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ARTICLE

Structural, magnetic and electrical transport properties of non-conventionally prepared MAX phases V_2AlC and $(V/Mn)_2AlC$

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Supplementary Information

Experimental details

For powder X-ray diffraction measurements, a small part of the densified pelled was ground resulting in a fine powder. The powder materials were subsequently loaded onto flat plat holders and measured with a powder diffractometer system STOE STADI P with monochromatized Cu radiation in transmission geometry. Rietveld refinements were obtained using the program TOPAS (Topas Academic v4.1, Alan Coelho, Brisbane, Australia).

High resolution EDX mapping is performed on different spots of the polished pellet of the bulk $(V_{1-x}Mn_x)AlC$ with x = 0.05, 0.1 and 0.15 in a Zeiss LEO 1530 with GEMINI column equipped with an Oxford Instruments MAX 80 mm^2 EDX system working with INCA 4.4 software. This system features a positon accuracy of better than 100 nm. All EDX data were taken at 20 kV with an energy resolution of 10 eV. The analysis of individual EDX spectra has error bars on the order of 0.5 at% for Al, V, and Mn. The C content is slightly overestimated due to increased sensitivity of the detector at low energies.

Aberration corrected scanning transmission electron microscopy (STEM) was carried out at 120 kV using a JEOL 200F. Atomic resolution high angle annular dark-field Z-contrast images (HAADF) were acquired using a convergence angle of 41.11 mrad and a 6C spot size. Energy-dispersive X-ray (EDX) spectra were acquired using a JEOL EDS-system JED-2300T system provided with a 50 mm^2 light-element-sensitive X-ray detector and an acquisition time of 60 s. A beam shower procedure was performed prior to the EDX acquisition to minimize errors in the carbon EDX quantification. Electron energy-loss spectra (EELS) were acquired with a convergence angle of 59.67 mrad and a collection angle of 10.5 mrad. The spectra were integrated 25x using an acquisition time of 2 seconds.

The TEM samples were prepared by conventional grinding and polishing followed by dimpling and ion milling to electron transparency. For STEM imaging a camera length of 6 cm, a 30 µm condenser aperture, a 3 mm bright-field aperture, and a 6C spot size were used. This yields a convergence angle α = 24.8 mrad, a maximum bright-field detector angle of 23 mrad and a high-angle angular dark-field (HAADF) angular detection range of 90–370 mrad. EELS and EDX experiments were carried out with a 70 µm condenser aperture corresponding to a convergence angle α = 59.21 mrad increasing the EELS signal.

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The corresponding detectors are a Gatan Enfina EELS spectrometer and a JEOL EDS-system JED-2300T system provided with a 50 mm^2 light-element-sensitive X-ray detector, respectively. The energy-resolution in EELS, as measured by the full-width half-maximum of the zero-loss peak, was about 0.8 eV. The camera length was reduced to 4 cm yielding a collection semi angle β = 10.5 mrad. For low-loss EELS a 1 mm spectrometer entrance aperture was used whereas for core-loss it was a 3 mm one. Wide range STEM-EELS spectra were acquired for measuring the Al-$L_{2,3}$, C.K and V-$L_{2,3}$ edges simultaneously using the following settings: 3 mm spectrometer entrance aperture, 2 s acquisition time per pixel, 25 integrated frames, and 0.5 eV energy dispersion.
High resolution EDX mapping is performed on different spots of the polished pellet of the bulk $(V_{1-x}Mn_x)AlC$ with x = 0.1 and 0.15 in a Zeiss LEO 1530 with GEMINI column equipped with an Oxford Instruments MAX 80 mm2 EDX system working with INCA 4.4 software. This system features a positon accuracy of better than 100 nm. All EDX data were taken at 20 kV with an energy resolution of 10 eV. The analysis of individual EDX spectra has error bars on the order of 0.5 at% for Al, V, and Mn. The C content is slightly overestimated due to increased sensitivity of the detector at low energies.
Electric transport and vibrating sample magnetometry (VSM) is measured in a Quantum Design Physical Property Measurement System (PPMS) at variable temperatures T = 2.5 – 370 K. Transport properties are determined with a custom made sample holder by 4 Au-coated spring pins slightly pressed in the pellet driving the current up to 10 mA through the sample and measuring the voltage drop between the inner pins. The cylindrical pellets with approximate diameter of 10 mm and thickness of 2 mm are cut in two halves to fit the sample holder. The material resistivity for the geometry of the measurements was calculated in accordance to Miccoli *et al.* [The 100th anniversary of the four-point probe technique: the role of probe geometries in isotropic and anisotropic systems, Miccoli et al,J. Phys.: Condens. Matter 27, 223201, 2015]. VSM is performed on 20-40 mg powders in standard PPMS capsules in variable fields $\mu_0 H$ up to ±9 T.

