The Concept of Trajectories in the Data Analysis of Non-axially Symmetric Nuclear Quadrupole Interactions

Tilman Butz

Universität Leipzig

HFI/NQI 2010

Conventional Data Analysis

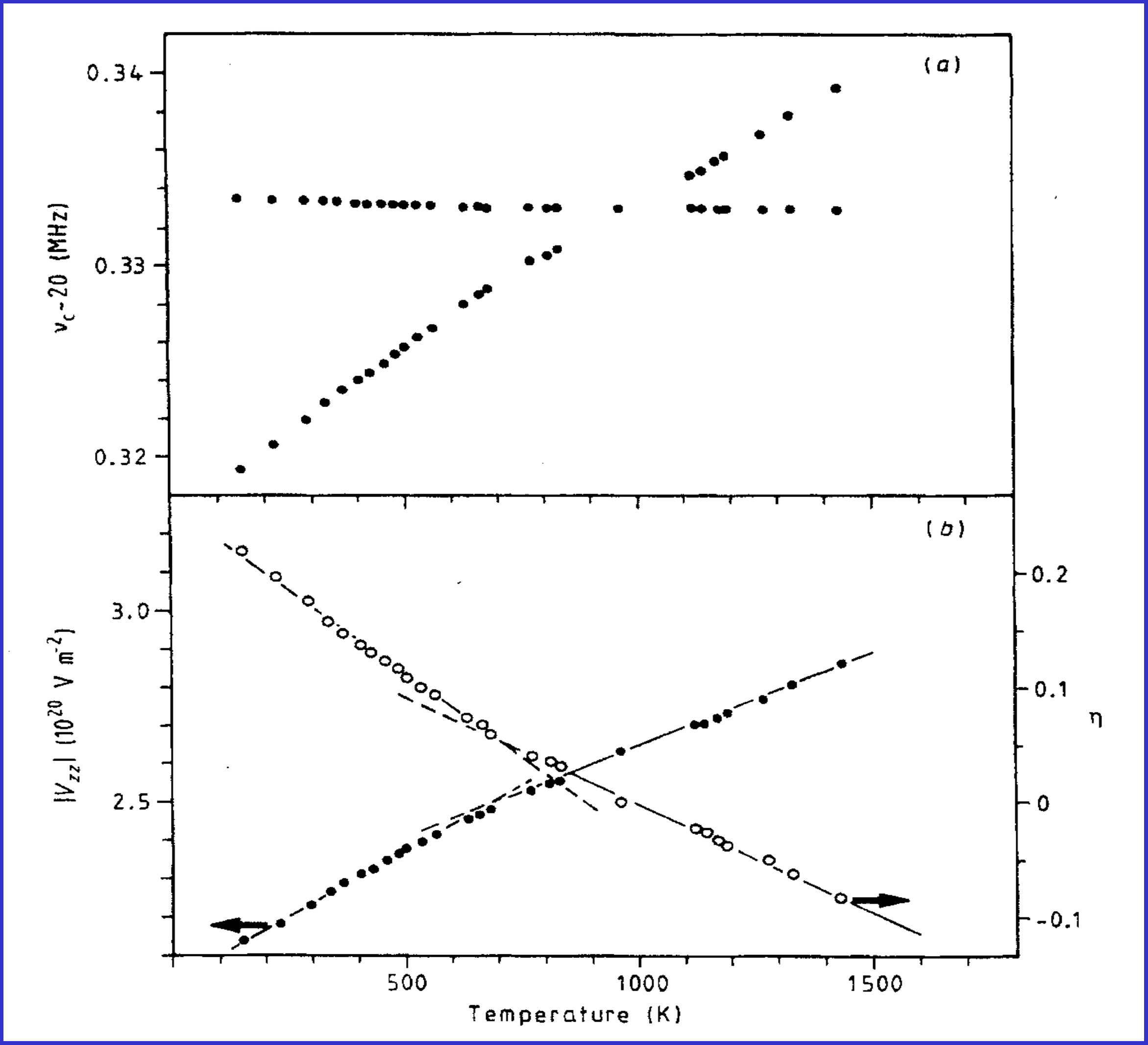
- The electric field gradient tensor for random powder samples is conventionally desribed by two parameters:

  V_{zz}: the largest component of the tensor in magnitude
  and
  $\eta = (V_{xx} - V_{yy})/V_{zz}$: the asymmetry parameter

