

Interpreting DSC Data

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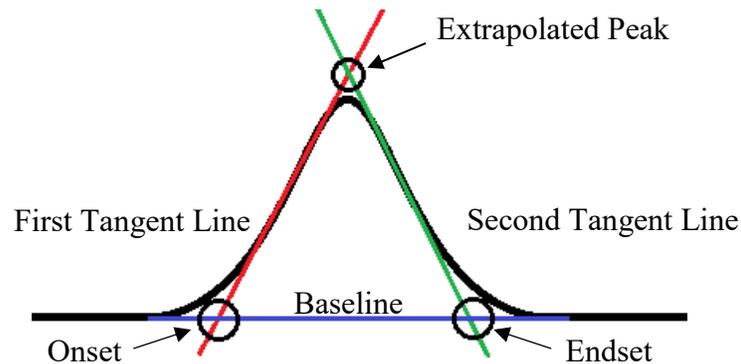
Interpreting DSC Data

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Interpreting DSC Data

Anatomy of a Peak



A DSC event peak typically contains the following components:

- **Baseline:** This is the expected signal (or change in signal) if no transition event occurs (e.g. if the enthalpy change of melting or H_{fusion} were zero). This is not always a flat line, as the specific heat capacity of a material is not guaranteed to be constant as temperature changes, or after a phase transition.
- **First Tangent Line:** This line is generated by an analytical program, (Proteus) and attempts to project a tangent along the most reasonable length of the phase transition's first peak. The criteria for "reasonable" in this scenario would be the longest length of approximately consistent slope.
- **Second Tangent Line:** Similar to the first tangent line, this is a projection along the second length of the peak using similar methods. This is also generated by an analytical program.
- **Onset:** The onset of a transition event is where the tangent line intersects the baseline. Users may want to use the first tangent line to look at the onset of a melting transition or use the second tangent line to look at the onset of a recrystallization event.
- **Endset:** The endset of an event occurs at the intersection of the tangent line with the baseline on the second half of a peak. Like the onset, users may choose the second tangent line to find the endset of a melting transition or the first tangent line to find the end point of a recrystallization event.
- **Peak Apex:** The location of the max peak value is subject to multiple variables. Its value is influenced by the thermal kinetics of the sample and the DSC system. The sample mass, shape, density, and crucible contact as well as the heating rate and gas environment will all impact at what temperature or time the phase transition will reach its maximum. As a result it is generally a poor indicator of a sample's properties.

