EPMA of Light Element #5—Boron: It Can Be Done

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Boron: Z=5, important in many materials.

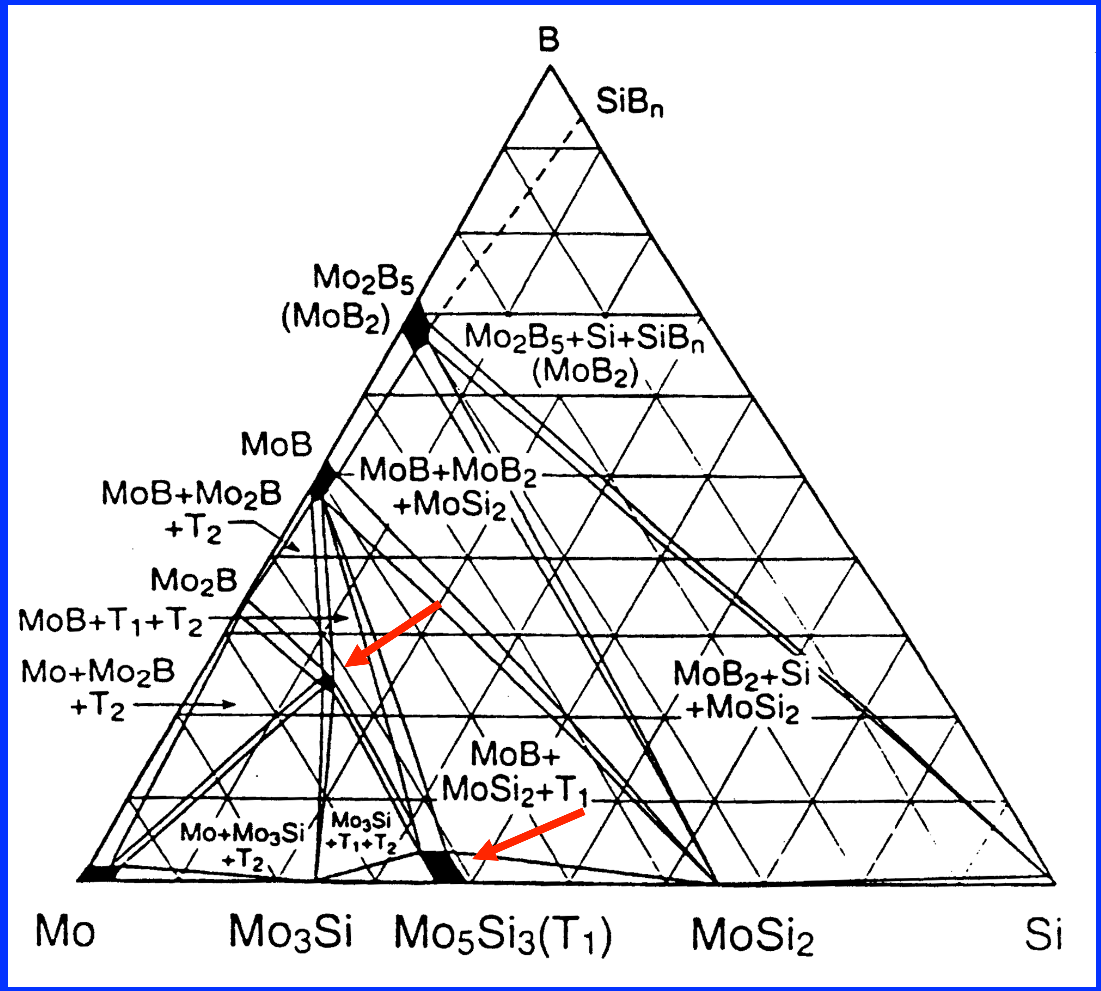
Previously difficult for EPMA:

😐 Long wavelength of B Ka (67.6Å) requires large 2d crystal or synthetic diffractor (100-200Å)