- If this tensor is measured as a function of an external variable, e.g. temperature (T) or pressure (P), 2N adjustable parameters are used for N data points

- Usually V_{zz} as well as η are plotted separately vs. T or P

Examples: ^{47,49}Ti in Rutile

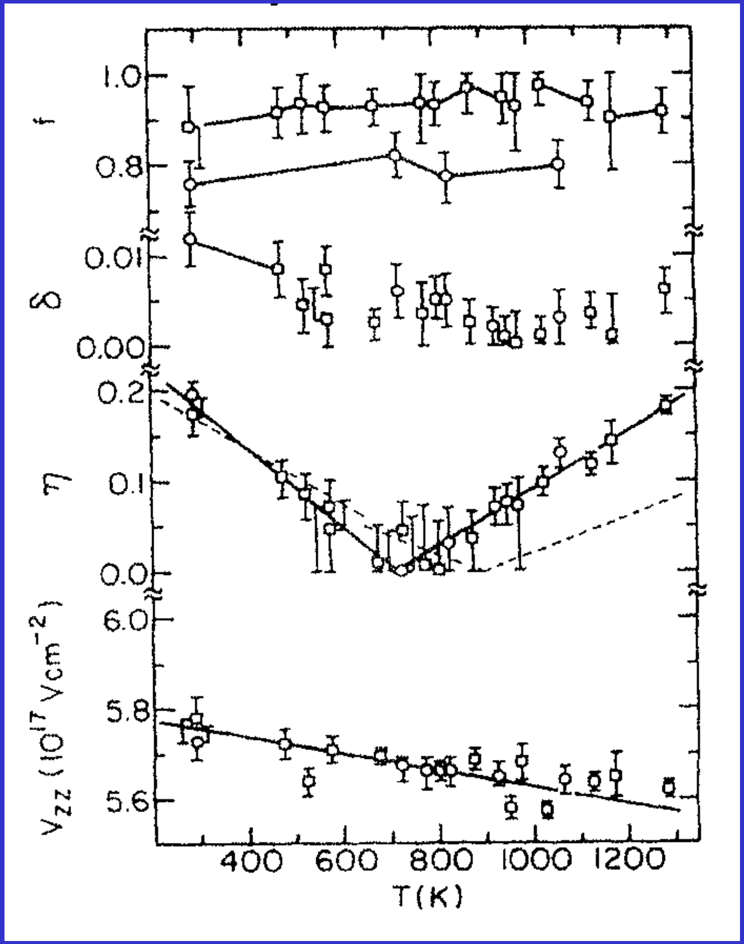


O. Kanert and H. Kolem

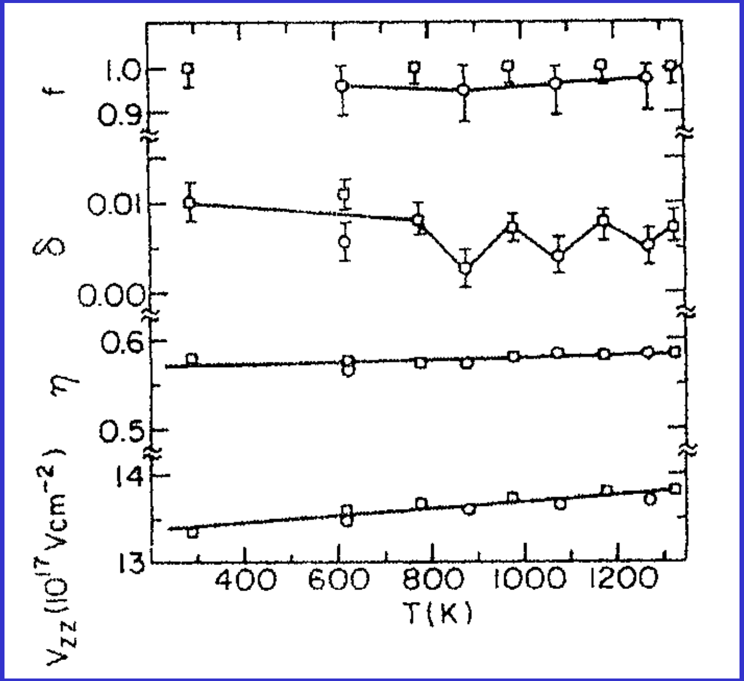
J. Phys.C 21(1988)3909

^{111}Cd and ^{181}Ta in Rutile

^{111}Cd



^{181}Ta



J. M. Adams and G. L. Catchen

Phys. Rev. B50(1944)1264

This Procedure is Tier 1 of the Analysis

This procedure looks very innocent, yet it could be utterly wrong to stop the data analysis at this stage!

