Supporting Information for design of semiconducting electrides via electron-metal hybridization: the case of Sc$_2$C

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Table S1:
We compared the predicted x-ray diffraction pattern for layered Sc₂C to the diffraction pattern in Rassaerts et. al.¹ and found that while many of the predicted peaks do match well with the published data, the 1967 pattern misses several intense peaks. These missing peaks are within 0.2° of other intense peaks which were observed. It is unclear whether the absence of neighboring peaks is due to instrumental broadening. Our inspection of papers from this era indicates that typical instruments had instrumental broadenings below 0.1° two-theta, and a larger width of peaks is indicative of higher structural disorder². We therefore expect that the absence of peaks 0.1-0.2° apart suggests the previously synthesized material was not layered Sc₂C.

| Index | McRae et. al. Sc₂C XRD shifts | Rassaerts et. al.¹ Sc₂C XRD shifts | McRae et. al. Sc₂C XRD intensities | Rassaerts et. al. Sc₂C XRD intensities |
|-------|-------------------------------|------------------------------------|-----------------------------------|--------------------------------------|
| (111) | 16.2°                         | 16.2°                              | 5,080 – weak                      | Weak                                 |
| (0-1-1)| 32.7° missing                 | 20,000 – very strong               | Missing                           |
| (222) | 32.8°                         | 32.9°                              | 7,000 – very strong               | Very strong                          |
| (211) | 38.0°                         | 38.2°                              | 20,000–very strong                | Very strong                          |
| (3-22) | 50.1° 50.3°                   | 1,300 – very weak                 | Very weak                         |
| (10-1) | 54.7°                         | 55.0°                              | 6,750 - strong                    | Strong                               |
| (332) | 54.9° missing                 | 5,890 - weak                      | Missing                           |
| (00-2) | 65.15° missing                | 2,300 - weak                      | Missing                           |
| (321) | 65.24° 65.6°                  | 4,290 – weak                      | Medium strong                     |
| (433) | 65.4° missing                 | 1,815 – weak                      | Missing                           |
| (0-2-2) | 68.4° 69.0°                   | 2,770 - weak                      | Medium weak                       |
| (422) | 81.1°                         | 81.5°                              | 1,370 - weak                      | Weak                                 |

Computational Methods
We explored the phase diagram of Sc-C computationally using the Universal Structure Predictor: Evolutionary Xtallography (USPEX)³ software. This is an algorithm that predicts stable and metastable phases within a given materials system. Structure optimizations were performed in the Vienna ab-initio Simulation Package (VASP) using the projector-augmented wave potentials to describe core electrons⁴,⁵. The generalized gradient approximation (GGA) PBE functional was used for relaxing structures and calculating energies⁶. We performed convergence tests for each USPEX structure. We ran a variable composition USPEX calculation where we allowed 5-10 atoms in the unit cell, and each generation had 1000 structures. The calculation ran for 60 generations before stopping, producing 60,000 structures. We found that there were many compositions with structures close to the hull, so we then ran fixed composition calculations on these compositions, where we explored unit cells up to 25 atoms.

For each density functional theory (DFT) calculation, a structural relaxation was performed followed by a more rigorous single-point energy calculation. The plane-wave energy cutoff was 650 eV and a Monkhorst-Pack k-point grid was used. The break condition for the energy in the electronic SC-loop in the relaxation step was 10⁻⁸ eV and for the energy calculation was 10⁻⁹ eV. The zero damping DFT-D3 dispersion correction of Grimme was used⁷ and a U parameter correction of 3 eV was placed on Sc since the Sc 3d orbitals are localized⁸.

The properties of the stable structure for Sc₂C were calculated using the GGA PBE functional for work function and mechanical properties, the GGA PBEsol functional⁹ for lattice
parameters, and the hybrid density HSE-06 functional\textsuperscript{10} for electronic structures and electron localization functions.

Work functions from thin slabs of 12 (hkl) planes of Sc\(_2\)C surrounded by 12 (hkl) planes of vacuum were calculated using the method from Fall \textit{et. al.}\textsuperscript{11}. These values were converged with respect to the number of layers. VASP\textsuperscript{kit} was used to calculate the vacuum level\textsuperscript{12}.

We used the ab initio scattering and transport (AMSET) package to calculate scattering rates and electrical conductivity\textsuperscript{13}. Three types of scattering were calculated: acoustic deformation potential scattering (ADP), ionized impurity scattering (IMP), and polar optical phonon scattering (POP). Density functional perturbation theory\textsuperscript{14} was used to calculate the static and high-frequency dielectric constants necessary for IMP and POP. The elastic constant matrix was calculated using the finite difference method.

