

Ion Formation in Electronic Sputtering from Decane

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ABSTRACT

Electronic sputtering of volatile organic substances like decane and phenol have been investigated in experiments recently. Some results indicate different formation conditions for positive and negative molecular and cluster ions. The observations are explained by applying electronic transport theory and elementary scattering theory.

INTRODUCTION

K. Wien presents in this volume his experiments about the temperature dependence of PDMS spectra of light volatile molecules. These made use of the possibility to cool samples in the spectrometer in a somewhat controlled way, a feature we had originally intended to use in obtaining spectra of frozen sediment samples from the Wadden Sea. The new data of K. Wien, which are described in this volume contain considerable information about the dependence of electronic sputtering from outer physical conditions for volatile organic samples. Of the many interesting and unexplained points, we selected one interesting topic, which can be investigated on the basis of previous, more general theoretic work. Electronic sputtering from a pure decane sample yields very different positive and negative secondary ion spectra: while the positive ion spectrum shows quite sharp peaks but nearly no cluster series, the negative ion spectrum contains a series of very broad lines which can be assigned to multiples of the molecular weight.

A theory of ion formation requires basic information about the physical conditions which are formed in the desorption process and which determine the behaviour of the molecules while being ejected. As an outcome of previous theoretical (still unpublished) work we can provide more precise information about the dimensions of the regions which are involved in sputtering, electron and molecular temperature and the time scale of molecular excitations. This theoretical background can be outlined only briefly; a detailed presentation is in completion [1].

Observations

Figure 1 shows positive and negative ion spectra at comparable conditions. The coincidence of very broad lines and clustering might be interpreted in different ways:

- cluster ions can decay during acceleration (variation of mass during acceleration),
- clusters need a longer time for formation than molecular ions (variation of ejection time),
- cluster ions are produced in molecule collisions in the gas phase (variation of kinetic energy and mass).

The above observations can be completed by the results found in kinetic energy measurements by Matthäus and Moshhammer [2]. It seems to be a very general phenomenon that negative ions are ejected with lower velocities than positive ions.

Our theoretical explanation for these observations is that positive and negative ions are produced from different spatial regions, the former from the inner ion track where atoms are positively ionized, the latter from the outer ion track, where the slow secondary electrons are stopped. In later stages of the desorption mechanism electronic transport of heat and charge causes an expansion of the excited zone and a partial equilibration of charge imbalance. Due to the transport properties of decane still at higher electron temperatures (but below the ionization energy) the charges can stay separated until molecules and clusters are ejected.

Note that this approach implies that ion pair formation does not contribute to the ion yield. This assumption makes sense for the spectra observed here; we do not extend it to samples with molecules which are used to show ion pair reactions (e.g. salts).

To give possible reasons for the experimental observations from the theoretical point of view, we need at first a short discussion of the processes which form the conditions of ion sputtering.

GENERAL PHYSICAL PRECONDITIONS

Elastic Scattering of Secondary Electrons

As discussed in many review articles, the impact of a ^{252}Cf fission fragment causes an energy deposition in the range of about $1 \text{ keV}/\text{\AA}$. Contrary to the conventional view of the situation, where the electronic energy density in the ultratrack is assumed to follow a r^{-2} -law down to short distances [3, 4], we assume that a broader spatial energy distribution is formed. The reason is the elastic scattering of the secondary electrons with initial energies of about 50 eV and below, which dominate the SE spectrum, and which have a short mean free path in organic matter. The consequence of elastic scattering is that the motion of the SE has a diffusive rather than a linear character, and the width of the spatial energy distribution results from the distance they need to be stopped by *inelastic* scattering.

Elastic electron scattering cannot be neglected in condensed matter in the region around the ion track. One can estimate its role from the elastic cross section, which can be calculated as in the Lenz model [5, 6]. The quantum mechanical differential scattering cross section (proportional to the spatially Fourier-transformed potential) becomes