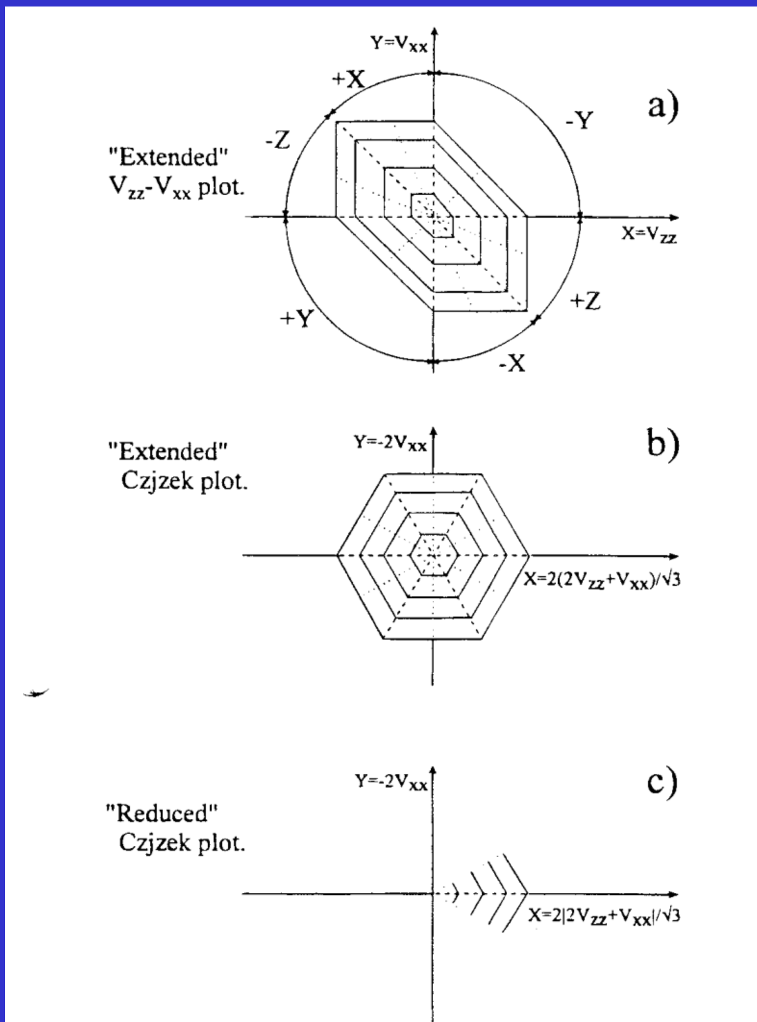
What is needed is a check for EFG tensor component interdependencies!

The conventional parametrization is perfectly suited to hide such interdependencies!

Trajectories and Parameter Landscape

- A 2-dimensional plot of V_{xx} vs. V_{zz} with the implicit parameter T or P would reveal eventual interdependencies
- An even better plot is the Czjzek-plot which is also a linear plot of tensor components
- Each pair of V_{xx} and V_{zz} constitutes a point in the Czjzek-plot
- Connecting the points by a line constitutes a trajectory

The Czjzek-plot G. Czjzek, Hyperf, Interact. **14,** 184, (1984)



(T. Butz et al. Phys. Script. 54(1996)234)

