Some links between GD-OES fundamentals, instrumentation and applications

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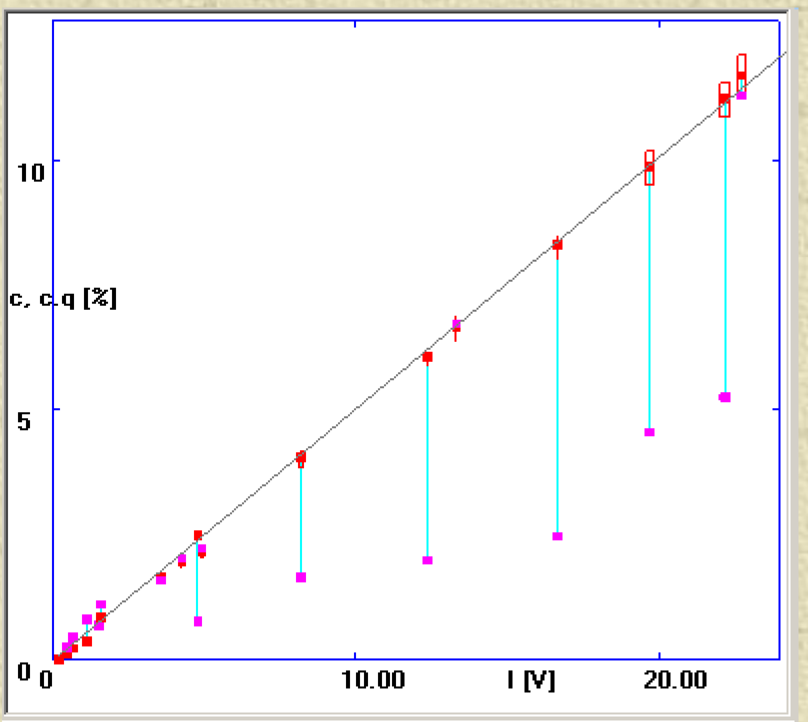
Example 1: back to basics:

formalism of the 'multi-matrix' calibration (the standard model):



sputter rate correction

$c \rightarrow c^*q$

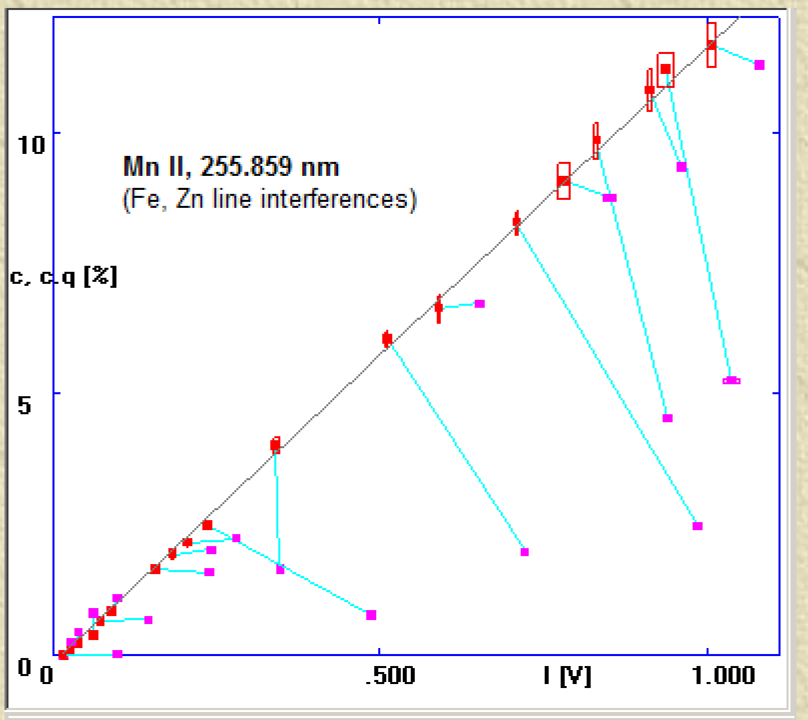
$I_\lambda = R_\lambda \, . \, (c_{Mn}.q)$

R_λ ~ 1 / (slope of the cal. curve) ...

... emission yield

Example 1 (cont.):

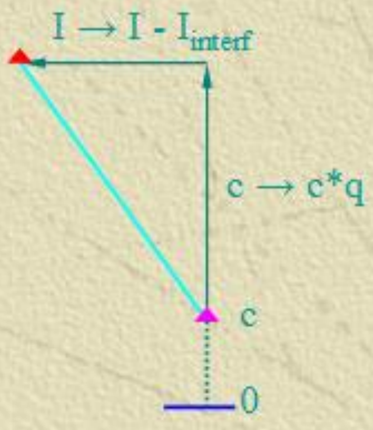
calibration if line interferences are involved



