

Valence and core-loss EELS combined to *ab initio* calculations for the rationalization of the electronic properties of nanolaminated conducting ceramics.

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1. INTRODUCTION

The $M_{n+1}AX_n$ phases (where M is an early transition metal, A an element from the group III-V and X is C or N), are nanolaminated ceramics. They crystallize in the $P6_3/mmc$ space group and can be described as the stacking of “n” MX octahedra layers ($n = 1$ to 3) interleaved between pure A layers (see fig. 1(a)). Because of their peculiar crystallographic structure, which results in complex charge transfers between the M, A and X elements, these materials combine the best properties of metals and ceramics. $M_{n+1}AX_n$ phases are thus intensively investigated for diverse applications including structural materials for nuclear power plants, high temperature ohmic contacts on SiC, or as magnetic nanolaminates.^{1,2} For all of these applications, the anisotropy of the unit cell - and related physical properties - and the versatility of the accessible chemical compositions are key parameters to be investigated.

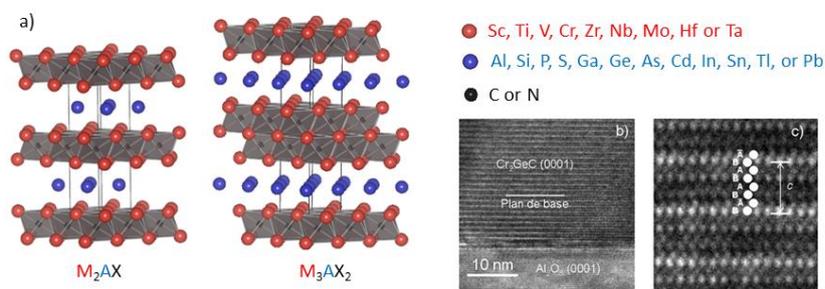


Figure 1: a) Schematic of MAX phases unit cell with $n = 1$ or 2. b) and c) high resolution TEM micrographs of a Cr_2GeC thin film epitaxially grown on a Al_2O_3 substrate.

In this context, we use electron energy-loss spectroscopy (EELS) in order to investigate the electronic structure of these materials at the nanometer scale, with controlled crystallographic orientation. Both valence and core electron excitations are studied in order to obtain a complementary picture related to the global valence electron gas behavior and the site projected electron density. The valence EELS (VEELS) and energy-loss near edge structures (ELNES) signals are quantitatively interpreted using *ab initio* simulations. In particular we show that, when focusing on the electronic structure projected within the basal plane of the structure, these ceramics can be described as atomic scale superlattices built on independent MX and A layers: this simple picture is discussed in terms of the physical properties of MAX phases, with particular emphasis on solid solution effects on their electronic transport properties.

2. RESULTS

2.1 Experimental and calculation details

The following MAX phases, corresponding to the $n=1$ or 2 stacking sequences (see fig. 1a), have been investigated: Ti_2AlC , Ti_3AlC_2 , Ti_2AlN , Cr_2AlC as well as $Ti_2AlC_xN_y$ solid solutions. TEM samples were prepared either in cross-sections or plane views in order to investigate the anisotropy of the electronic structure. Experiments were performed in a JEOL 2200 FS microscope equipped with an in-column omega filter and operated at 200 kV. The energy resolution, determined from the zero-loss peak full width at half maximum is 0.8 eV. For each sample, both the VEELS signal and the C or N-K edges were acquired.

Simulations of the experimental data were performed using codes based on the density functional theory. For the VEEL spectra, different approximations going from the independent particle approximation (IPA) up to an accurate treatment of many-body (MB) effects using either time-dependent DFT or the Bethe-Salpeter equation formalism were used.³ The ELNES were simulated using a real space multiple scattering approach as

implemented in the FEFF code:⁴ fine structures are thus analyzed in terms of the different coordination shells around the excited atom.

2.2 Results and discussion

Numerical investigations of the VEELS signal were used to optimize the experimental acquisition conditions (zone axis, collection angles) in order to disentangle the anisotropy of the MAX phases' dielectric tensor from MB effects. By doing so, data mainly determined by the basal plane dielectric response with minimized MB effects were collected. From the direct connection between the ground state electronic structure and the VEELS signal, an effective medium (EM) approach describing the MAX phase as an atomic scale superlattice $[MX/A]_p$ is shown to reproduce both the *ab initio* calculation and the experiment (see fig2 (a) for Cr_2AlC). The EM approach is also relevant to other compositions. The analysis of core-loss spectra supports this superlattice picture: FEFF calculations, in good agreement with the experiments (see fig2 (b-c)), show that the ELNES at the X element K edge are insensitive to the A element. They are thus a direct probe of the electron density within the MX layers.^{5,6}

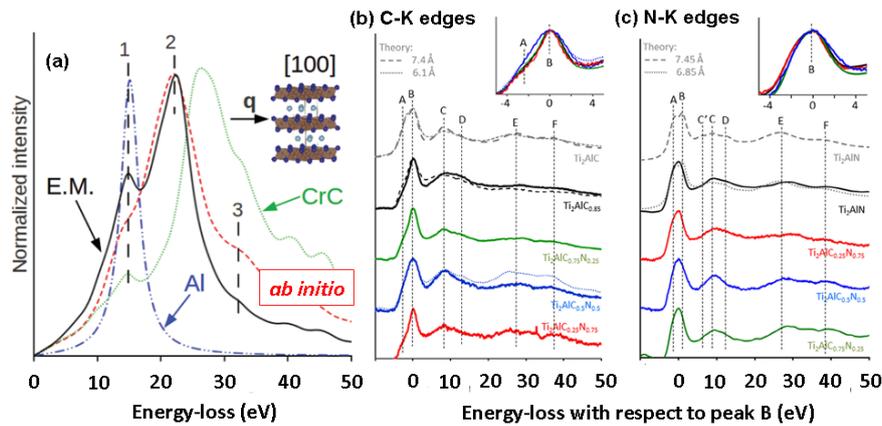


Figure 2: (a) Comparison between the basal plane VEELS signal deduced from the effective medium approach (black line) and the *ab initio* calculation (red dashed line). The Al (blue dashed-dotted line) and CrC (green dots) theoretical VEEL spectra are also given for comparison. ELNES at the (b) C-K and (c) N-K edges in $Ti_2AlC_xN_y$ solid solutions. The corresponding simulations are given in gray.

Since electronic structure calculations show that the charge carriers involved in MAX phases transport properties mainly result from the MX layers,⁷ the X element K-edge is used to investigate solid solution effects on the electronic structure and related transport properties in the $Ti_2AlC_xN_y$ systems. The very weak changes observed experimentally (see fig. 2 b and c) give evidence of a small perturbation of the MX layer electronic structure.⁶ These observations give support to simplified *ab initio* calculations, which allow for an estimation of the relative weight between charge carrier concentration and electron-phonon coupling effects in the variation of the resistivity of the system as a function of the composition.⁶

3. CONCLUSION

From the combination of valence and core-loss EELS with *ab initio* calculations, the electronic structure of MAX phases is rationalized in terms of their elementary building blocks. The site projected electron density, as probed in ELNES, is then used to investigate solid solution effects in the electronic transport properties of the $Ti_2AlC_xN_y$ system. EELS data give support to a simple numerical approach allowing for an estimation of the relative contributions between charge carrier concentration and electron-phonon coupling effects in the evolution of the resistivity as a function of the composition.

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