**Experimental Methods**

**Synthesis of Sc\(_2\)C**

All steps were performed under inert atmosphere (Ar). Before use, scandium (Alfa Aesar, distilled dendritic, 99.9\%) was arc-melted to form one large piece of scandium, which facilitates subsequent arc-melting. The scandium was combined with graphite (Sigma-Aldrich, \textasciitilde 100 mesh flakes, 99.9\%) in a typical ratio of 67.3 at. \% and 32.7 at. \% for scandium and graphite, respectively. This includes a slight excess of scandium (<1 at. \%) to account for scandium ablation in the melting process. The pellet after melting was loosely wrapped in Ta foil (Sigma-Aldrich, 0.025 mm thick, \textgeq 99.9\%) and sealed in a fused quartz ampule under 1 mBar Ar. The ampule was then heated to 1373 K at a ramp rate of \textasciitilde 3.5 K/min. The temperature was held for 7 days, and then cooled back to room temperature at the same rate. The pellet was then ground into a powder in a mortar and pestle for further analysis.

**Characterization of Sc\(_2\)C**

All analyses were performed under inert atmosphere except for studies of sample oxidation. Powdered samples of Sc\(_2\)C were characterized by x-ray diffraction (XRD) at room temperature in a Bragg-Brentano geometry across a range of 30–130° using Cu K\(_\alpha\) (\(\lambda=1.54056 \text{ Å}\)) in a Rigaku Smartlab diffractometer. The Sc\(_2\)C was covered with Kapton tape to keep the sample air-free. The pattern was indexed and refined using the PDXL software from Rigaku. Samples for transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were prepared by suspending Sc\(_2\)C powder in 1,3-dioxolane and sonicating for 30 minutes. Three microliters of the suspension were drop-cast onto a lacy carbon grid and dried under vacuum for 16 hours. The samples were loaded into a Thermo Scientific Talos F200X Transmission Electron Microscope and studied at room temperature under high vacuum at an accelerating voltage of 200 kV. STEM samples were probed with a 7 nm condensed beam. Electrical conductivity measurements were performed using a chunk of Sc\(_2\)C before grinding. Bare copper wire (Arcor Electronics, 38 AWG, >99\%) was attached to the chunk using electrically conductive adhesive (MG Chemicals, Silver & Epoxy) in a van der Pauw geometry\textsuperscript{15}.

Thin films were characterized by x-ray photoemission spectroscopy (XPS) using a Kratos Axis Ultra Delay-Line Detector spectrometer with a monochromatic Al K\(_\alpha\) source. For these measurements, the powder was pressed into indium substrates. High resolution XPS data were
collected at a pass energy of 20 eV, and a charge neutralizer was used for charge compensation. All data were corrected to the C 1s peak at 284.6 eV. All XPS lines except those from the s orbitals occur as doublets due to spin-orbit coupling. Doublets originating from 2p orbitals will consist of the 2p$_{3/2}$ and the 2p$_{1/2}$ peaks, and typically, the intensity ratios will be 2:1, and the full width at half maximum (FWHM) of both peaks in the doublet will be the same. This results in a 2:1 area ratio of the 2p$_{3/2}$ and the 2p$_{1/2}$ peaks. In the case of the Sc 2p peaks, however, it has been reported that the Sc 2p peaks do not follow these rules. The Sc 2p$_{1/2}$ peak is typically wider than the Sc 2p$_{3/2}$ peak, and the peak splitting varies somewhat depending on the Sc species\textsuperscript{16}. This data informed our peak fitting process.

After 11 days of oxidation, the Sc sample showed a single doublet which we assume is from the fully oxidized species. This data was fit with two peaks (GL(30) function in Vision Processing software) that were not constrained in any way. Once the peak positions, widths, and heights were optimized, the relative peak positions, relative FWHM and peak heights were fixed with respect to each other (Component A).

This constrained doublet was then applied to the data obtained at the initial time point. The data required an additional component, which we assume to be a carbide component, given the prominent carbide peak present in the C 1s spectra. An asymmetric doublet (AS(80,0.4) function in the Vision Processing software) was added, but the two peaks in the doublet were not constrained in any way. The asymmetry function was varied, and the AS(80,0.4) function provided the best fit, especially when considering the peak at ~398 eV which is better resolved. These peaks were then constrained so that their relative peak positions, FWHM, and heights were fixed to each other (Component B). With these two doublets (fully formed oxide and carbide), there was still unfitted intensity in the data. A third doublet was added, which we assume is an intermediate species as the carbide transitions to the fully formed oxide. Again, peaks were added without constraint, allowed to vary, and once a best fit was obtained, they were fixed with respect to each other (Component C). Finally, there was a small peak at low binding energy (395 eV). It is unclear if this is Sc or possibly N, since the binding energy of this peak is low for either element. We fit this as a fourth doublet (Component D). Its intensity is low, and it doesn’t affect the quality of the peak fit much. The relative peak positions and relative FWHM values for the Sc 2p$_{3/2}$ and Sc 2p$_{1/2}$ peaks were compared to literature data\textsuperscript{16}, and found to match reasonably well (Table X). It should be noted that an asymmetric peak shape was used to fit the carbide component because the cubic phase (ScC$_x$) is known to be metallic and because it looked like the data warranted it. Elemental Sc also shows an asymmetric peak shape\textsuperscript{16}.