Density functional theory calculations were carried out with the Wien2k package [P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvaniscka, and J. Luitz, WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties (Technische Universität WIEN, Austria, 2001)]. The exchange and correlation were taken into account using the Perdew-Burke-Ernzerhof (PBE) parametrization [J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).]. The convergence parameter RMT Kmax, which controls the size of the basis set for the wave function, was set to 7.0. The muffin-tin sphere radii of V, Al and C have been chosen as 2.11, 2.42 and 1.73, respectively. The number of k points was set to 50000 for good convergence in the full Brillouin zone resulting in 2541 in the irreducible part. The self-consistent cycle was converged below 0.0001 for the energy and below 0.001 for the charge.

Magnetization curves for all samples at different temperatures

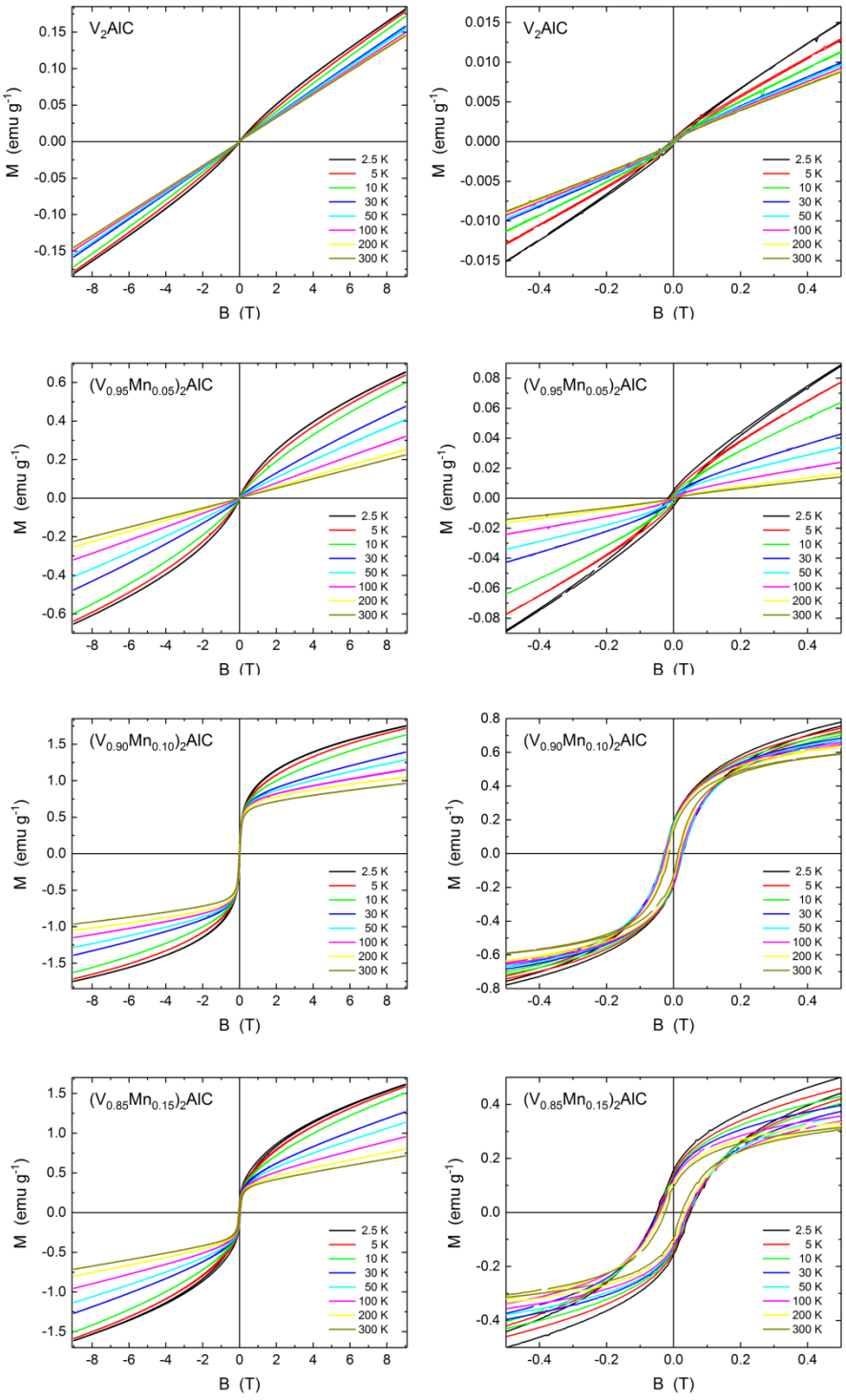

Figure SI-1: Magnetization as a function of magnetic field at different temperatures for all samples studied. Note that nominal compositions are given in the figure. Right panels show a magnification around zero field.

Calculated density of states of V_2AlC

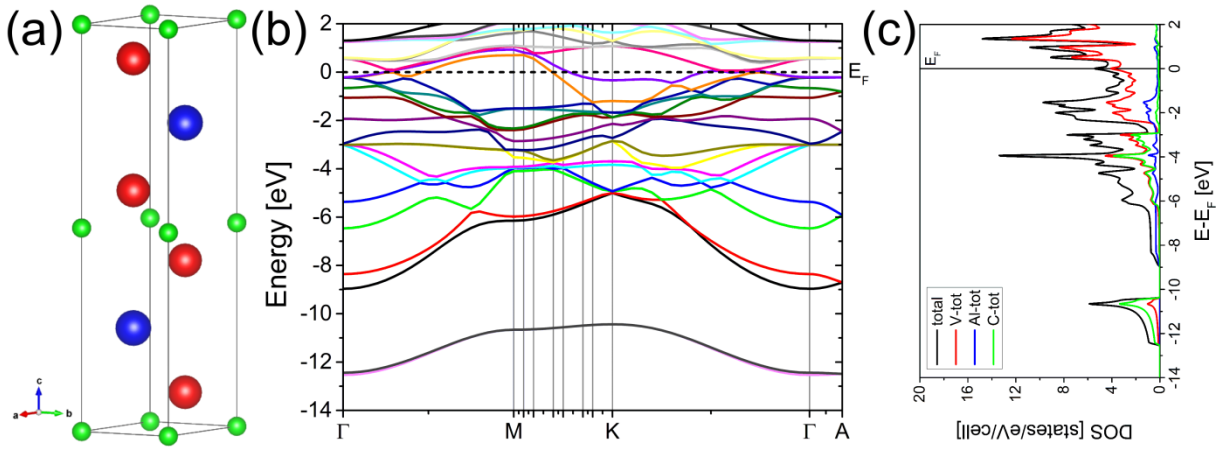

Figure SI-2: (a) Unit cell of V_2AlC with V atoms in red, Al atoms in blue and C atoms in green [K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," J. Appl. Crystallogr., 44, 1272-1276 (2011).]. (b) Calculated band structure along the standard hcp path. (c) Total calculated density of states (per element) using the WIEN2k code [P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvaniscka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Technische Universität WIEN, Austria, 2001).].