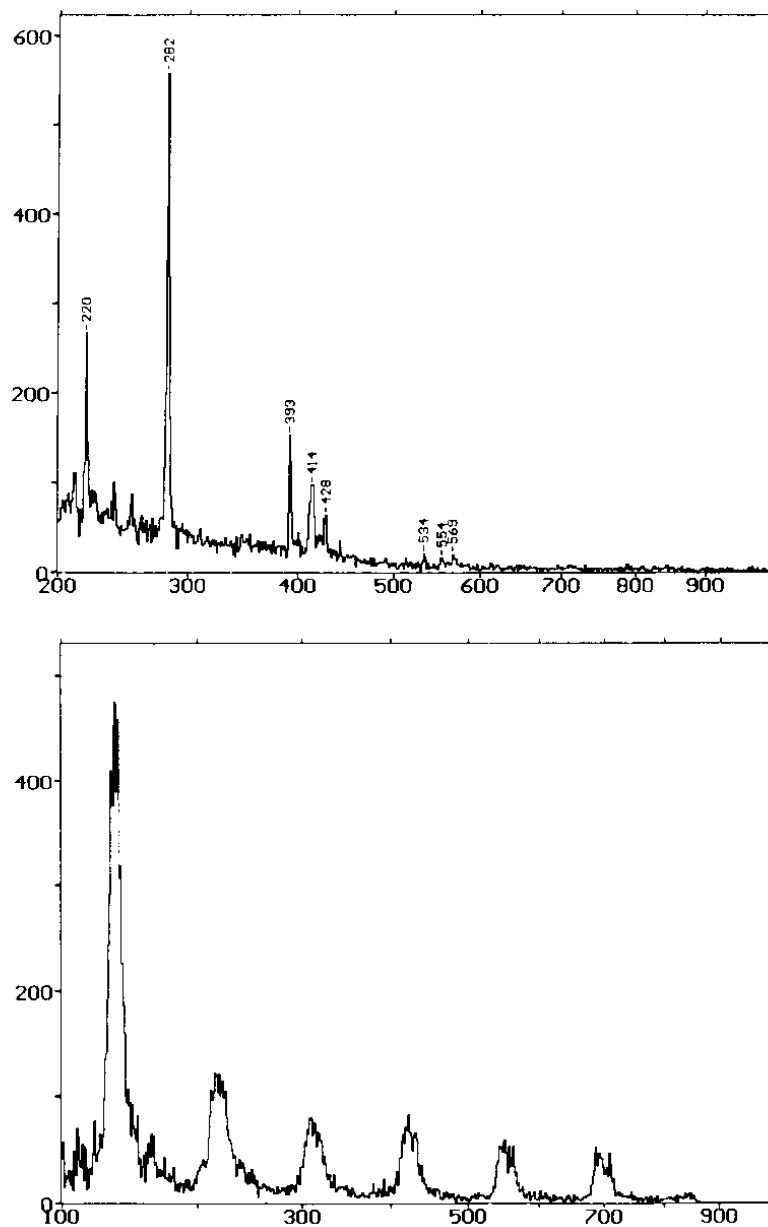


Figure 1 Positive (top) and negative (bottom) PDMS-Spectra from a decane sample at -180°C

$$\begin{aligned}\frac{d^3\sigma}{dv^3} &= \left| \frac{m_e \tilde{V}(m_e v/\hbar)}{2\pi\hbar^2} \right|^2 \delta\left(\frac{v^2 - v'^2}{2}\right) \\ &= \left| \frac{4\pi m_e Z e^2}{(m_e v/\hbar)^2 + \lambda^2} \right|^2 \delta\left(\frac{v^2 - v'^2}{2}\right)\end{aligned}$$

The screening parameter λ is (owing to Thomas–Fermi–theory) taken as $Z^{2/3}/a_0$. From this formula one can derive a cross section σ_2 for the deflection of a collimated beam of electrons by a target. σ_2 is defined by

$$\Delta v^2 = \sigma_2 n_A D v^2$$

(n_A =atomic density, D =target thickness) and gives

$$\sigma_2 = \frac{2\pi Z^2 a_0^2 \epsilon_0^2}{E^2} \left[\log(1 + E/E_Z) - \frac{1}{E_Z/E + 1} \right]$$

with

$$E_Z = \frac{Z^{2/3} \epsilon_0}{4}$$

Note that the total scattering cross section (giving the number of all scattering events) scales with $Z^{4/3}$, but σ_2 is weighted with the momentum transfer proportional to λ^2 .