Disadvantage: different segments allocated to x,y,z

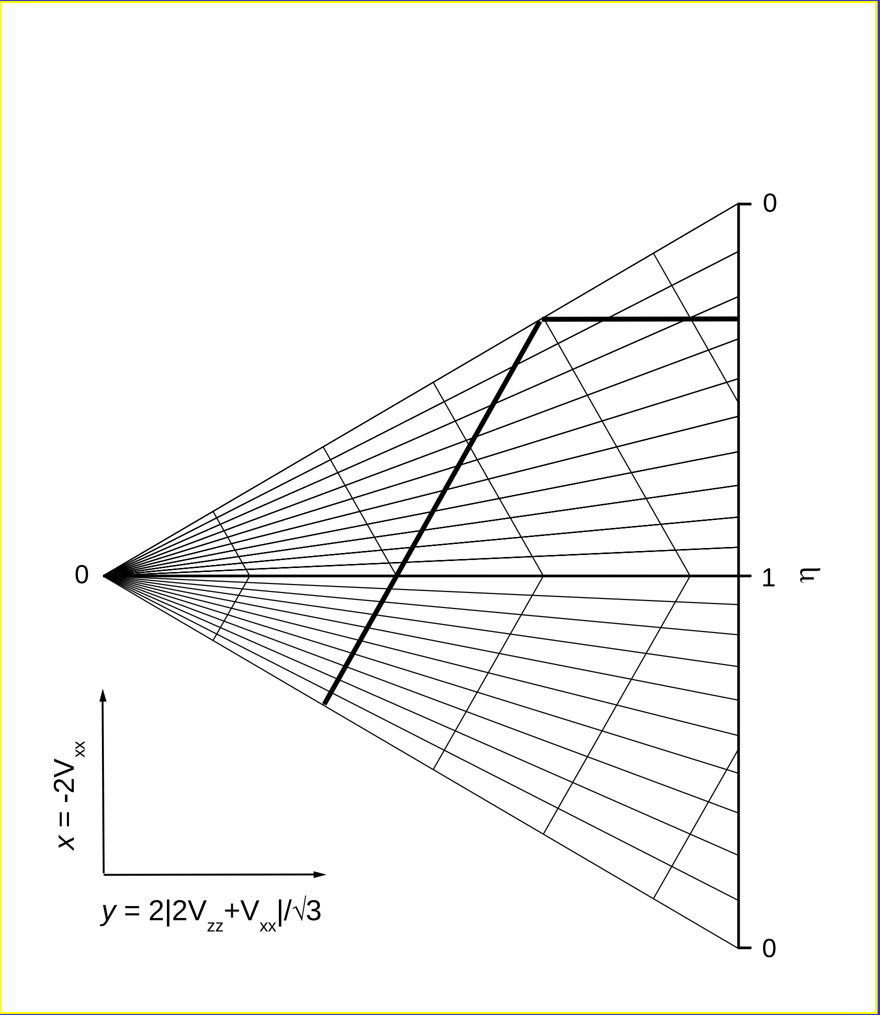
By choosing a suitable linear combination of V_{xx} and V_{yy} for the abscissa identical segments are obtained

If orientation of tensor is unknown two wedges suffice

Absolute sign in abscissa guarantees connectivity across $\eta = 1$ line

If sign is unknown upper wedge suffices

Example: The Czjzek-plot with a linear trajectory



Trajectory starts at lower boundary with constant V_{zz},

crosses the η = 1 line, and continues with increasing V_{zz} while η decreases towards 0

then is reflected at the upper boundary and continues horizontally

and finally η = 1 is reached asymptotically

New Parametrization

$$V(T) = \text{constant}\cdot(V_1 + \alpha(T)\cdot V_2)$$

Both tensors are **diagonal simultaneously**

They can both be chosen to have a norm of two

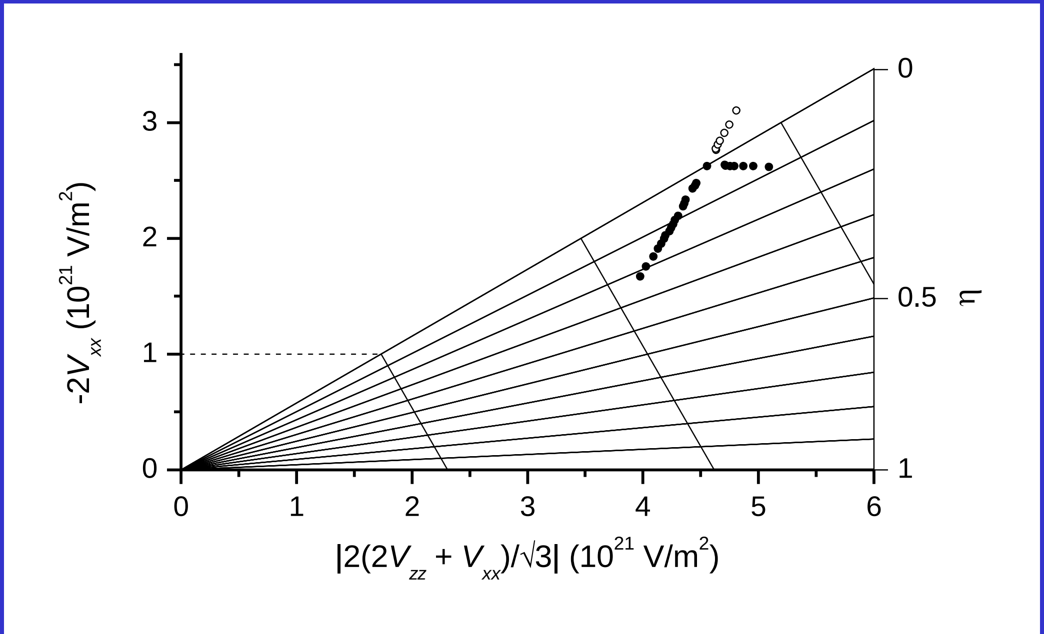
V_1 defines the origin of the trajectory (can be chosen arbitrarily)