Resistivity as function of temperature in logarithmic scale

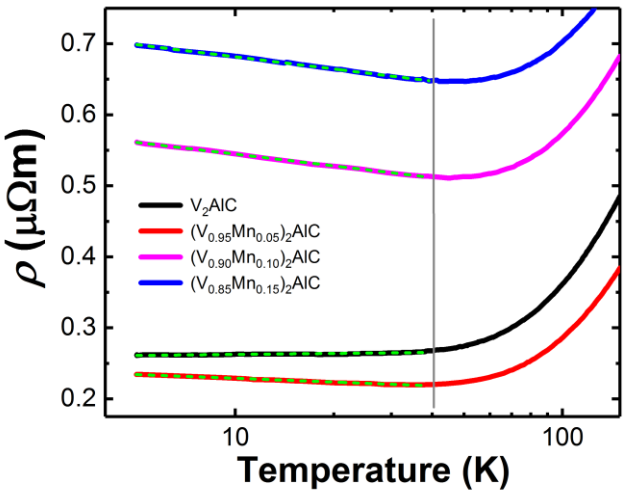

Figure SI-3: Resistivity as function of temperature in logarithmic scaling of the four investigated samples. While the parent V_2AlC compound has a constant resistivity between 5 K and 40 K, the Mn-doped samples show a logarithmic decrease at low temperatures as indicated by dashed green linear fits in this scaling. Note that nominal compositions are given in the figure.

Field-cooled magnetization in B = 1 T

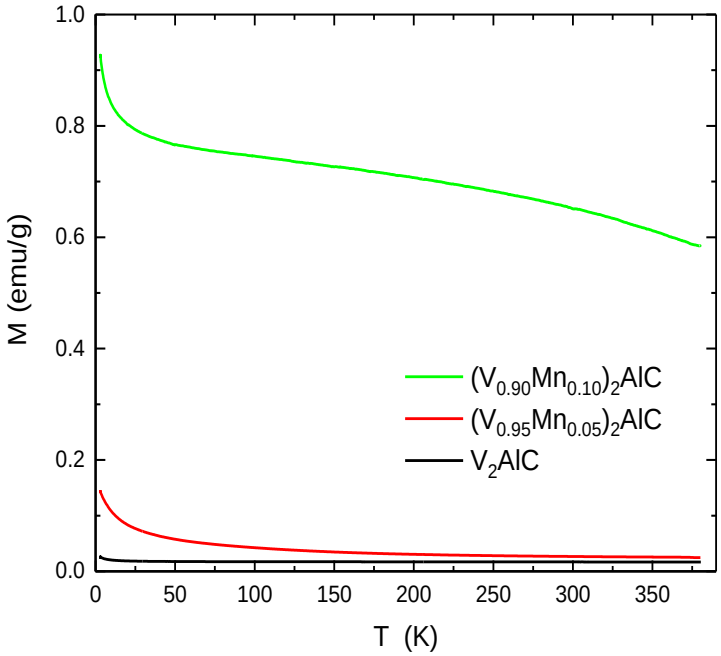

Figure SI-4: Magnetization as function of temperature in B = 1 T for the parent compound and doping levels of 0.05 and 0.10. The curves were measured while cooling the sample down from 380 K to 5 K (field cooling). The phase pure samples V_2AlC and $(V_{0.96}Mn_{0.04})_2AlC$ have a very low magnetization while for the sample with precipitates the signal rises by about an order of magnitude and show a characteristic curvature of a ferromagnetic with a Curie temperature of 500-600 K. Note that nominal compositions are given in the figure.