The character of motion of an electron beam can be qualified by a dimensionless parameter $\alpha = |\langle \mathbf{v} \rangle|/v$ which gives the relative contribution of “straight” motion. For an isotropic velocity distribution, expected after many scattering events, $\langle \mathbf{v} \rangle = 0$. From a Boltzmann–equation applied to the distribution function for a single electron it follows that

$$\dot{\alpha} = -n_A \sigma_2 v \alpha = -\nu \alpha$$

or — in terms of the total distance s , $ds = v dt$:

$$d\alpha = -n_A \sigma_2 ds$$

The mean distance of the electron to the place of its production is $\langle R \rangle = |\langle \mathbf{x} \rangle| = |\int \langle \mathbf{v} \rangle dt|$, and $\Delta R^2 = \langle \mathbf{x}^2 \rangle - \langle \mathbf{x} \rangle^2$ can be calculated from

$$\frac{\partial \Delta R^2}{\partial t} = 2\Delta(\mathbf{x} \cdot \mathbf{v}) = 2[\langle \mathbf{x} \cdot \mathbf{v} \rangle - \langle \mathbf{x} \rangle \cdot \langle \mathbf{v} \rangle]$$

and

$$\frac{1}{v} \cdot \frac{\partial \Delta(\mathbf{x} \cdot \mathbf{v})}{\partial t} = -\nu \Delta(\mathbf{x} \cdot \mathbf{v}) + \Delta v^2$$

One can compare the action of elastic and inelastic scattering by using the energy loss formula (which finally defines ds):

$$dE = -n_A \sigma_E ds$$

with

$$\sigma_E = \frac{4\pi Z E_0^2}{E} \log\left(\frac{E}{Z E_0}\right)$$

(the I -value in this formula is approximated by $Z E_0/2$ which makes an error of some 10% for lighter elements). Due to the different scaling with Z it becomes clear that elastic scattering has a strong effect:

$$d\alpha = -\frac{\sigma_2}{v^2 \sigma} dE$$

scales with Z . Figure 2 shows the dependence of $\sqrt{\Delta R^2}/\langle R \rangle$ on the energy. Electrons starting with a certain energy E_0 (given in Ry units) lose a small fraction of E_0 until the radius of the area they are distributed over exceeds their mean distance from the ion track; very fast electrons never reach this point.

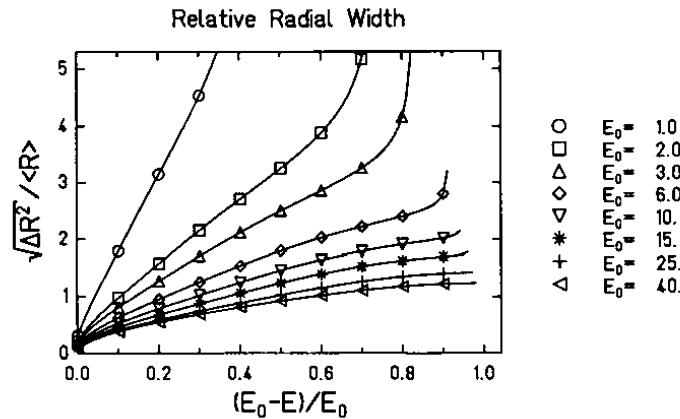


Figure 2 Change of $\Delta r/\langle r \rangle$ with decreasing energy (increasing $(E_0 - E)/E_0$). The initial energies are given in Ry units.

Initial Distribution of Charge and Energy

There are two main contributions to the spatial distributions of charge and energy, which are caused by direct or indirect action of the projectile. *Close* to the path atoms can be excited directly as they are ionized. The radius of this close excitation zone is v_p/ω_E where $\hbar\omega_E$ is the mean excitation energy, here (where the projectile is relatively slow) the ionization energy is 10 eV. From a plain wave Born approximation it follows that the secondary electron spectrum is weighted like $(E + E_I)^{-n}$ where n lies between 2 and 3 [7]. Within a radius of v_p/ω_I ($\hbar\omega_I$ =mean ionization energy) atoms are ionized; this is the radius where positive charges are concentrated initially. Secondary electrons carry charge and energy into *more distant* regions, where they are stopped. We take the respective radius from the mean SE energy which comes to about 30 eV for a ^{252}Cf fission fragment on a decane sample ($v_p = 0.5v_0$). Electrons with this initial energy lose 90% of their energy within a radius of 50 Å. While this gives the width of the *negative* contribution to the charge distribution, the SE contribution to the *energy distribution* has a mean radius of 30 Å (this is the distance where secondary electrons produced with the mean energy have lost 50% of their energy).