V_2 defines the asymptotic η for α going to ∞

$\alpha(T)$ is the control parameter; it is the only temperature dependent variable; there is isometry

Fit parameters: N values for α at N temperature points using a **simultaneous** fit of all spectra plus the asymmetry parameter of V_2 plus the constant (scale factor), i.e. N+2 instead of 2N parameters in conventional analysis

Example: ^{47,49}Ti in Rutile

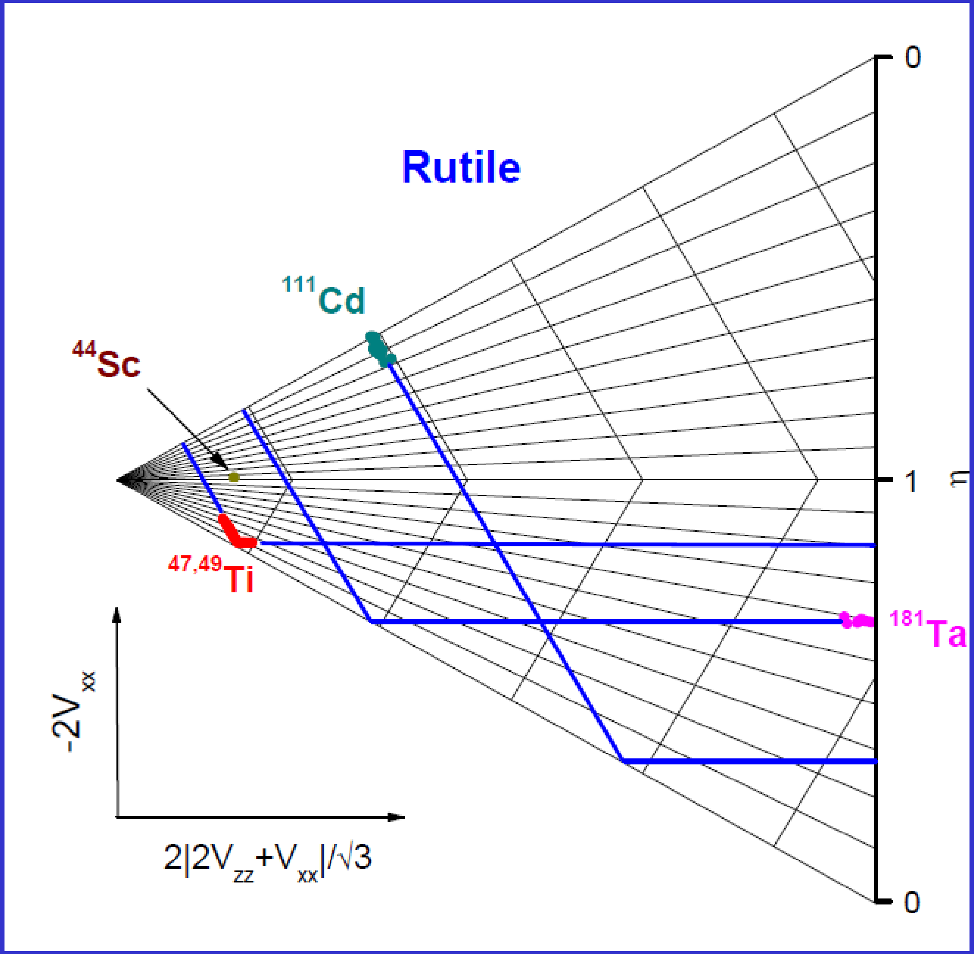


Czjzek-plot of the NQI of ^{47,49}Ti in rutile (O. Kanert and H. Kolem J. Phys.C 21(1988)3909) in the studied temperature range from 300 K to ~1400 K. V_{zz} increases with temperature.