The 4 sets of doublets used to fit the as-made data were applied to the 1-day data. They did not fit perfectly by just allowing the constrained doublet heights, widths and positions to vary, so one by one, the components in each doublet were allowed to vary, optimized, and then fixed with respect to each other. The resulting relative peak positions and relative FWHM values for the Sc 2p$_{3/2}$ and Sc 2p$_{1/2}$ peaks were compared to literature data\textsuperscript{16}, and found to match reasonably well, with the exception of the intermediate phase (Component C). In this case, the peak separation for the Sc 2p$_{3/2}$ and Sc 2p$_{1/2}$ peak was 4.0 eV, when it is more commonly reported as 4.5 eV for scandium oxides. In addition, the relative peak areas, which should be 2:1 were closer to 1.2:1. Attempts were made to constrain the peaks in this doublet to more reasonable values, but the peak fit was noticeably worse. The cause is unclear, but perhaps another intermediate species is also
present. However, it's not clear from the data where this would be, or how this would improve the fit. Chi squared values for the resulting fits were 3.5 (as-made), 3.7 (1 day) and 4.8 (11 day).

Table S2: Scandium XPS peak positions

|       | 11 days (eV) | 1 day (eV) | 0 days (eV) | Literature (eV) |
|-------|--------------|------------|-------------|-----------------|
| 2p^{1/2} A | 406.1        | 406.0      | 405.9       | 406.2^{16}      |
| 2p^{3/2} A  | 401.6        | 401.5      | 401.4       | 401.7^{16}      |
| 2p^{1/2} B  | 402.5        | 402.4      |             | 401.8^{17}      |
| 2p^{3/2} B  | 397.8        | 398.0      |             | 398.5^{17}      |
| 2p^{1/2} C  |             |            | 403.6       | 403.9           |
| 2p^{3/2} C  | 399.5        | 399.4      |             |                 |
| 2p^{1/2} D  | 400.5        | 400.1      |             |                 |
| 2p^{3/2} D  | 396.0        | 395.6      |             |                 |

Table S3: Scandium XPS peak splitting

|       | 11 days | 1 day | 0 days | Literature |
|-------|---------|-------|--------|------------|
| A     | 4.48    | 4.48  | 4.48   | 4.45^{16}  |
| B     | 4.66    | 4.66  |        |            |
| C     | 4.03    | 4.48  |        |            |
| D     | 4.48    | 4.48  |        |            |

Table S4: Scandium XPS FWHM 2p^{3/2}:2p^{1/2}

|       | 11 days | 1 day | 0 days | Literature |
|-------|---------|-------|--------|------------|
| A     | 0.79    | 0.79  | 0.79   | 0.75^{16}  |
| B     | 0.94    | 0.94  |        |            |
| C     | 0.85    | 0.79  |        |            |
| D     | 0.79    | 0.79  |        |            |
Figure S1: XRD pattern of typical arc-melting synthesis without annealing

| Occupancies  | Sc | C  | Quant |
|--------------|----|----|-------|
| Cubic ScC    | 1.00 | 0.5 | 59%   |
| Layered ScC | 1.00 | 1.00 | 41%   |

Figure S2: XRD pattern of Sc$_2$C$_{0.95}$

| Occupancies  | Sc | C  | Quant |
|--------------|----|----|-------|
| Cubic ScC    | 1.00 | 0.5 | 48.7% |
| Layered ScC | 1.00 | 1.00 | 51.3% |
Figure S3: XRD pattern of Sc$_2$C$_{1.13}$

| Occupancies  | Sc | C | Quant   |
|--------------|----|---|---------|
| Cubic ScC    | 1.00 | 0.5 | 88.1%   |
| Sc$_4$C$_3$   | 1.00 | 1.00 | 11.9%   |

Figure S4: 2D electron localization functions of Sc$_2$C, Y$_2$C, and Al$_2$C
The band structure of $\text{Y}_2\text{C}$ as compared to $\text{Sc}_2\text{C}$ has the same general shape with the difference in spins and electronegativity of the cations as the primary reasons for the different electronic properties. We would expect to see less dispersion in $\text{Y}_2\text{C}$ because yttrium is larger than scandium, but one spin is dispersed while the other is less disperse. The lower electronegativity of Y leads to a higher energy valence band and a lower energy conduction band, which likely leads to the semi-metal behavior we see in the $\text{Y}_2\text{C}$ system.