The resulting distribution of charge shows a narrow peak in the center of the ion track where positive ions remain after the projectile has passed. The negative charge contribution is a gaussian with a width of 50 Å. Electronic energy is highly concentrated in the *close region* and the SE contribution is distributed by a Gauss function with a width of 30 Å. This is the physical situation one femtosecond after the passage of the projectile. About 50 charge units per Å are removed from their initial positions, causing a strong electrostatic field which is 90% screened outside a radius of 100 Å by the stopped secondary electrons.

Diffusion of Heat and Charge

Scattering and stopping of secondary electrons happens within a very short time (about 10 times the inverse Bohr frequency), while an excitation of molecular motion requires at least multiples of the typical molecular vibration period (in the picosecond range). This time gap is closed by *thermal* evolution of the electron system. Electronic heat is distributed over a growing volume by diffusion, while at the same time energy is transformed into molecular heat by electron-phonon and exciton-phonon coupling. Both processes — diffusion as well as molecular and lattice coupling — decrease the electron temperature and are thus competing processes. The conditions which are “seen” by ejected molecules are a product of electronic heat diffusion with a time scale in the picosecond range.

Generally, one may distinguish two stages in this diffusion phase: the first at a temperature comparable to the ionization energy, when a “free-electron-plasma” determines the transport behaviour. Once the temperature has decreased so far that only the lowest levels are populated, the solid state properties come into effect. For ordered crystals, conduction band and hole transport will still play a role; where an exciton spectrum exists, exciton diffusion will contribute to energy transport. The latter is strongly affected by exciton self-trapping: where excitons couple strongly to the lattice, they are trapped immediately and diffusion happens only by rare hopping events. This condition holds in aliphatic solids, where in contrast to aromatic molecules, electronic states are localized to single atoms or covalent bonds. Therefore effective heat diffusion is limited to a temperature comparable to the ionization energy, where the system behaves like a plasma. Once it has been cooled down so that the energy distribution “freezes”, the conditions for later molecule sputtering are formed.

So we start with a large radial gradient of electron density and temperature. Contrary to earlier models we do not treat the return of the electrons in a ballistic way, assuming that they carry their full potential energy inside the center of the ion track. Even in organic solids the motion of electrons is limited by scattering, and generally in solid bodies the energy they can get in an external field is limited to the band width. Therefore electron motion must be treated by transport theory, as well as heat transport.

Diffusion is described by Fick's laws

$$\begin{aligned} \mathbf{J}_n &= -\alpha_{nn} \text{grad } n - \alpha_{nT} \text{grad } T - e\beta_n \mathbf{E} \\ \mathbf{J}_E &= -\alpha_{En} \text{grad } n - \alpha_{ET} \text{grad } T - e\beta_E \mathbf{E} \end{aligned}$$

and the continuity equations

$$\begin{aligned} \dot{n} &= -\text{div } \mathbf{J}_n \\ \dot{E} &= -\text{div } \mathbf{J}_E - e\mathbf{J}_n \cdot \mathbf{E} \end{aligned}$$

The electrostatic field is connected to the electron density by

$$\text{div } \mathbf{E} = 4\pi en$$

In the frame of a simple plasma theory the transport coefficients are calculated as

$$\begin{aligned} \alpha_{nn} &= \frac{\partial \gamma_n}{\partial n} & \alpha_{nT} &= \frac{\partial \gamma_n}{\partial T} \\ \alpha_{En} &= \frac{\partial \gamma_E}{\partial n} & \alpha_{ET} &= \frac{\partial \gamma_E}{\partial T} \\ \beta_n &= \frac{1}{n_M} \langle \mathbf{v}^2 \tau f' \rangle & \beta_E &= n_M \frac{1}{n_M} \langle E v l_f f' \rangle \end{aligned}$$

from

$$\gamma_n = \frac{1}{3}n_M \langle v l_f f \rangle \quad \gamma_\epsilon = \frac{1}{3}n_M \langle E v l_f f \rangle$$

where f is the Fermi-function $[\exp\{(E - E_F)/T\} + 1]^{-1}$ and f' its derivative $f(1 - f)$. Due to the short mean free path of slow "free" electrons for inelastic scattering, l_f is taken as the lattice dimension. For cylindrical symmetry and axial translation invariance (in z -direction)

$$\dot{\mathbf{E}} = 4\pi e \mathbf{J}_n$$

results, and thus

$$\dot{\mathbf{E}} = -4\pi e^2 \beta_n \mathbf{E} + \alpha_{nn} \Delta \mathbf{E} - 4\pi e \alpha_{nT} \mathbf{grad} T$$