Using Proteus

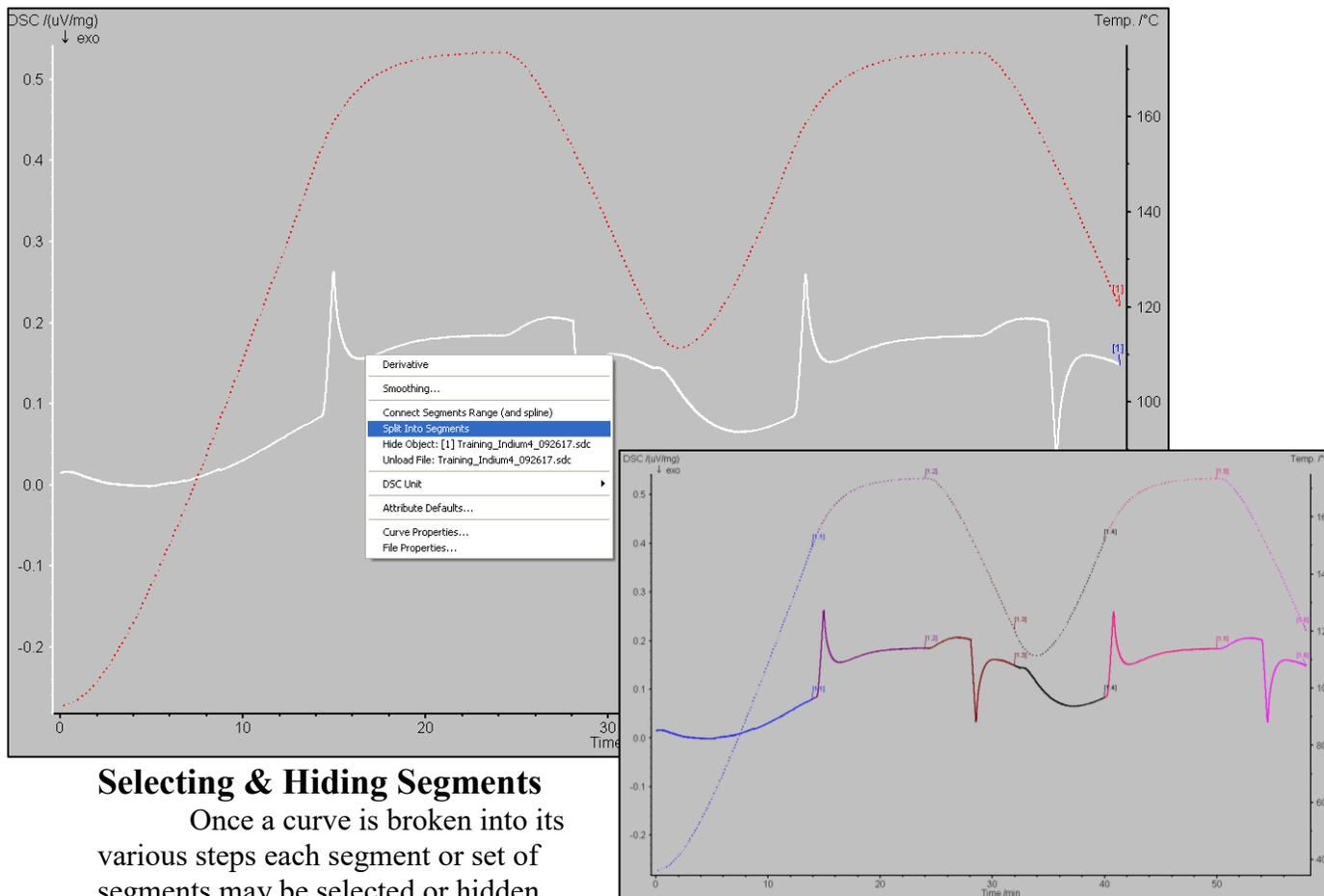
Identifying Transition Events

When a file is first opened in Proteus the default display use an x-axis of time and both temperature and signal along either y-axis. For the purposes of analyzing transition events users will find it useful to change the x-axis to temperature. This requires users will to first split the segments, hide isothermal portions and, if needed, spline segments together.

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Splitting a Curve into Segments

To cut a measurement curve into segments users will need to left-click on their curve of interest, causing it to turn white. Then, users will right click on the same curve to display a menu. From this menu select the “*Split Into Segments*” option. The curve should now be cut into multiple segments, of different colors, corresponding to each step in the programmed measurement. That is each segment corresponds to a dynamic or isothermal step according to the program used to gather the data.



Selecting & Hiding Segments

Once a curve is broken into its various steps each segment or set of segments may be selected or hidden.

Right clicking on the background of the graph (the gray area) will open another menu allowing users to open the Segments window. This window will show a list of the various segments that the curve has been cut into. Selecting or deselecting the check boxes next to each segment will allow users to hide or portion.

Generally if users are interested in looking at transition events they can uncheck the initial heating periods and any isothermal segments that do not contain portions of the relevant peaks. For transition events with peaks that spill over into two segments, the segment will needed to be splined.