😐 Problems with first order interferences and background modeling

😐 Low energy and large mass absorption; only some MACs well characterized

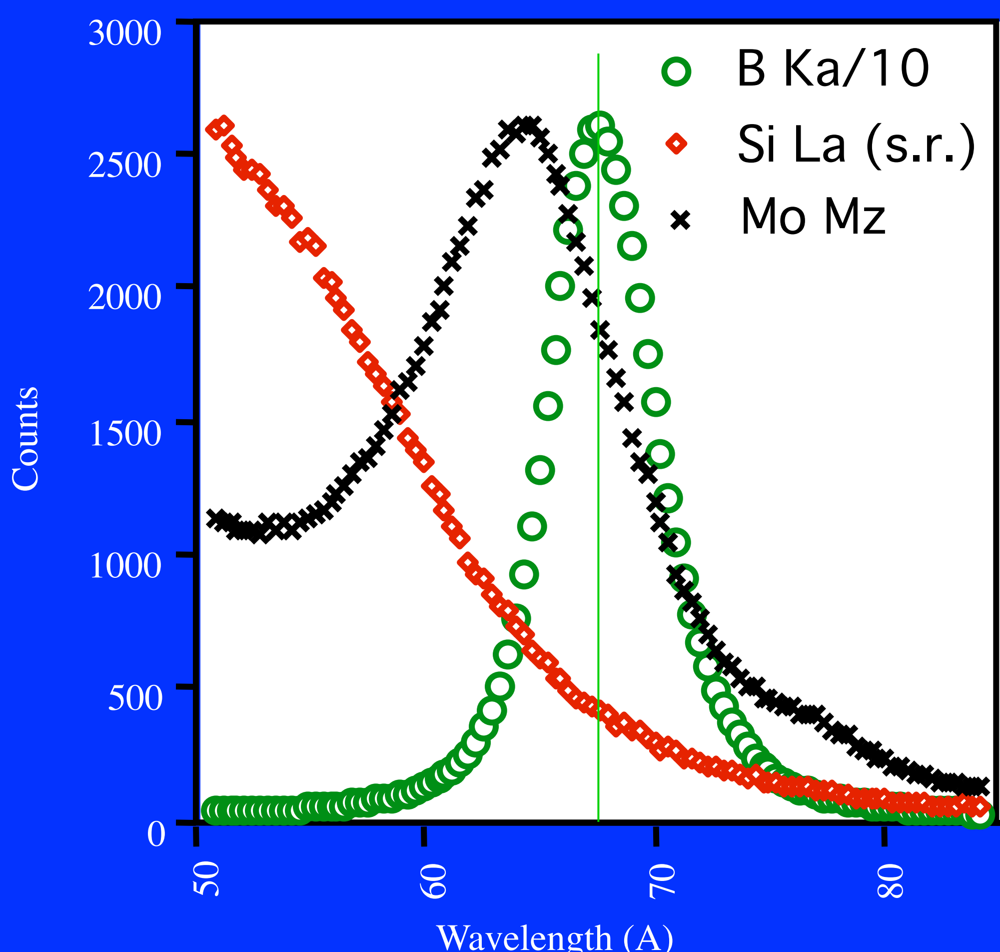
First case: precise, accurate analysis of Boron in 2 Mo-Si-B phases, T_1 and T_2



(previous: B by difference, or assumption based upon starting material…???

The major problem: pathological Mo Mz* interference + intense "background" signal from specular reflectance of Si La

