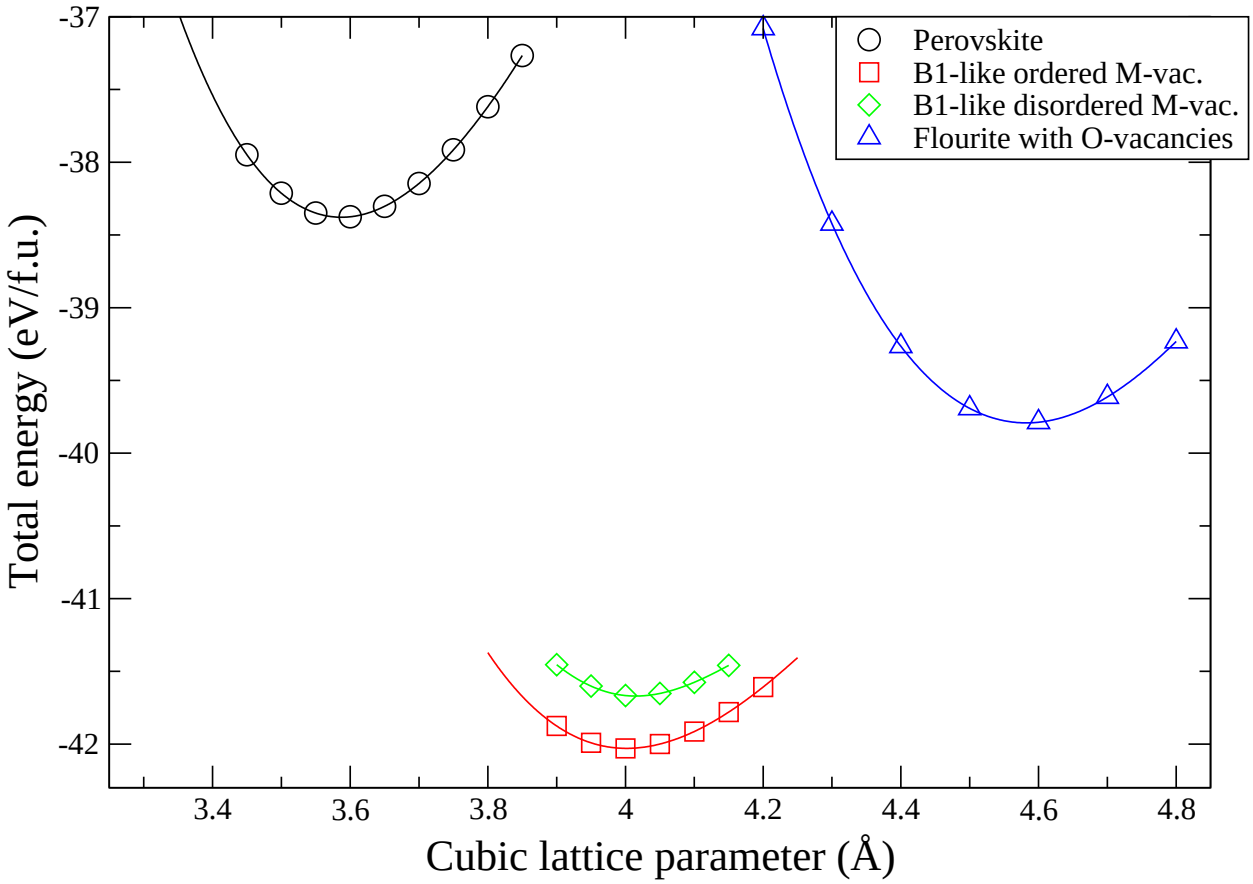

FIG. 1. (Color online) Calculated energy versus cubic lattice parameter for perovskite, B1-like and fluorite like $(Cr_{0.5}Al_{0.5})_2O_3$ structures, the latter two including metal and oxygen site vacancies.