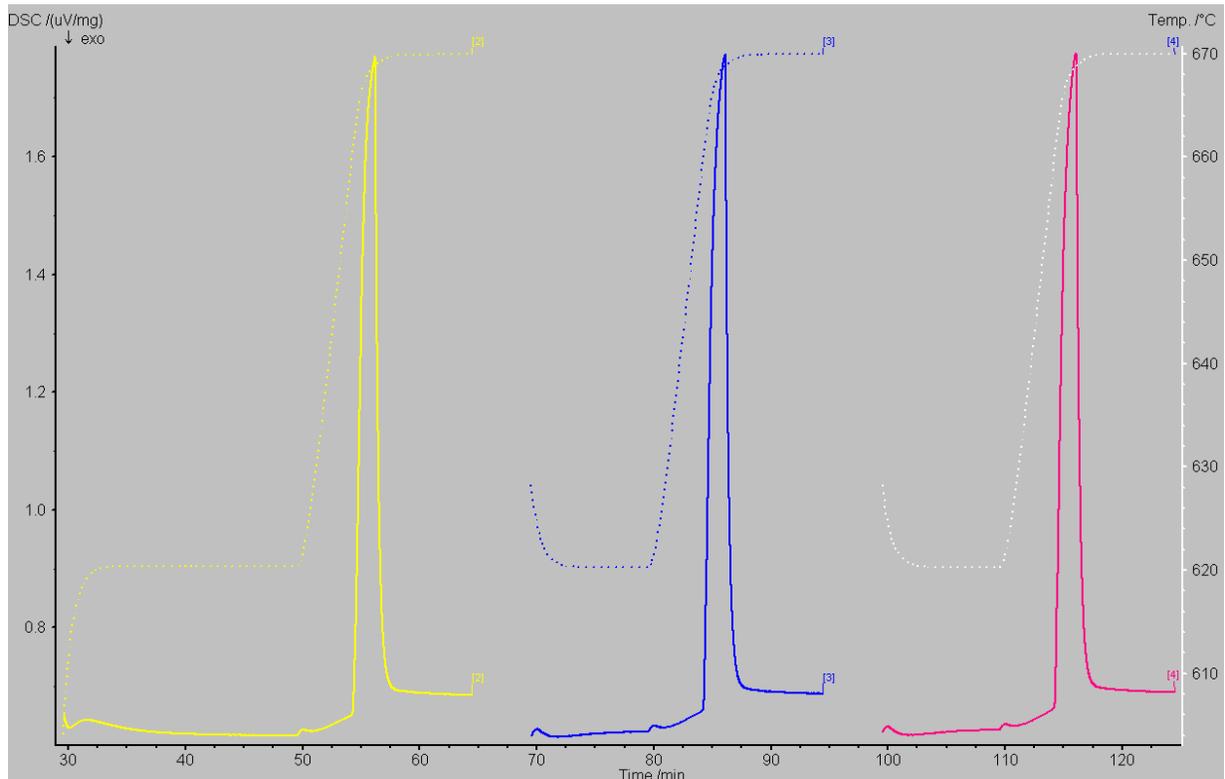
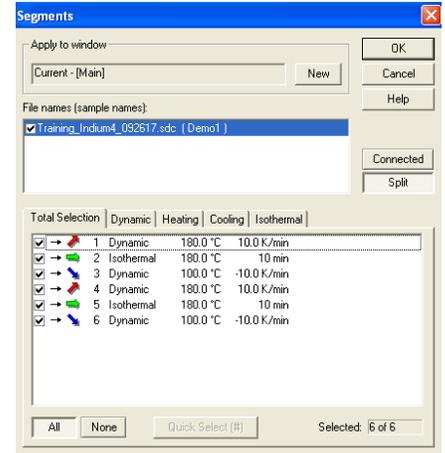
Interpreting DSC Data

Splining Segments

In the Proteus analysis software, splining a set of segments will create a new line whose points include the data from the original segments. This new line can then be treated as a dynamic step and manipulated accordingly.

To spline your segments:

- Deselect any segments that you are not interested in so that they are hidden in the data display.
- Right click on any of the displayed segments to display a menu.
- Select “*Connect Segments Range (and spline)*” from the menu.
- A tool should appear at the top of the main display window, listing the segments you are about to connect. Continue connecting segments as needed.
- After deciding on each segment, the connected lines should now be present with the original components hidden. The original line segments can always be restored by right clicking on the main background again and returning to the segments window.