resolution ca 0.07 nm

sputter rate correction
$c \rightarrow c^*q$

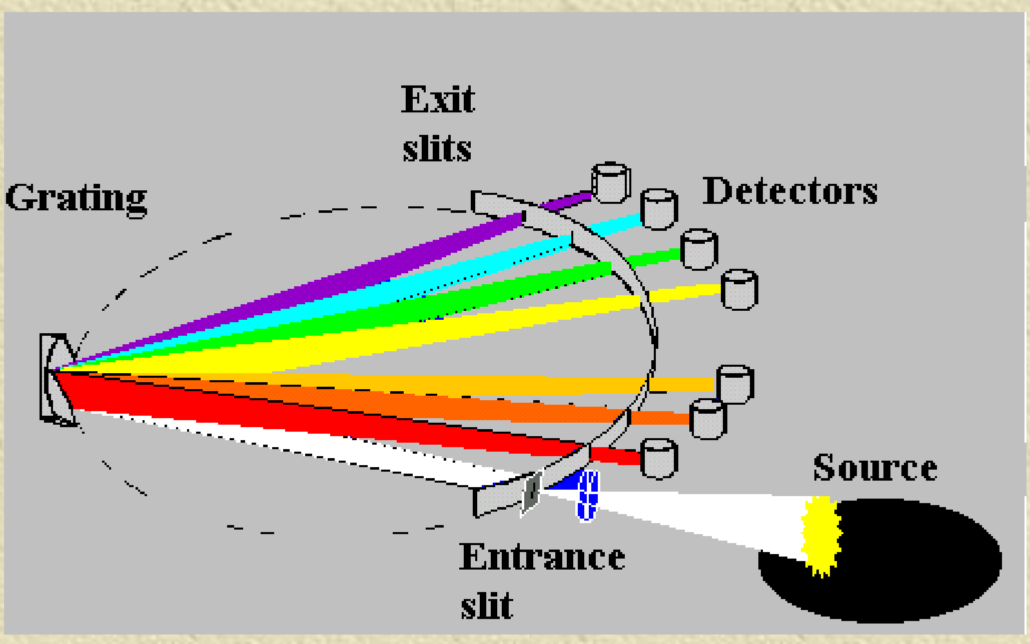
correction for line interference
$I \rightarrow I - I_{interf}$



We need the calibration model to be accurate !!

Example 1: instrumentation

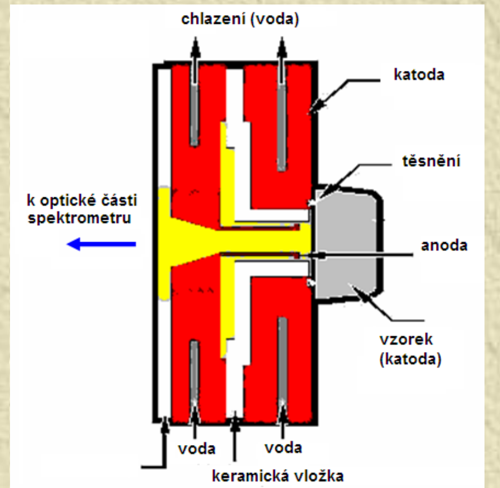
Grimm-type GD source + Paschen-Runge polychromator



- 1970s-1980s:
  spark source replaced by GDS
- mostly atomic resonance lines,
  typically 1-2 lines per element

W. Grimm, *Spectrochim. Acta, Part B*, 1968, **23**, 443

(45 years ago)



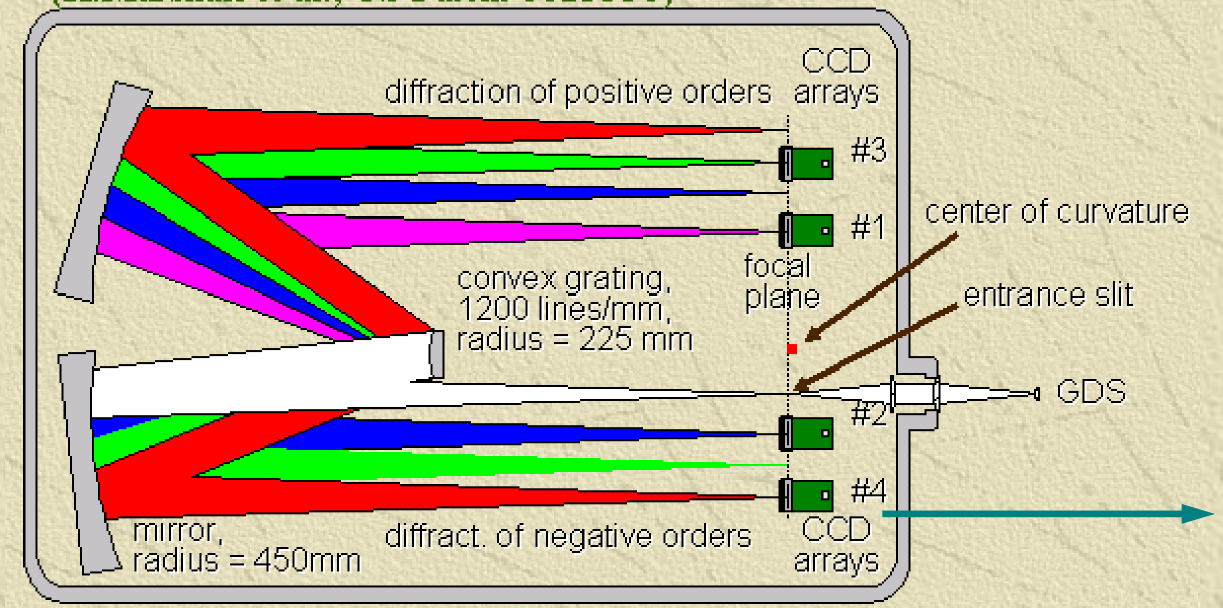
Example 1: (cont.)

- methodology:
  - bulk analysis: methodology taken over from spark
  - "mode 3": I/I_M versus c/c_M + normalization to 100%
- but a different physical context than in spark:
  - atom number densities in the plasma preserve stoichiometry of the sample
  - excitation independent of the cathode (in many cases)
  - the "mode 3" follows from the standard model
  - as an exercise: prove that ! ☺

Example 2 (since early 2000s):

advent of CCD instruments

(K.Marshall et al., US Patent 6023330)