*$M_{IV,V}$-$N_{II,III}$



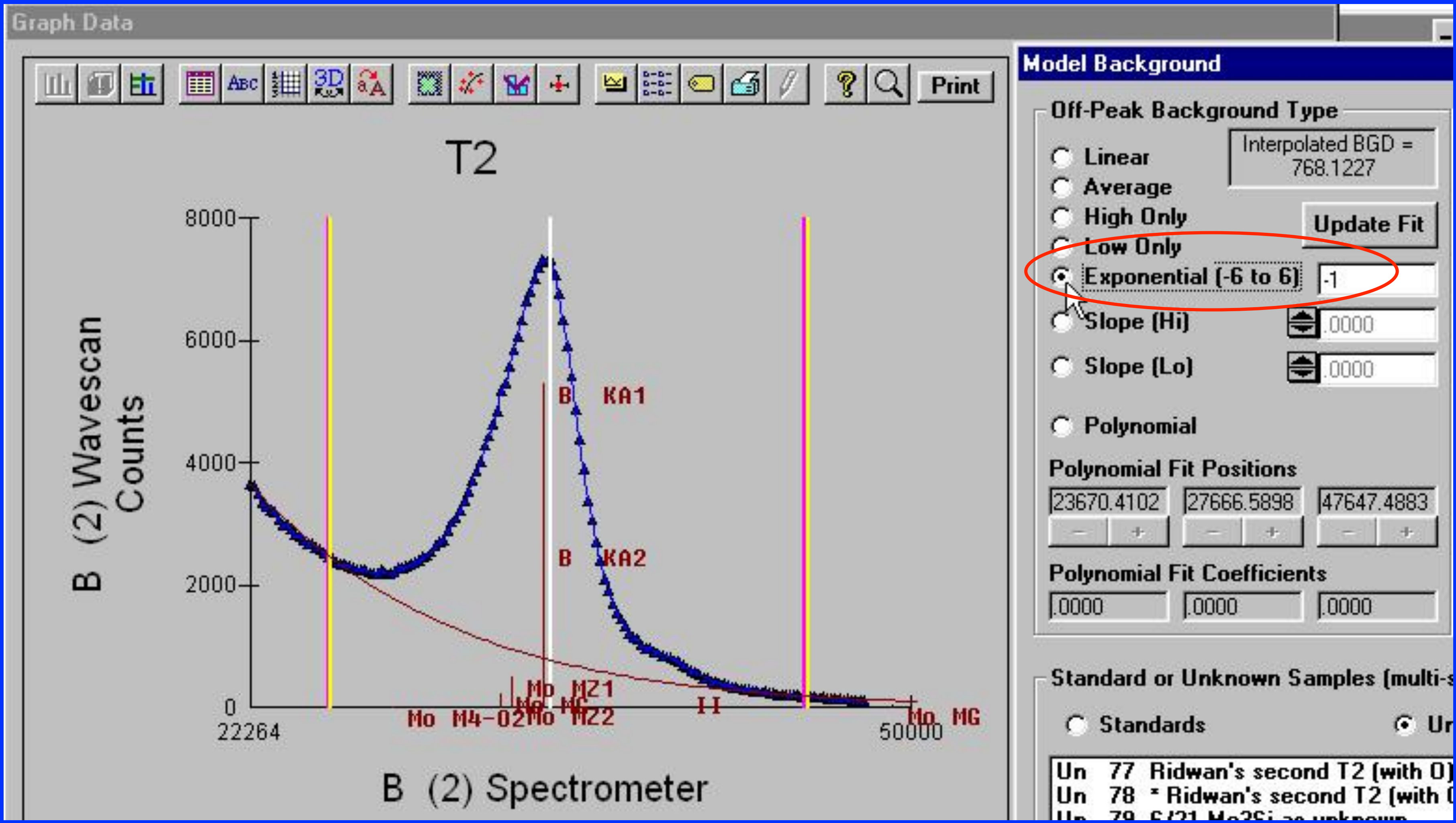
→Mo M interference on B ka
→ complex low side back-ground due to Si L specular reflectance & other Mo lines

Line	λ	I
Mo MZ1,2	64.35 A	1.0
Mo M4-O2	54.8 A	0.5
Mo M3-N1	37.5 A	1.0
Mo M3-M4	74.7	1.0
Mo M3-M5	74.9	0.1
Mo M3-N1	75.0	0.3
Si L (specular reflectance)		