Sign not known from NQR data (theory says negative).

Open symbols show that straight trajectory continues beyond upper boundary where V_{xx} and V_{yy} are interchanged.

Example: ^{47,49}Ti, ^{111}Cd, ^{181}Ta in Rutile



Czjzek-plot of the NQI of ^{47,49}Ti, ^{111}Cd, ^{181}Ta in rutile (dots) in the studied temperature ranges from 300 K to ~1400 K. Signs are from S.-b. Ryu et al., Phys. Rev. B77 (2008) 094124

Solid lines are extrapolated trajectories.

For ^{44}Sc in rutile the data point at 300 K is indicated. It is predicted that the temperature dependence follows a 120° line.

Extension to Non-linear Trajectories

$$V(T) = \text{constant}\cdot(V_1 + \alpha(T)\cdot V_2)$$

Both tensors are NOT diagonal simultaneously

They can both be chosen to have a norm of two

V_1 defines the origin of the trajectory (can no longer be chosen arbitrarily, must be selected by physics)

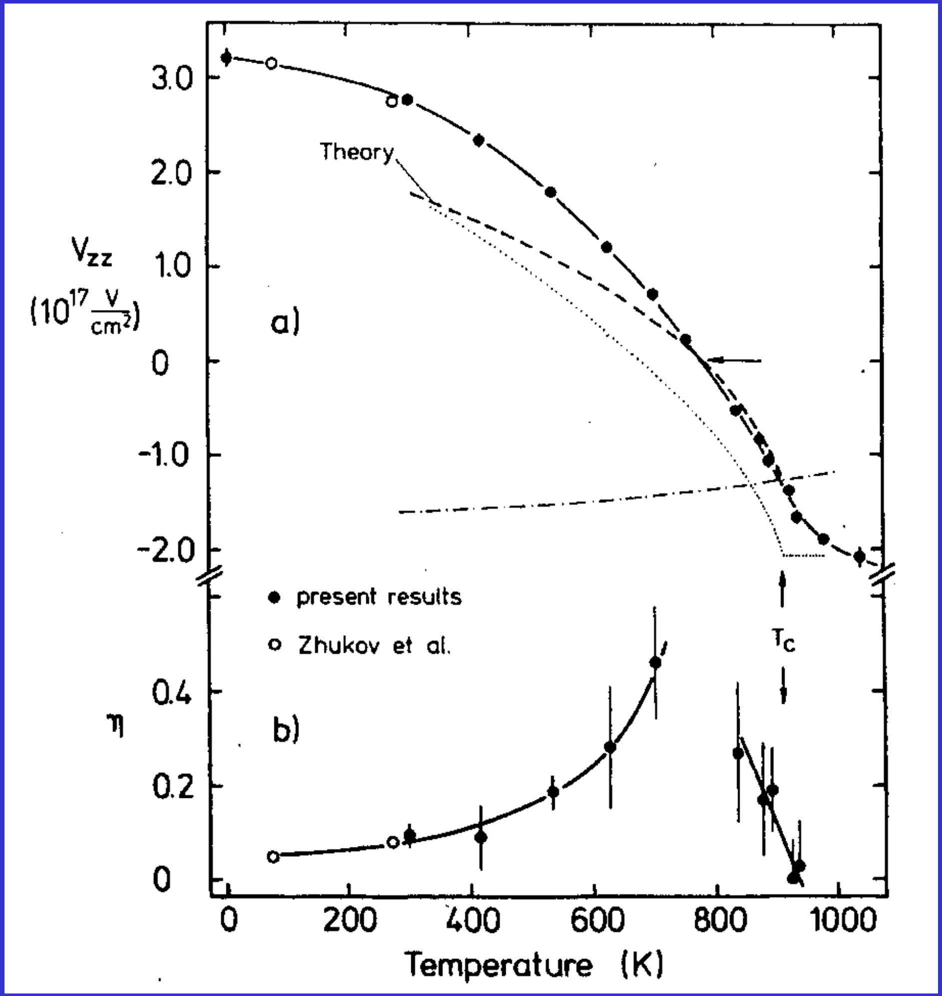
V_2 defines the asymptotic η for α going to ∞