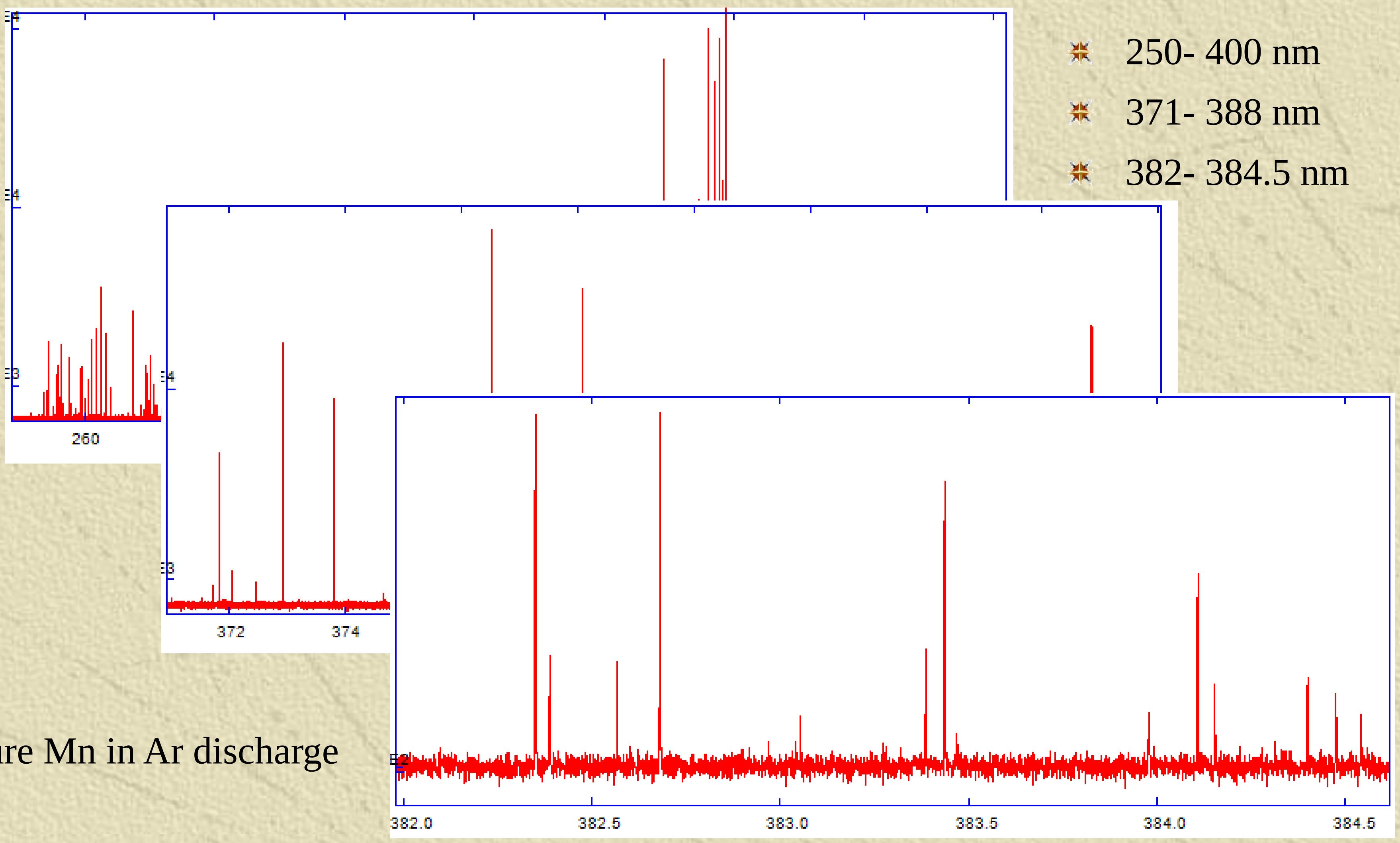


- continuous spektrum, (LECO GDS500A: 165-465 nm)
- an unlimited number of channels
- a great flexibility, lots of potentially useful information

<u>Example 2</u> : Manganese (by FTS)

the nature of GD spectra

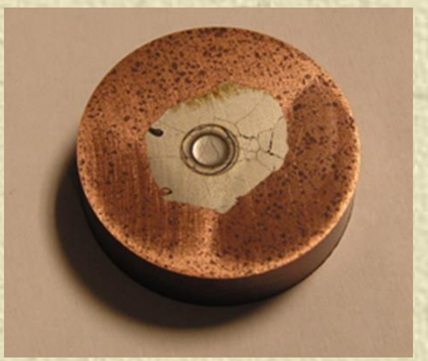
- 250- 400 nm
- 371- 388 nm
- 382- 384.5 nm



pure Mn in Ar discharge

Mn spectrum: a summary

- observed: 220 Mn I lines, 345 Mn II lines, 450 Ar lines
- everything between 160 and 610 nm,
  altogether 1015 lines in the spectrum (by FTS)



- how to sort out this amount of information ??
- which lines to use for what purpose ??
- and why ? (... what is happening in the plasma ?)

- excitation:
  - collisional-radiative models
  - typically 30-50 types of processes considered for Ar-M plasma, many of them energy-dependent or concerning specific terms/levels (i.e. many of one type)
  - would be nice to identify few of them, controlling the pattern of excitation