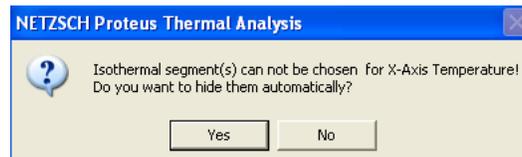
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Changing to a Temperature X-Axis

In the Proteus toolbar, at the top of the window, select the Temperature / time x-axis button. It should resemble a T / t with an arrow beneath it. The display will change the axis for you.



After selecting this button, if isothermal segments are still present, then users will be given a warning. Continuing through this warning will automatically hide any isothermal segments.



Identifying the Event Onset Temperature

First select the segment you are interested in analyzing by left clicking on the curve. Once selected the curve should turn white. From the Proteus toolbar select the Onset icon. This will bring up two bounds on the main display as well as show the first derivative of your selected segment and add a second toolbar. The boundaries serve to identify which peak you want the software to analyze.



Drag the first bound to the left of the peak, making sure to include a sizeable portion of your baseline signal. Place the second boundary at the apex or maximum value of the peak and then select "Apply". The interpreted onset temperature should be automatically added to the main display screen.

Identifying the Event Endset Temperature

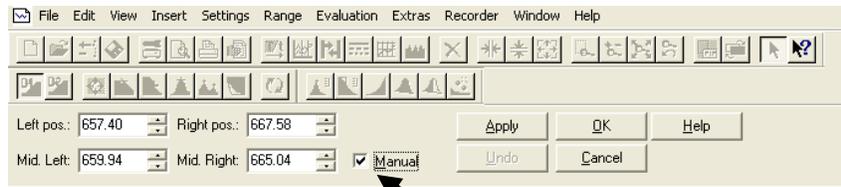
The event endset is more relevant to transition events that occur moving from a high temperature state to a lower temperature, such as recrystallization. Similar to the onset, a curve is selected and then the "Endset" button is selected from the toolbar. This time the left-side boundary is placed at the peak's maximum value and the right bound should include a portion of the apparent baseline. Selecting "Apply" will place the calculated temperature.