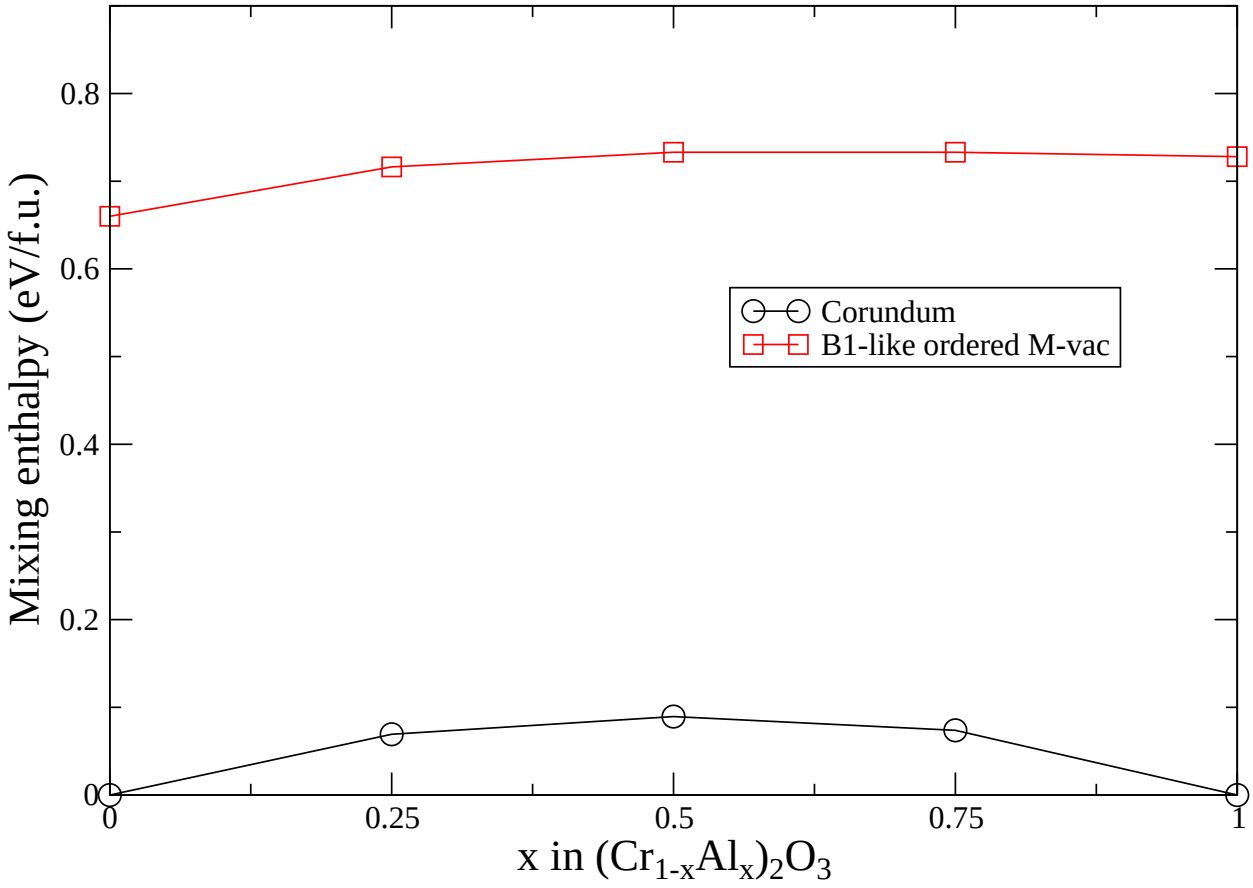

FIG. 2. (Color online) Mixing enthalpies of the B1-like structures with ordered vacancies as compared to corundum solid solutions.