Excitation, line intensities, transition rates

line intensity:
transition i → j

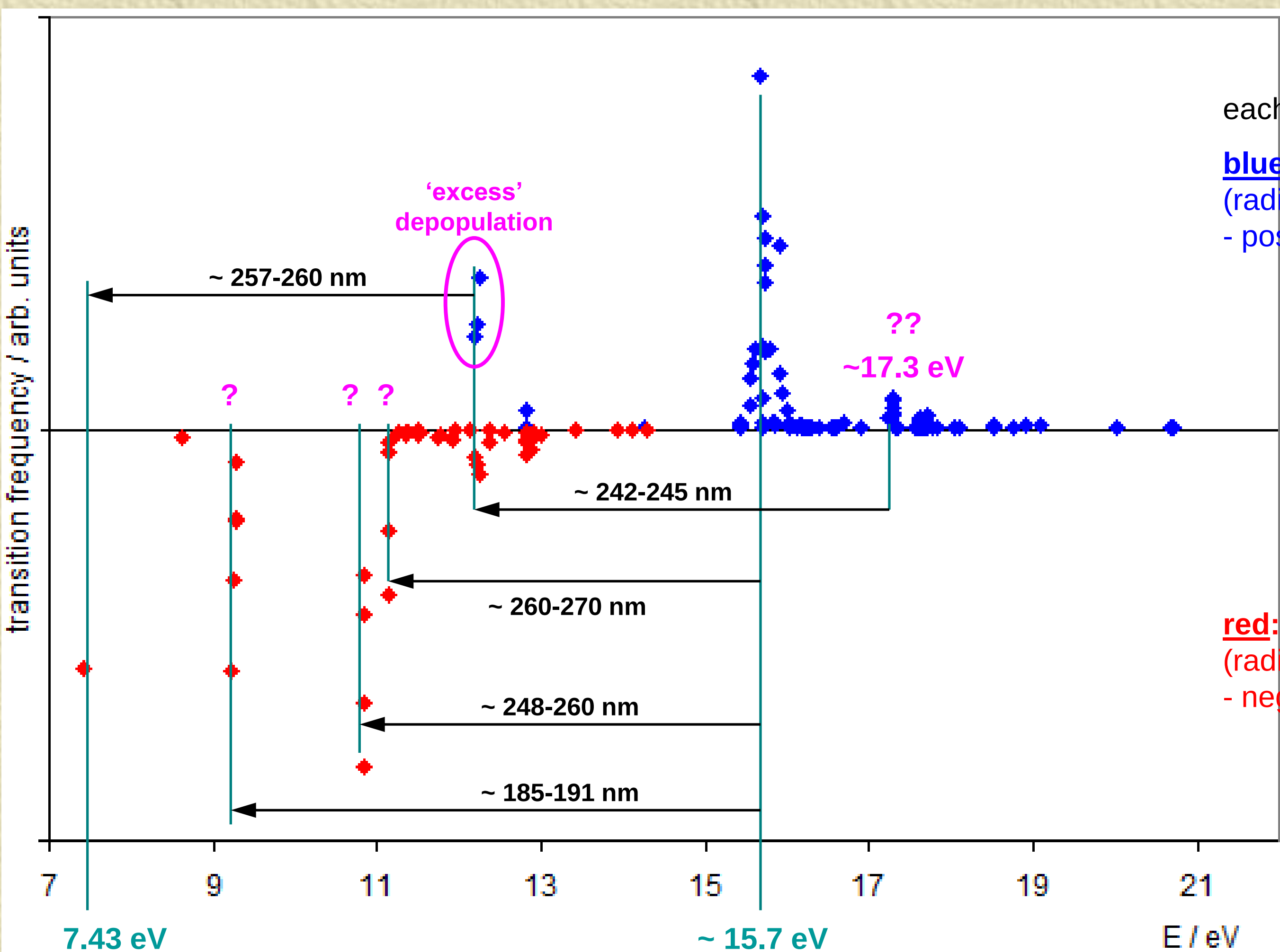
$$I(\lambda_{ij}) \sim \frac{hc}{\lambda_{ij}} . n_{i \to j}$$

transition rate
for i → j

$$n_{i \to j} \sim \lambda_{ij} I(\lambda_{ij})$$

- ‘true’ intensities: radiometric calibration is needed
- which radiative transitions occur and how frequent they are

Mn II transition rate diagram



charge transfer: $Mn^0 + Ar^+ \rightarrow Mn^{+*} + Ar^0$

each transition: two points

blue: upper level
(radiative depopulation)
- positive

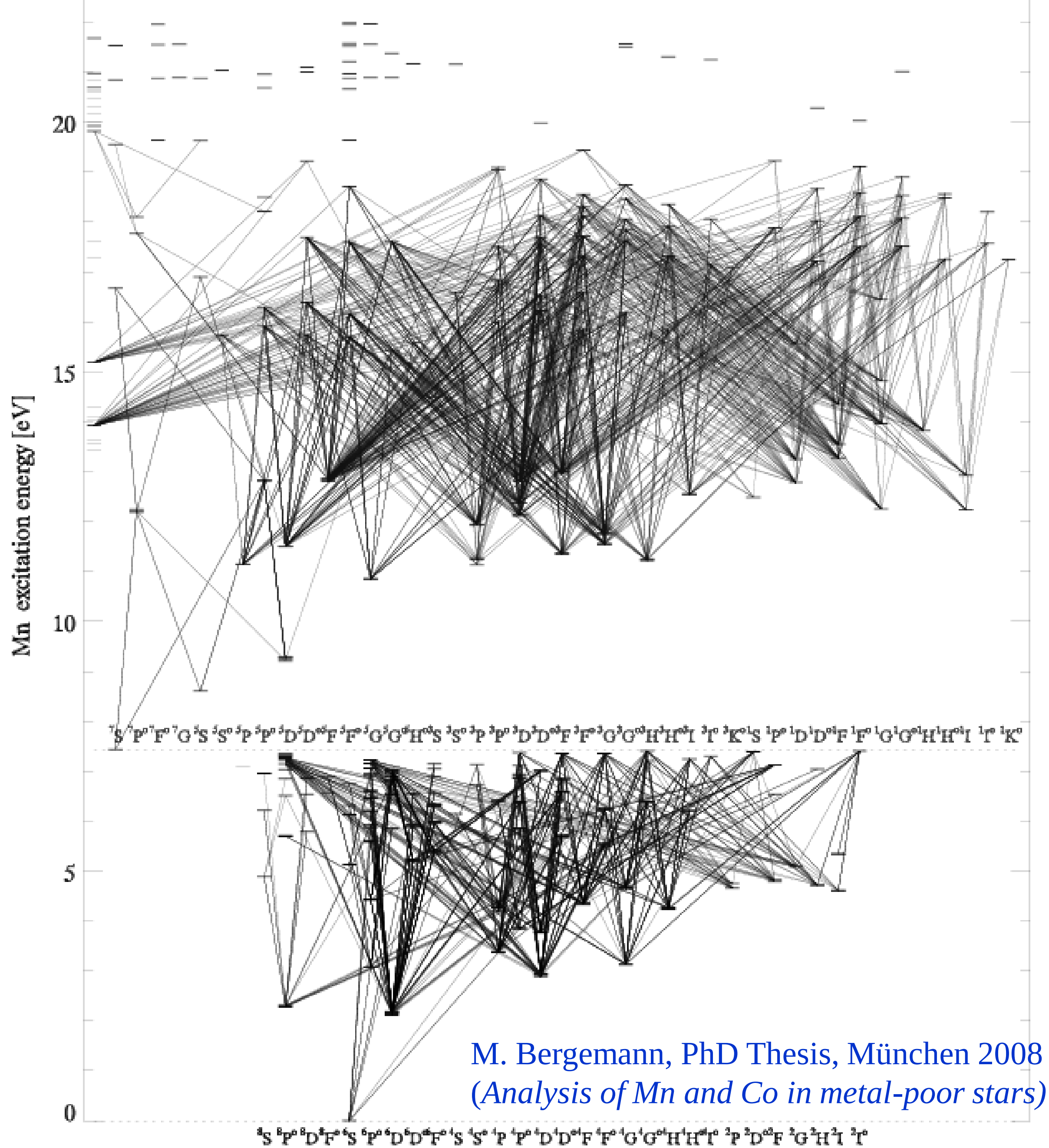
red: lower level
(radiative population)
- negative