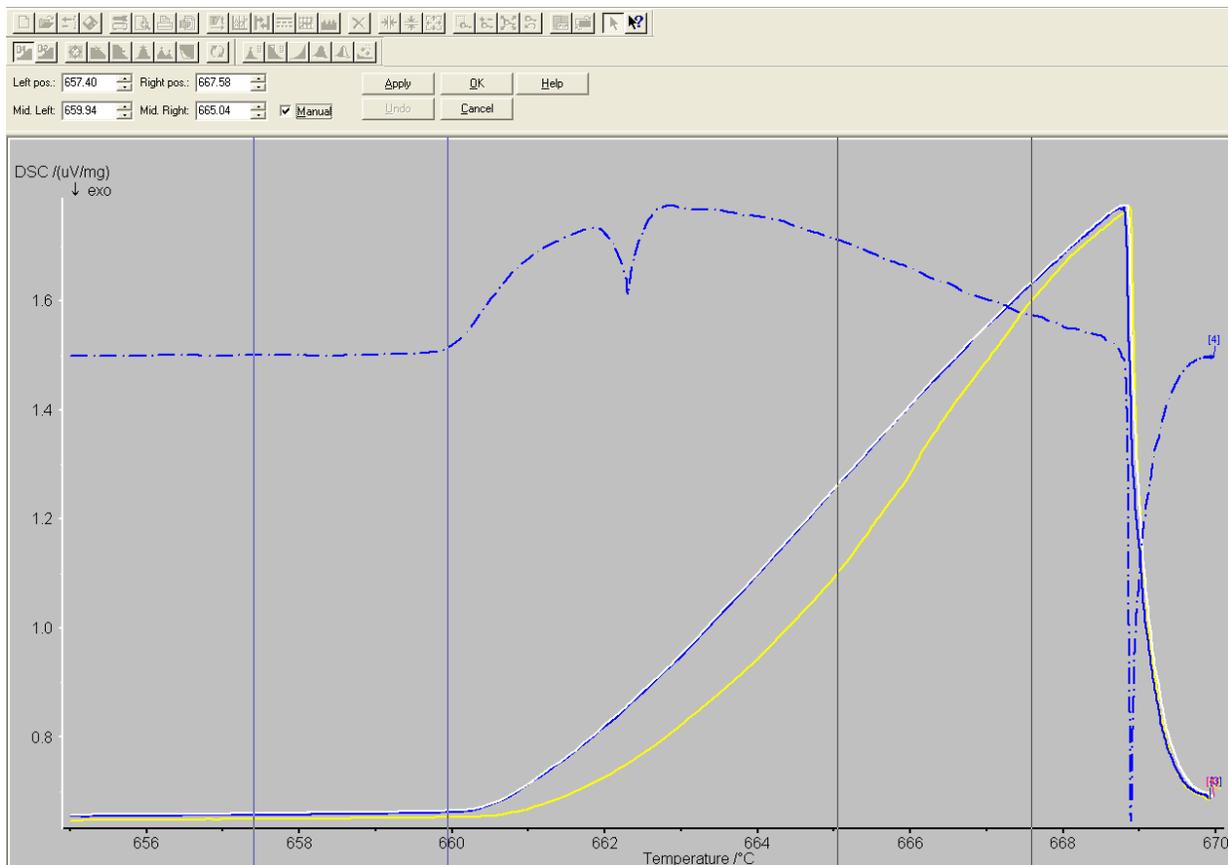
Interpreting DSC Data

Using Manual Select

The automated onset and endset tools are both susceptible to the inclusion of errors. Users may find that they are able to obtain more accurate results using the manual option with both of these tools. To use the manual select, click the curve of interest and select the onset or endset tool. In the toolbar that drops down check the box next to “*Manual*”.



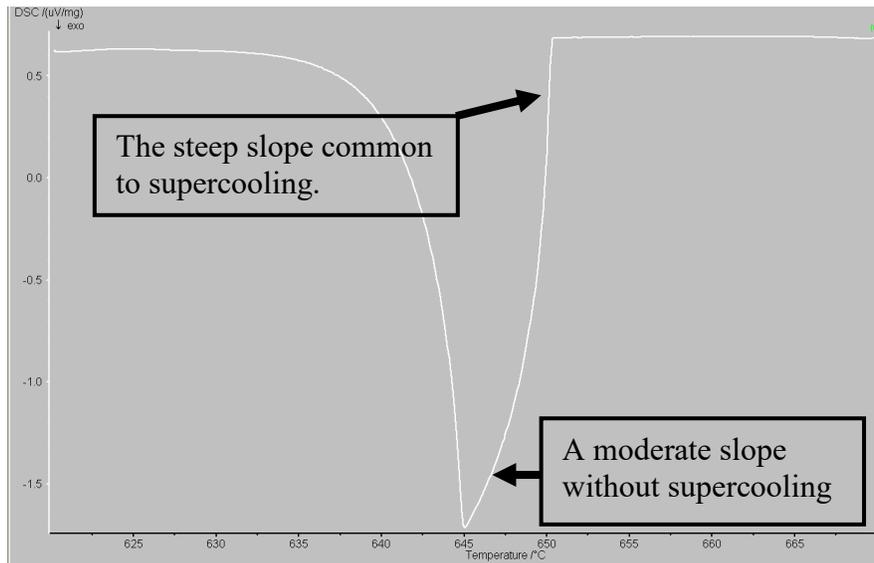
There should now be two set of bounds present on the display; a blue pair and a black pair. The blue bounds identify the portion of the curve that the software will use as the peak baseline. Ideally the user should highlight a region with a mostly consistent slope that is not too far from the peak. The black bounds are used to highlight the portion of the peak that would produce a tangent line most resembling the slope of the peak. Selecting apply will draw the new tangent line and give the event’s temperature value.