This means that $4\pi e^2 \beta_n$ gives the inverse of a relaxation time constant τ_E ; when this time scale has expired, the electron current has become negligible and the electrostatic fields are compensated. The remaining electric field is then (for a classical, nondegenerate electron gas)

$$\mathbf{E} = -\frac{\mathbf{grad} T}{e}$$

and the charge per unit length associated with this field, $\sigma = dQ/dz$ (where $\mathbf{E}_{rad} = e\sigma/R$), has the order of magnitude of T/e^2 , i.e. less than one per Å when T is below 14.4 eV. τ_E results from an effective plasma frequency as can be seen from its definition:

$$\tau_E^{-1} = \left\langle \frac{4\pi f(1-f)n_A e^2}{m} \cdot \frac{m v l_f}{T} \right\rangle \approx \frac{4\pi f n_A e^2}{m} \cdot l_f \sqrt{\frac{m}{2T}}$$

It was assumed that $f \ll 1$ and $\langle v \rangle = \sqrt{2T/m}$. Obviously τ_E increases with $\exp\{E_I/T\}$, so the conditions for electron transport are principally different with respect to a temperature larger or smaller than E_I .

In plasma physics the condition $\mathbf{J}_n = 0$ means that electron pressure and electrostatic fields are in balance. So τ_E can be used to check if the initial charge separation is important for ion sputtering. Immediately after the projectile has passed, T is less than the ionization energy in the negatively charged region, while it is larger in the inner excited region. When the inner excited zone expands, positive charges move along, thus minimizing the electrostatic energy as far as possible that way. Electronic transport comes to an end where the peak temperature gets below the ionization energy; diffusion does not stop abruptly, but runs now as slow as the excitation of molecular motion. The resulting distribution of charge is then the (nearly) unchanged negative contribution as above and is gaussian for the positive charges with a width D which fulfills the condition

$$\frac{T_0 R_0}{D} = E_I$$

As assumed in earlier models the motion of the electrons in the electrostatic field (equivalent to a decay of that field) releases potential energy; since the respective process is electron-lattice-scattering we assume that the molecular system is heated in that way. The amount of energy transferred in that way is (per unit length)

$$d\Delta V = e^2 \sigma^2 \log\left(\frac{R_2}{R_1}\right)$$

where the positive charge is inside a radius R_1 before and R_2 after. In our case this gives 50 eV/Å; note that this amount of energy is transported towards the center of the ion track since the associated process is a drift motion of electrons back inside.

In aliphatic solids all outer-shell electrons are involved in σ -bonds. This means that lattice (or molecular) forces are nearly always created where electrons are excited. The respective exciton band widths are small, but the deformation energy is large as are the phonon frequencies. Following Rashba, these are typical conditions for the formation of "light" self-trapped excitons with a low self-trapping barrier. This means that excitons are rapidly trapped, at a rate comparable to molecular oscillation frequencies (since the required activation energy is small). This makes the case simple: one can assume that the electron energy distribution in which T is less than the ionization energy, is the "final" one; the one which produces the spatial distribution of *molecular* energy.

CLUSTER AND MOLECULE SPUTTERING AND BREAKING

Cluster Formation and Molecular Heat

The temperature dependence of PDMS spectra should be rather small, since the energies deposited at each bond are large compared to the temperature of the lattice. However, due to the change of the solid structure we still expect different support of a shock wave. With increasing lattice temperature the compressibility of the material decreases as does its density. Both will decrease the shock transport effectiveness. However this should be tested by molecular dynamics calculations. (See that section.)

We have estimated the sublimation of volatile frozen material starting from the Clausius Clapeyron equation. However, since this stems from comparing vapour and solid in equilibrium, one has to correct for vacuum by subtracting the vapour pressure term. With realistic equations of state we find about the same results as for v.d. Waals-like substances. That is, in terms of the critical temperature, pressure, and density, the rate of sublimation rises most quickly at about .5 of the critical temperature of the respective material. Thus this is a good estimate for the temperature at which the spectral lines for the molecular ion should disappear in PDMS, as the sample is heated.