ACT-excited lines (15.4-15.9 eV) account for

- 54 % of total Mn intensity
- 76 % of total Mn transition rate

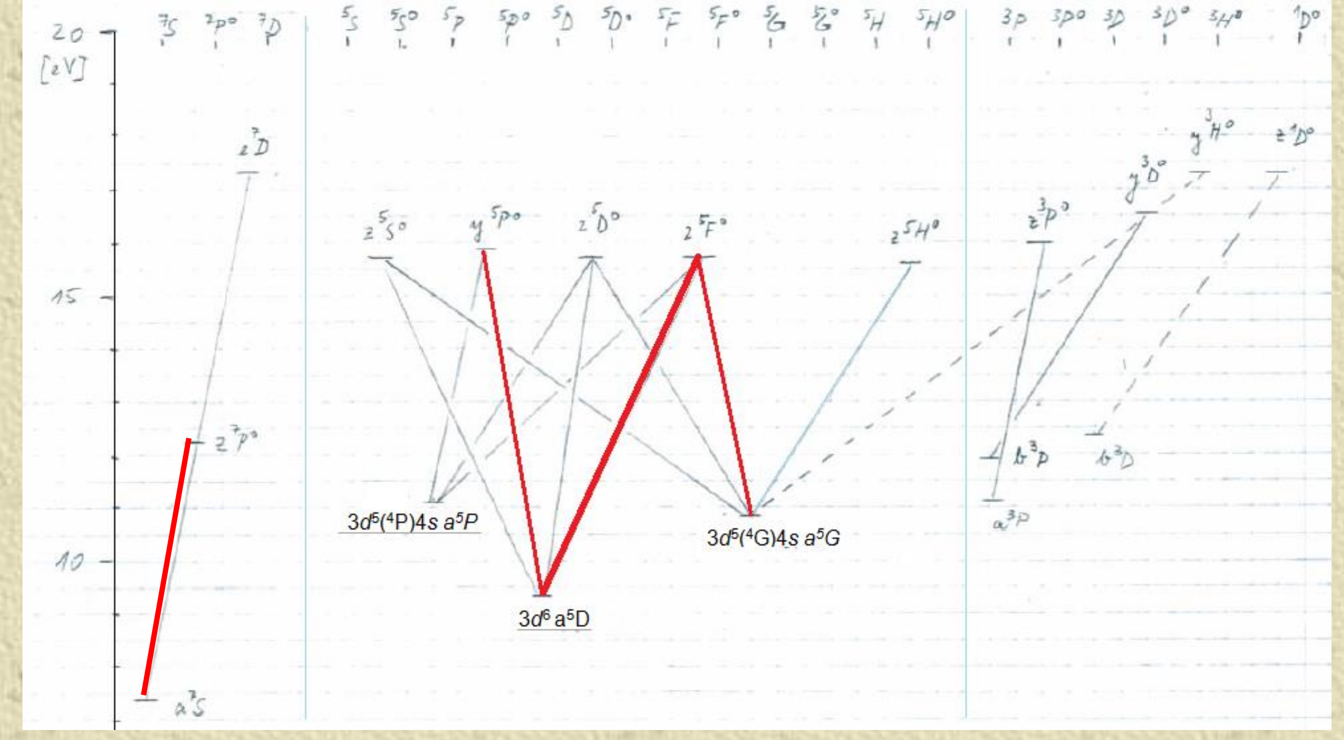
Mn I, Mn II
Grotrian diagram

- the term structure, possible radiative transitions
- in Ar plasma, only some transitions are excited



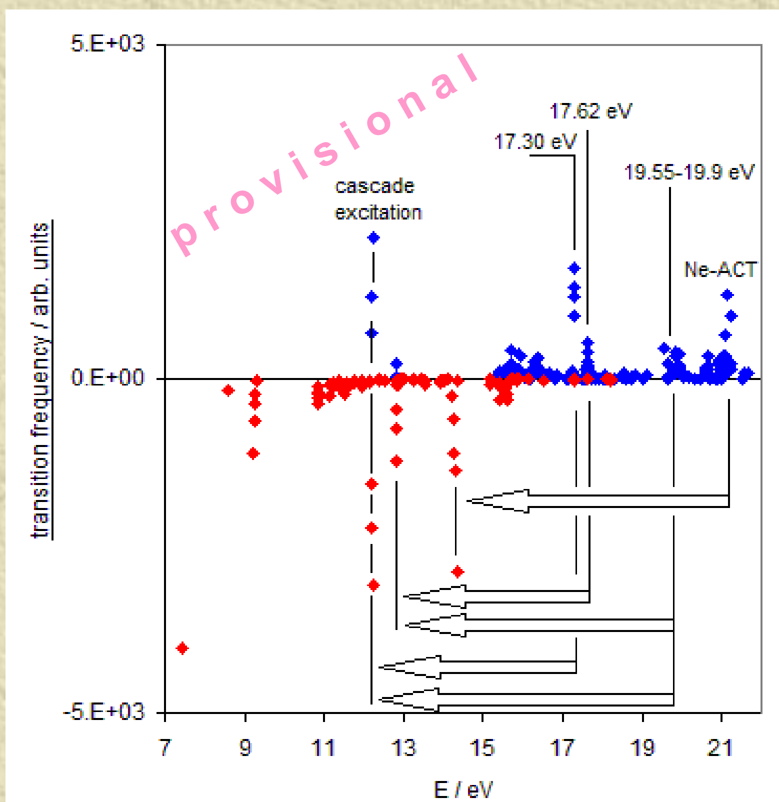
M. Bergemann, PhD Thesis, München 2008
(Analysis of Mn and Co in metal-poor stars)