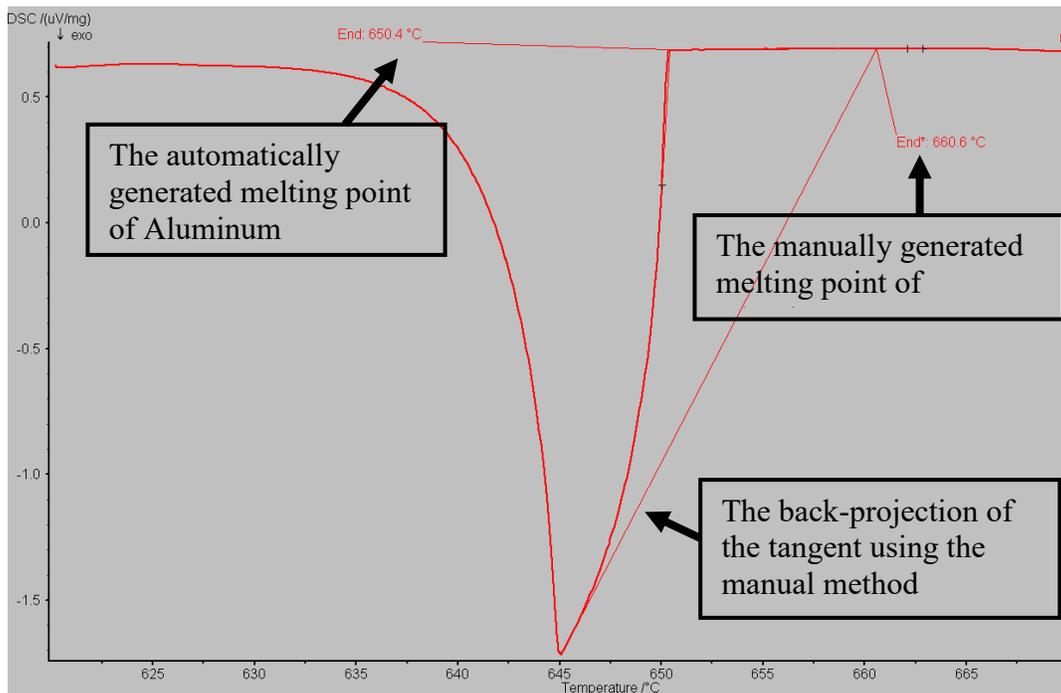
Interpreting DSC Data

Recrystallization Events

During recrystallization transitions it is common to see the sample demonstrate some level of supercooling. Because of the likelihood of such a phenomenon the determination of an endset temperature necessitates the use of the manual selection option. Supercooling may be identified by a sudden and sharply vertical slope on a recrystallization peak before shifting to a more reasonable value.



In this scenario the moderate slope region of the recrystallization peak should be used to generate a tangent line for the event. This will cause the software to project the line further back and provide a more accurate event temperature value. An example of this is given in the next image using a sample of pure aluminum (Melting Point 660.3 °C).



Interpreting DSC Data

Melting Point Peaks

Melting peak characteristics will vary in response to many variables. The melting points of pure materials are often characterized by an almost straight or linear line on the low temperature side of the peak. Impure or polymeric samples will display more concave sides and longer tails, while amorphous materials will display broader peaks due to size distribution of their internal structural components (i.e. crystal grains or polymer chains).

Peak width is also useful for data characterization. A pure crystalline material would be expected to have a sharp peak with a peak half-width range of 1-10 K. Polymers may demonstrate melting point peaks with half-widths of 10 K or broader.

Multiple Melting Point Peaks

Samples may appear to indicate multiple melting points if other phase transition events occur within the measured temperature range. These may include phenomena such as glass transition points, Curie points or changes in crystallographic structure. A possible source of error may be sample dispersion. Samples which are not compacted, or which contain air bubbles will appear to show multiple melting points. This is more likely to appear in powder samples and is often resolved after the first melting point measurement.