$\alpha(T)$ is the control parameter; it is the only temperature dependent variable; isometry is lost because linearity is lost due to diagonalization

Fit parameters: N values for α at N temperature points plus the asymmetry parameter of V_2 plus the constant (scale factor) plus 1-3 off-diagonal elements of V_2 (V_1 is chosen diagonal)

Now the principal coordinate system rotates with temperature

Example: ^{181}Ta in $LiTaO_3$



$LiTaO_3$ is a ferroelectric with perovskite structure

It becomes paraelectric above T_c = 906 °C

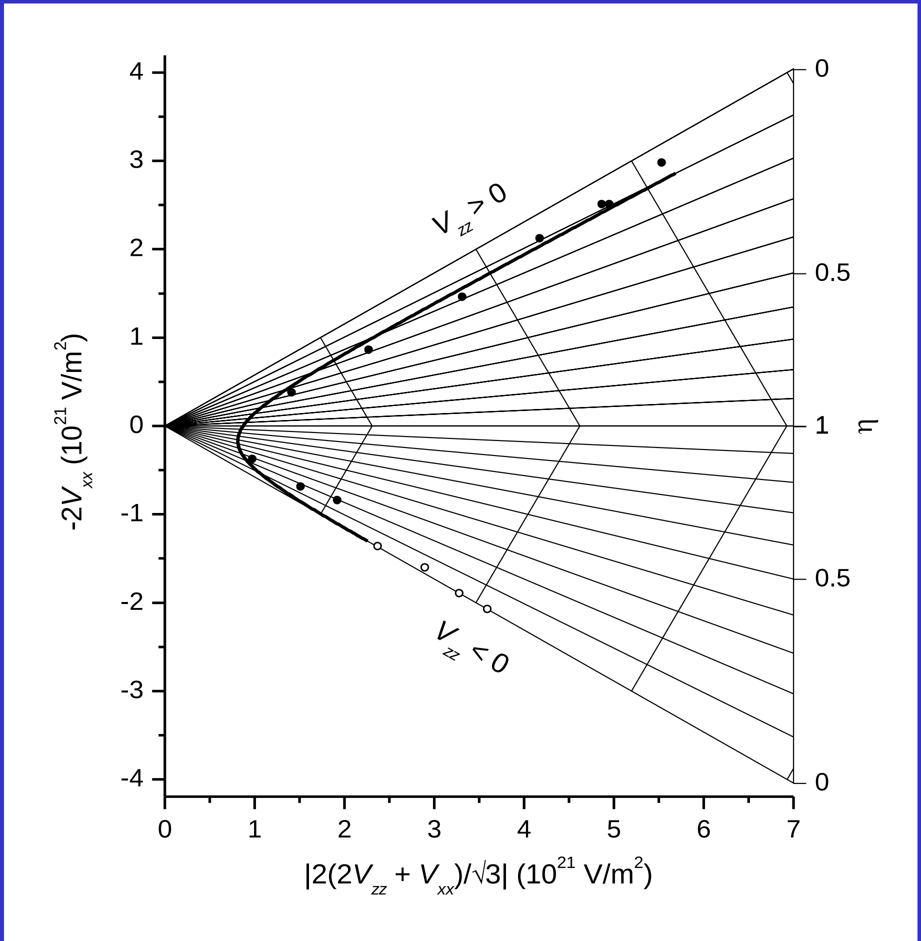
Mössbauer data from:

M. Löhnert, G. Kaindl, and

G. Wortmann

Phys. Rev. Lett. 47(1981)194

Czjzek-plot for ^{181}Ta in $LiTaO_3$



Data start at Tc = 906 °C at lower boundary where η = 0 and end at 77K in the upper wedge

Solid line is a hyperbola which osculates the lower boundary

Note that the η = 1 line is crossed (sign change of V_{ZZ})