Aliphatic Molecule Fragmentation

For a first rough attempt to understand the fragmentation pattern of positive vs. negative decane PDMS spectra, we made use of a new program, CRUNCH, written in our group by K. Kruse and A. Dullweber. We assume the storage time of energy in the molecules to be so short in PDMS, that each chemical bond gets its own energy share independent of that of the others. This short time or *entropic* energy deposition is in contrast to the more common *thermal* energy deposition, where over a much longer time than the lattice oscillation times, relatively little energy is offered to each bond, favouring the excitation of collective vibrations, leading eventually to breaking as well.

CRUNCH calculates the fragmentation pattern for a given chemical structure. For the positive spectra, following the ionization arguments of the previous sections, we give each chemical C-C bond the same breakup probability. Then the calculation yields almost equal peak heights for all fragment lines. This is in contrast to the experimental PDMS spectrum, which looks rather similar to the well known EI spectrum. Thus we have to assume an internal excitation energy, which contributes thermally to breaking up the molecule. In fig.3 we give the result for an assumed 'temperature' of 0.2885 in the expression $w = \exp(-(\mu T)^{-1})$, for the breakup probability w , given by the reduced mass of the fragment pair μ and the parameter T . This seems to give the best fit to the EI spectrum (also shown in figure (3)), as well as to the experimental PDMS data.

For larger T the molecular line fades away, disappearing for $T = 500$, and for lower

T all fragment groups become more equal. For this simple model study we used CH_2 and CH_3 as building blocks.

We conclude that positive spectra indicate that the decane molecules are internally excited by PDMS.

For the negative spectra we tried to start from a lattice of Decane molecules. For simplicity we assumed an idealized perfect 'three-cluster': each molecule has three v.d.Waals type bonds to other molecules. If we assume a **low** internal excitation and set the PDMS entropic breakup probabilities to be inversely proportional to the direct breakup channel level densities, giving for the C-C bond about 1/20th of the probability for a van der Waals bond, we end up with a multimer series of peaks of slowly decreasing amplitude. Since this resembles the experimental PDMS finding, it may be interpreted as an indication that negative ions are internally colder than positive ions.

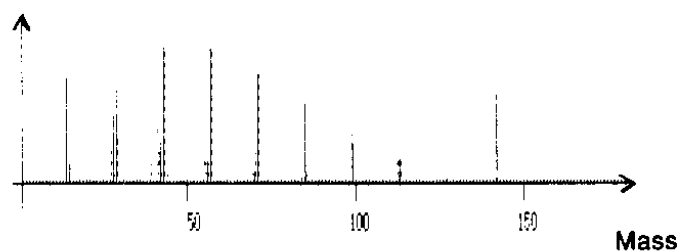


Figure 3 PDMS spectrum by CRUNCH program (full lines) versus the experimental EI-spectrum (broken lines)

CONCLUSIONS

It is a strong simplification to assume that ion formation in electronic sputtering is dominated by the charge separation which is caused directly by the projectile. Even for samples with molecules (or atoms) which normally form ions in usual chemical reactions, there is no need to exclude such effects when regarding ion desorption. There is, however, not yet any clear evidence for direct ion pair formation as a source of sputtered ions. The decane sample we investigated in this paper should clearly be free from such reactions, except perhaps ions which require much energy to be formed and are more exotic than molecular ions and simple fragments.

Despite the necessary restriction to our hypothesis on the current state of its development one should point out some of its interesting aspects. If ions are formed when the respective charge and electronic energy is in excess, this would be a natural explanation for the rare observation of multiply charged ions, because mobile charges tend to be distributed in a way that coulomb energy is minimized. This means that matrix properties could be exploited by combining probe molecules for positive ion observation with matrix molecules with a higher level density above the Fermi-edge, so that they can keep the excited electrons. For negative ion observation the matrix should have a lower

level density than the probe molecules to “offer” electrons to them.

The specific mechanism we described should also enable the use of plasma desorption in cases where usual ionization methods fail because of the specific material properties. The general behaviour of the sample would then be governed by its solid state (transport-) rather than its chemical properties.

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