It is also possible that a sample may show two apparent melting point peaks during one run and not another. If two melting points are apparent in the first trial and not in succeeding measurements it may be indicative of the removal of an oxidative layer from the material. It is typical for most metals to hold an oxide layer on their surfaces but usually these would not be expected to be destroyed or greatly altered during melting.

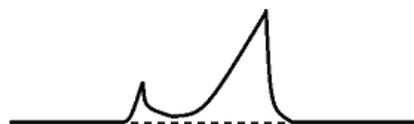
Samples which did not originally demonstrate two melting peaks on their first trial but do so on their second and third measurements may be the result of two possibilities.

- 1. Oxidation:** Users should verify that the correct gas is connected, (Ultra High Purity Argon) and that the gas is flowing at the correct rate. After verifying this and checking that they have purged their sample chamber users considering a possible leak should contact a TEMPO employee for help.
- 2. Eutectic Formation:** Samples may be reacting with the crucible material to form a eutectic. This is highly likely to damage the instrument (and destroy the sample). Users should verify their samples will not react with their crucibles by consulting either the crucible selection guide located on Gauchospace or the appendix included in this manual.

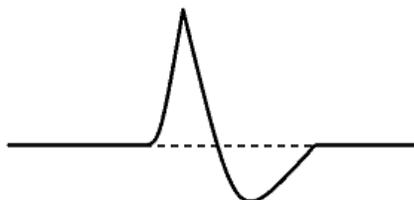
Melting Point Peak Examples



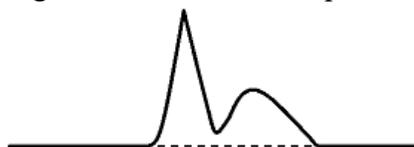
Pure Non-Organic Crystalline Material



Signs of a Eutectic Impurity



Signs of Possible Decomposition



Signs of Possible Decomposition



Semi-Crystalline Polymer Material

Interpreting DSC Data

After performing a measurement visual inspection of the sample may confirm if a eutectic is being formed. Samples may demonstrate discoloring or altered crystalline appearance. For eutectics, the appearance of multiple peaks should decrease as cycles continue and homogeneity is established however the final peak will be representative of the newly formed sample's properties and not the original materials.

Polymorphism

Solid samples capable of existing in more than one form or crystal structure may produce two noticeable peaks (and onset points) during phase transitions. In this scenario the baseline used to interpret the first peak is also used on the second.

Overlapping Peaks

If two events or peaks overlap a better resolution may be achieved by alternating heating rates during the measurement. Either higher or lower heating rates may be used. The measurement could also be rerun with a smaller quantity of sample.

Interpreting DSC Data

Recrystallization Point Peaks

Integration of recrystallization peaks should produce an area similar in size to the corresponding melting point peaks. Some differences may appear as a result of supercooling but the peak area should not deviate by more than 20%.

It is common for samples to show some level of **supercooling** effects during recrystallization. This is typically manifested by a difference between measured melting point and recrystallization. A reasonable range of disagreement would be 1-50 K. Substances that crystallize rapidly after nucleation would be expected to have a sharp and vertical peak before establishing a more gradual slope. Because of this supercooling effect users looking to establish a recrystallization point will need to project backwards from a region with more moderate slope.

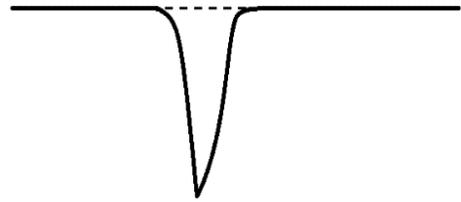
Materials that demonstrate **amorphous solidification** (i.e. form glasses on cooling) will not demonstrate easily noticeable peaks but instead will show a sudden change in specific heat capacity or shift in the baseline. Samples with eutectic impurities which solidify this way don't show their characteristic two peaks.