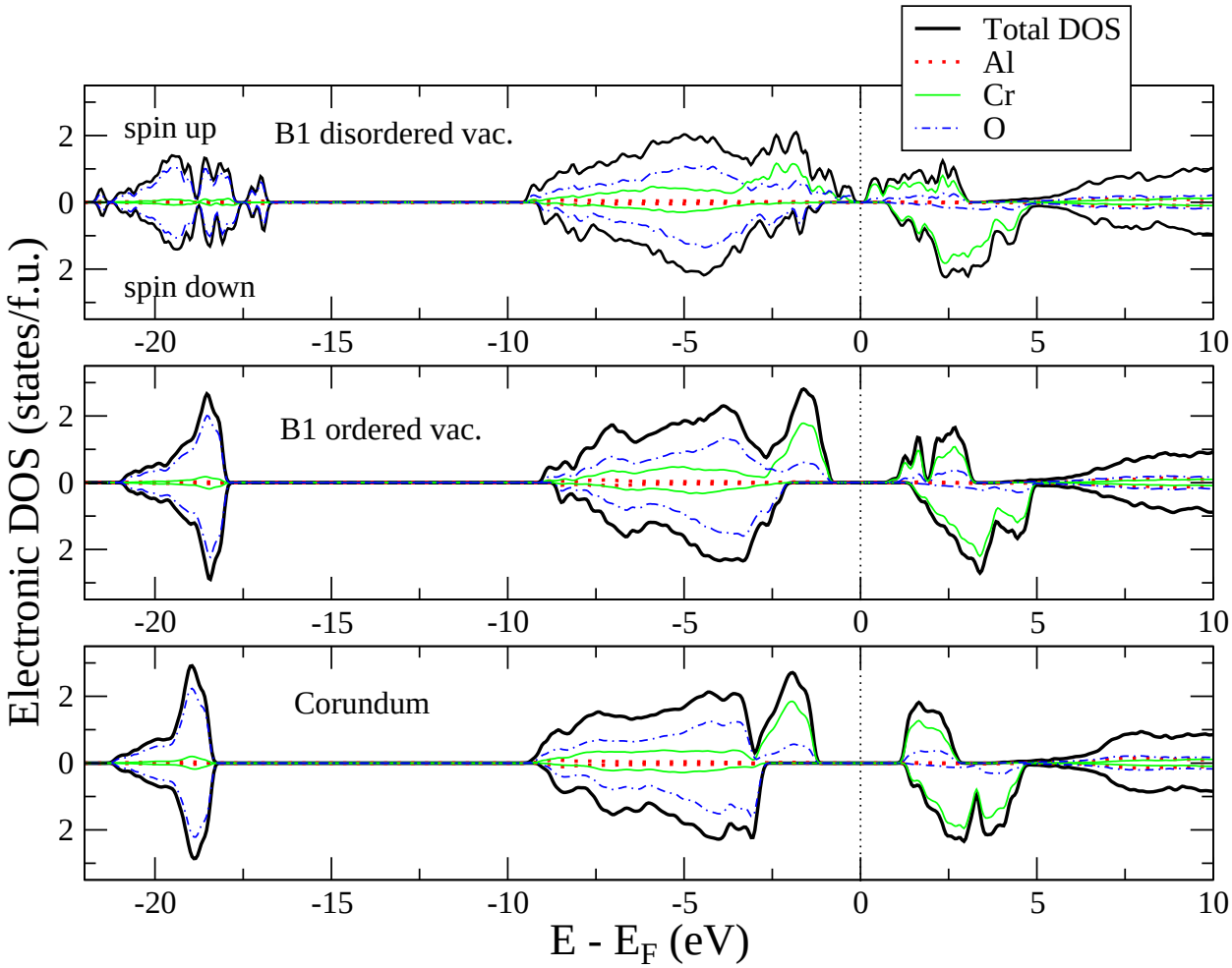

FIG. 3. (Color online) Calculated electronic density of states for $(Cr_{0.5}Al_{0.5})_2O_3$ solid solutions in B1-like structures with disordered and ordered metal vacancies, as well as in the corundum structure. The total DOS, and the average site projected DOS on Al, Cr, and O atoms are shown.