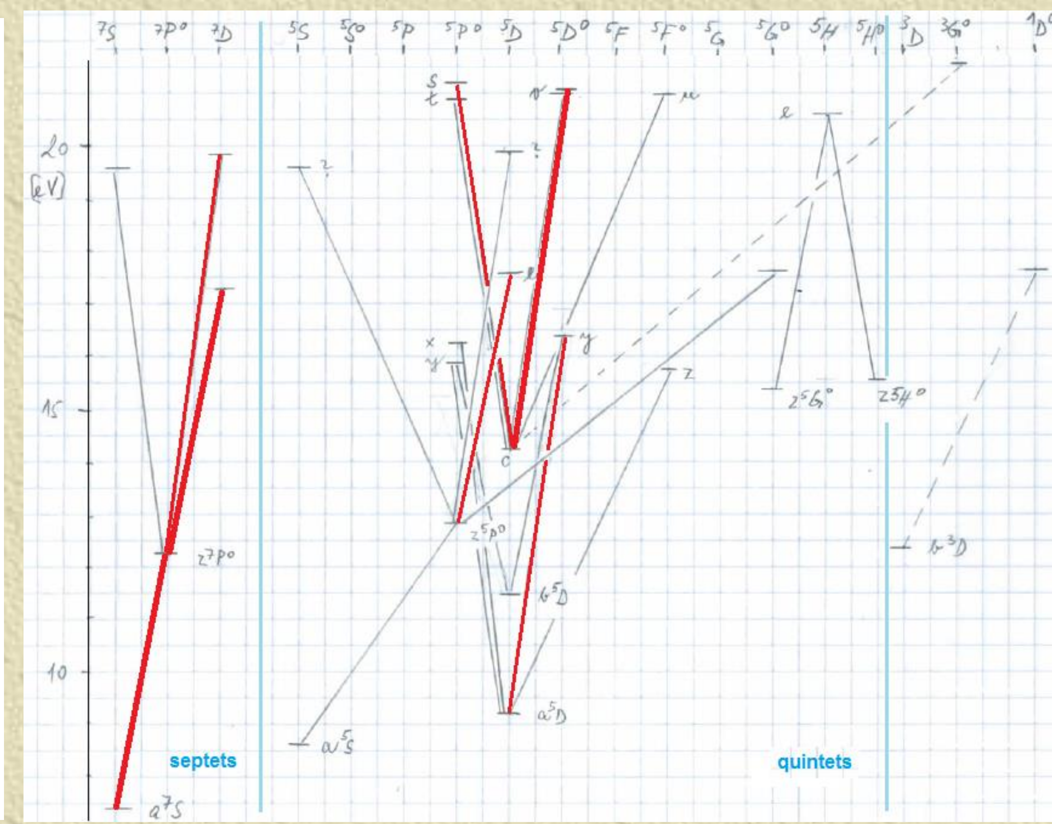
Mn II: transitions with highest transition rates