Multiple Recrystallization Point Peaks

Samples that don't completely cover the crucible floor or which use small quantities of noble metals can form individual drops in their liquid phase. Each of these drops can exhibit different levels of supercooling and form a series of smaller recrystallization peaks. The total area under these peaks should still approximately match the of the melting point. Measurements may benefit from rerunning the sample using more material or ensuring even distribution across the crucible floor.

Recrystallization Point Peak Examples

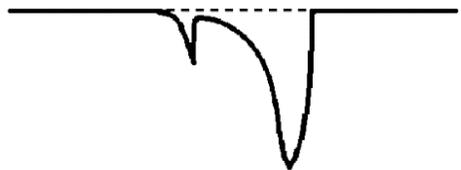
a Pure Non-Organic Crystalline Material



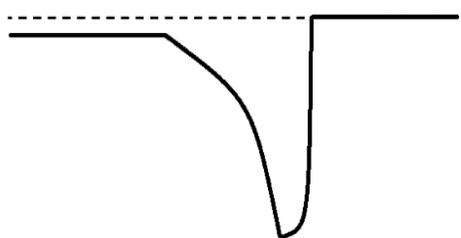
a Material Showing Multiple Supercooling Effects



a Material with a Eutectic Impurity



a Semi-Crystalline Polymer Material



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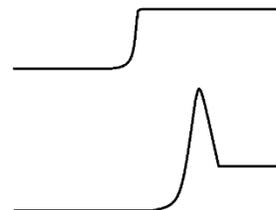
Other Possible Peak Events

Glass Transition Points (T_g)

The **glass transition point** is the temperature at which an amorphous material undergoes a transition from a brittle or hard state to a rubber-like viscous state. The transition is reversible and is known as **vitrification**. Measurements for glass transition points will typically follow two possible patterns.

1. **Glass Transition:** Peaks will show an abrupt and linear rise in signal before quickly leveling out.
2. **Glass Transition with Enthalpy Relaxation:** After the initial climb, the signal will drop again before leveling out. This is more commonly seen in samples that have been stored for a long period of time below the glass transition temperature. Samples undergoing repeated cycles should only show this event in the initial heating.

a Glass Transition Event



a Glass Transition Event with Enthalpy Relaxation

Transition events will typically occur over ranges of 10-30 K. Users suspecting that an event might be a glass transition point can verify this by using a furnace or other heating source to heat their samples to the event temperature and observing if the material has assumed a noticeable elastic, softened or liquid like quality. Users should not use the DSC to do this, as the furnace cannot be raised during a measurement or when the temperature exceeds 100 °C.

Reporting the temperature of the glass transition is, to some degree, based on preference. No standard is currently established about which point along the curve is considered the official “temperature”. Papers typically report either the onset, midpoint or endpoint temperature of the transition.

It is also important to note that the glass transition temperature will vary by instrumentation and technique. Measurement by means of a physical instrument, such as dynamic mechanical analysis (DMA) will often report a higher temperature than a DSC. This is due to the sensitivity of the detection method (mechanical versus electrical) and both measurements can be considered accurate and precise. Users reporting a glass transition temperature should also include the instrumentation and means of determining the temperature.

Curie Transition Points (T_C)

Lambda transitions, or second order solid-solid transitions, can be difficult to detect on a DSC. Users looking to establish the temperature of a **ferromagnetic Curie transition** might find the TGA is capable of providing more exact data however the DSC may be of use for measurements looking to quickly find a temperature range at lower cost.

a Curie Transition Event



The Curie transition temperature (T_C) is the temperature at which a permanent magnetic material loses its magnetic properties. The ordered magnetic moments found in ferromagnetic materials become disordered above the Curie temperature effectively terminating the net dipole. T_C peaks are usually slight and easily missed in data. Users should be careful to give a large buffer range when designing measurements to obtain the Curie temperature as artifacts may hide or alter the data.