The band structure of $\text{Al}_2\text{C}$ differs from the band structure of $\text{Sc}_2\text{C}$ primarily at the L point, where the valence band is lower in energy at the L point compared to B$_1$, whereas in $\text{Sc}_2\text{C}$ has a higher energy L point than B$_1$. 

Figure S5: Band structure of $\text{Y}_2\text{C}$

![Band structure of $\text{Y}_2\text{C}$](image)

Figure S6: Band structure of $\text{Al}_2\text{C}$

![Band structure of $\text{Al}_2\text{C}$](image)
Justification for “emergence of semiconducting character in electrides”

We compared the metal-metal distances in $Y_2C$, $Sc_2C$, and $Al_2C$ to understand the orbital overlap between the metal and electride. The Y-Y distance in $Y_2C$ is 111% compared to that of yttrium metal, whereas the known electride $Ca_2N$ has a metal-metal distance of 113% compared to its calcium counterpart. This decreased metal-metal distance could explain the observation of hybridization in $Y_2C$ as the expected orbital overlap between the metal and the electride would be increased. The Sc-Sc distance in $Sc_2C$ compared to scandium metal is 109%, which would indicate even greater orbital overlap, thus greater hybridization, in this system. We wanted to further explore a possible electride structure with a similar, yet more electronegative metal, aluminum (1.61). A layered $Al_2C$ has a similar structure to that of both $Y_2C$ and $Sc_2C$ with a space group of $R\bar{3}m$, and there is observed electron localization in this structure between the layers of $Al_2C$ (Figure 5e). The Al-Al distance is larger in this material (108%) than Al metal, indicating that there is a small amount of electride character present in this material, but with a greater degree of hybridization than the other systems described.

Also, we considered the cationic radii of two $Al^{3+}$ (1.35 Å), two $Sc^{3+}$ (1.77 Å), and two $Y^{3+}$ (2.08 Å) along with the electride electron radius of ~2.5 Å\textsuperscript{18}. The metal-metal distances of 3.96 Å in $Y_2C$, 3.53 Å in $Sc_2C$, and 3.09 Å in $Al_2C$ do not allow for the electride to sit between the metals without some overlap.

Figure S7: Work function of $Sc_2C$ for (0001)
Table S5: Interlayer and Intralayer stiffness tensors for Sc$_2$C and Y$_2$C

|                | Sc$_2$C | Y$_2$C$^{19}$ |
|----------------|---------|---------------|
| Intralayer stiffness (GPa) | 286.8   | 150           |
| Interlayer stiffness (GPa)   | 136.7   | 104           |

Table S6: Mechanical Properties of Sc$_2$C and Y$_2$C

|                | Sc$_2$C | Y$_2$C$^{20}$ |
|----------------|---------|---------------|
| Bulk Modulus (GPa)     | 82.7    | 68            |
| Shear Modulus (GPa)    | 16.5    | 42            |
| Young’s Modulus (GPa)  | 46.3    | 104.5         |
| Poisson’s Ratio        | 0.407   | 0.24          |
| Bulk/Shear Ratio       | 5.027   | 1.62          |

Figure S9: TEM images of sonication experiments

In order to confirm the binding energy calculation showing that the layers of Sc$_2$C are too tightly bound for exfoliation, we performed an exfoliation process before TEM imaging. In previous work, the electride Ca$_2$N was shown to form two-dimensional sheets after exfoliation$^{21}$. We carried out the same exfoliation process on Sc$_2$C by sonicating in 1,3-dioxolane for 800 minutes under anhydrous and oxygen-free conditions. Three microliters were suspended on a lacy carbon TEM grid and dried in a vacuum chamber for 2 hours. When 2D sheets are observed in TEM, they are essentially transparent to the electron beam and have a constant thickness contrast throughout the particle. No Sc$_2$C particles were found that exhibited these properties after exfoliation. Figure S9a shows a low-magnification image of many Sc$_2$C particles, and no 2D sheets can be seen. Figure S9b shows a higher-magnification image of a thinner Sc$_2$C particle, but the thickness contrast of the particle shows a 3-dimensional “wedge” shape, rather than a 2D
The diffraction patterns in Figure S9c and S9d show two sides of the same crystal, showing that the crystal domains are, on average, greater than 1 µm.

**Figure S10: Complete XPS spectrum of unoxidized Sc$_2$C**
In the oxygen spectra, there are two peaks present at the initial timepoint, where the peak at 528.5 eV likely corresponds to ScₙOₓ or related species. The peak at 531.0 eV is in a binding energy region where many oxide species are possible, so we cannot associate this peak with any specific oxygen-type. However, the oxygen spectrum indicates that the amount of ScₙOₓ is not changing with exposure to air, as the intensity of the peak associated with the metal oxide does not change intensity with time.

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