- largely quintets and septets
- 3 quintet metastable levels

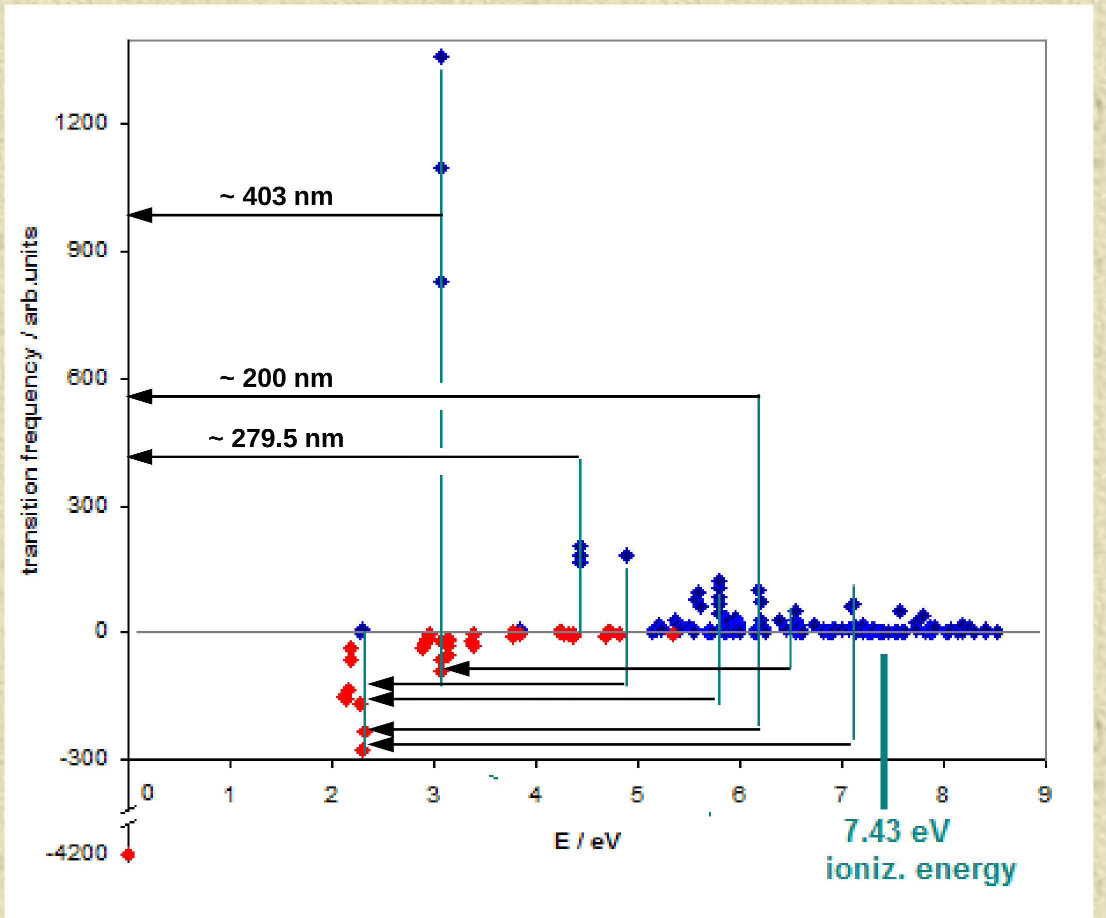
Mn II: the same for discharge in neon





- Ne-ACT at about 21.0-21.2 eV
- how the levels at ~16-17.5 eV are excited ?
- how the $3d^4 4s^2$ c^5D metastable levels at ca 14.25 eV are depopulated ?

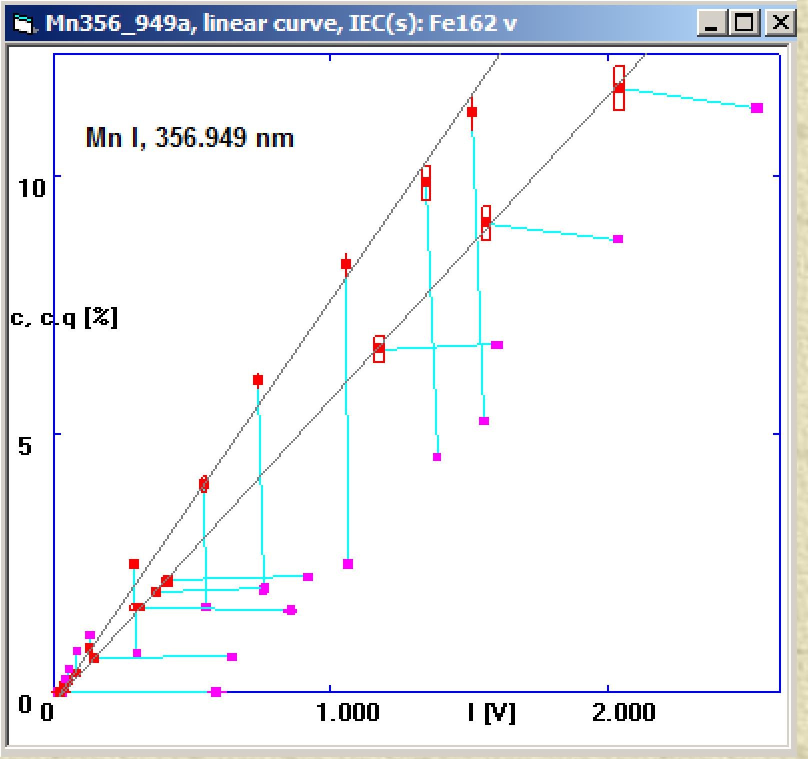
Mn I transition rate diagram (Ar discharge)



- the 3 lines at ca 403 nm account for ca 9% of total Mn intensity,
  23% of total Mn transition rate

a matrix effect in Mn I:

- Mn I, 356.949 nm (5.79 eV)
- the Fe-IEC calculated correctly (see the points close to zero)
- R-in-Fe > R-in-Cu
- also other Mn I lines with higher excitation energies ... there is a class of lines for which the standard model does not hold
- matrix effects like this were observed earlier for Cu, Zn, Al



Z. Weiss, *Spectrochim. Acta, Part B,* 62 (2007) 787–798

(LECO GDS500A)

Hydrogen effect(s) on Mn spectra

- $\gamma = R(Ar + 0.3\%\ H_2) / R(Ar)$
- all Mn I lines are enhanced
- most Mn II lines are suppressed
- similar pattern was observed for Zn