Open symbols: above T_c

Czjzek-plot for ^{181}Ta in $LiTaO_3$

$$V(T) = \text{constant}\cdot(V_1 + \alpha(T)\cdot V_2)$$

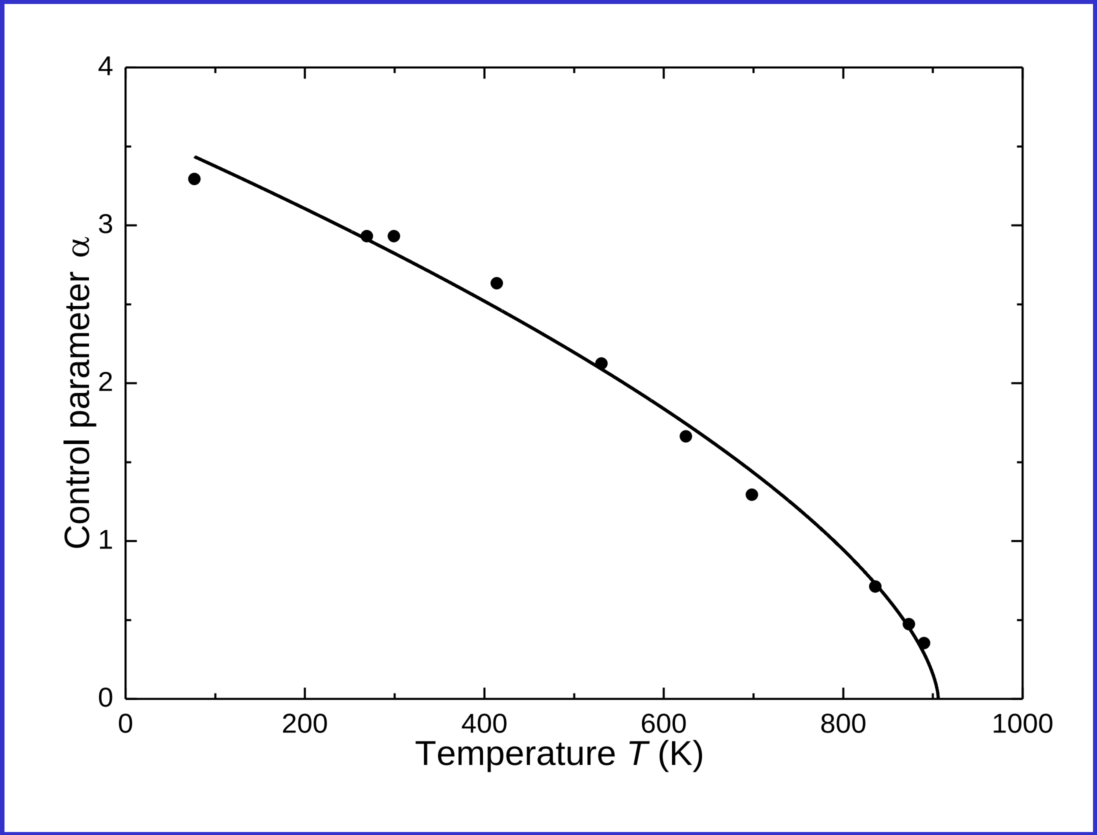
V_1 describes the paraelectric state (weak T-dependence ignored) and has the form: $\begin{pmatrix} 0.5 & 0 & 0 \\ 0 & 0.5 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ (negative V_{zz} from experiment)

V_2 has the form: $\begin{pmatrix} -0.5 & 0 & Vxz \\ 0 & -0.5 & Vyz \\ Vxz & Vyz & 1 \end{pmatrix}$ with constant $V_{xz}=V_{yz}$

Together with $\alpha(T)$ it leads to the total $V_{zz}(T)$, $\eta(T)$, and the rotation of the principal coordinate system with T

Fit parameters: N values for α at N temperature points plus the constant (scale factor) plus the off-diagonal element of V_2

Control Parameter vs. Temperature



Non-zero η is a hard proof that there is lateral displacement of Ta in addition to c-axis displacement

Control parameter is identical to an order parameter apart from normalization

Tilt angle: $0 \leq \phi \leq 17°$

Summary

- The Czjek-plot reveals interdependencies among EFG tensor components vs. an external variable
- A linear superposition of two tensors which are simultaneously diagonal and constant with a control parameter $\alpha(T)$ leads to linear trajectories
- Off-diagonal elements lead to non-linear trajectories and a rotation of the principal coordinate system
- The number of freely adjustable parameters is greatly reduced in a two-tiered data analysis

Summary (cont'd)

- There will be trajectories with symmetric asymptotes in all cases

- If a 2x2 matrix has to be diagonalized the trajectories are hyperbolae, otherwise they are third order functions and can even contain loops

- Trajectories are continuous, even for first order phase transitions
  More examples: see: T. Butz, Phys. Scr. **82** (2010) 025702

  Nature could have more phantasy than using linearity only!

Thank you very much for your attention