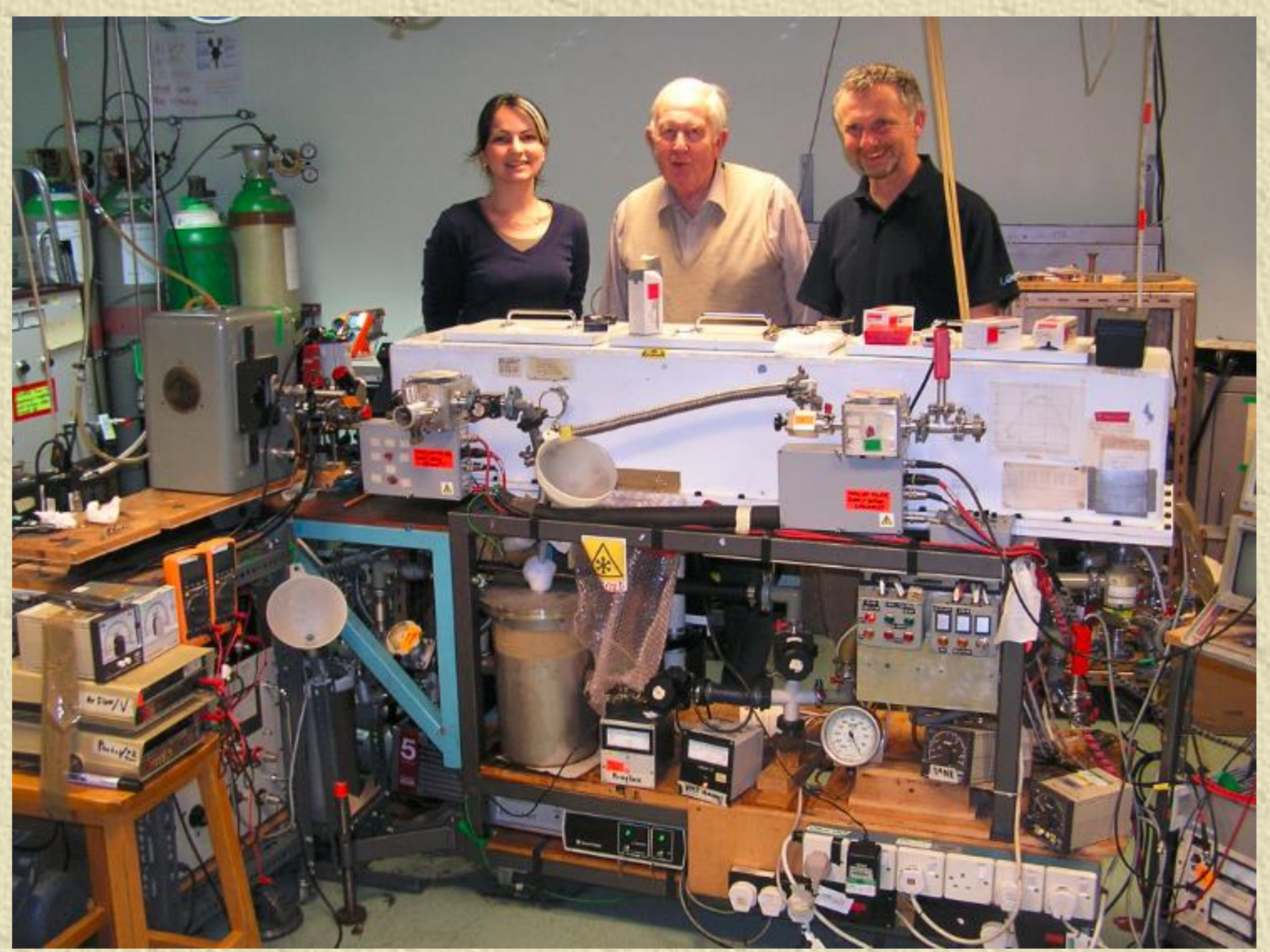
(Z.Weiss, *J.Anal.At.Spectrom.* 2005, 20, 839–846)

	Configuration	Term	Energy [eV] *)	γ **)	Lines used
Mn I	$3d^5(^6S)4s4p(^1P^\circ)$	y $^6P^\circ$	4.43	**2.17**	3
Mn I	$3d^6(^5D)4p$	z $^6D^\circ$	5.20-5.23	**1.05**	6
Mn I	“	z $^6F^\circ$	5.37-5.42	**1.49**	7
Mn I	“	z $^4F^\circ$	5.52	**1.40**	1
Mn I	“	x $^6P^\circ$	5.58-5.60	**1.52**	11
Mn I	“	z $^4D^\circ$	5.67-5.72	**1.49**	9
Mn I	“	y $^4P^\circ$	5.82	**1.43**	2
Mn I	“	y $^4P^\circ$	5.86	**1.46**	1
Mn I	$3d^54s(^7S)4d$	e ^8D	5.79	**1.43**	3
Mn I	“	e ^6D	5.85	**1.53**	5
Mn I	$3d^5(^4P)4s4p(^3P^\circ)$	y $^6D^\circ$	5.89-5.94	1.61	3
Mn I	“	v $^6P^\circ$	6.18-6.20	1.57	4
Mn I	$3d^5(^4G)4s4p(^3P^\circ)$	y $^6F^\circ$	5.98-5.99	**1.42**	5
Mn I	$3d^54s(^5S)5s$	f ^6S	6.13	1.52	2
Mn II	$3d^5(^6S)4p$	z $^7P^\circ$	12.21	1.39	1
Mn II	“	z $^5P^\circ$	12.81-12.83	**0.89**	9
Mn II	$3d^5(^4G)4p$	z $^5G^\circ$	15.42-15.43	0.16	4
Mn II	“	z $^5H^\circ$	15.55-15.59	0.20	4
Mn II	“	z $^5F^\circ$	15.68-15.73	**0.18**	10
Mn II	“	z $^3H^\circ$	15.83-15.85	0.21	3
Mn II	“	z $^3F^\circ$	15.84-15.85	0.23	4
Mn II	$3d^5(^4P)4p$	z $^5D^\circ$	15.70-15.78	**0.19**	6
Mn II	“	z $^5S^\circ$	15.73	0.25	1
Mn II	“	y $^5P^\circ$	15.90-15.92	0.18	4
Mn II	“	z $^3P^\circ$	15.99	0.22	3
Mn II	“	z $^3D^\circ$	16.21	(0.37)	1
Mn II	$3d^5(^4D)4p$	y $^5F^\circ$	16.15-16.19	(0.35)	3
Mn II	“	x $^5P^\circ$	16.28	0.21	1
Mn II	“	y $^5D^\circ$	16.36-16.39	0.21	2
Mn II	$3d^5(^6S)5s$	e ^7S	16.68	(0.68)	1
Mn II	“	e ^5S	16.90	(0.55)	2
Mn II	$3d^5(^6S)4d$	e ^7D	17.29-17.30	**0.45**	3

(LECO GDS500A)

Summary

- Mn I, Mn II spectra were described by transition rate diagrams
- the ‘standard model’ of calibration holds for Mn I, Mn II, except of Mn I lines with higher excitation energy
- charge transfer from Ar^+ ions is an important excitation mechanism for Mn II
- the work goes on



The FTS measurements were performed in summer 2010 at Imperial College, London, under the RTN Gladnet, Project P16

Gladnet

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Thank you for attention.

Danke für die Aufmerksamkeit !