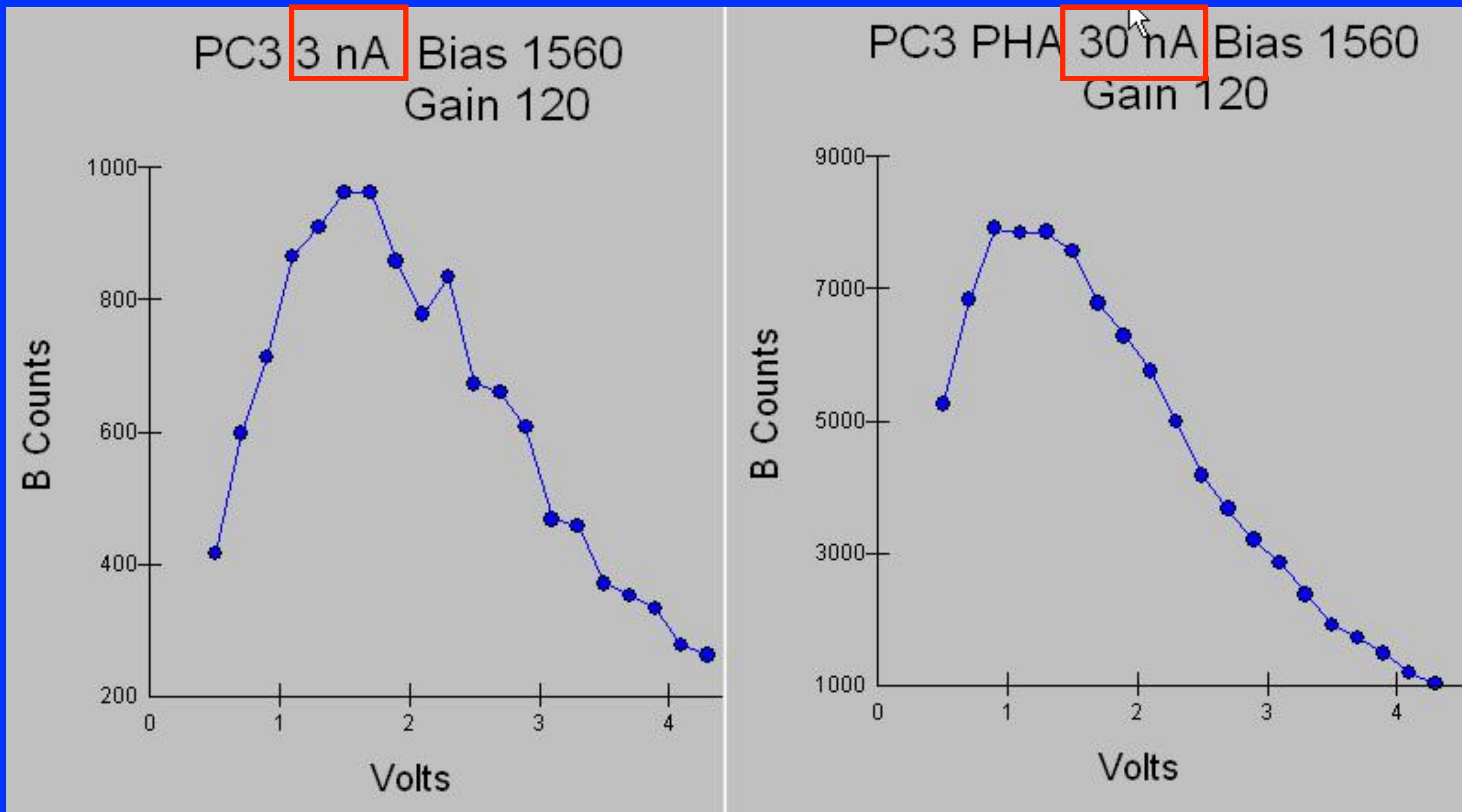
Analytical Conditions:

- ☸ 200 Å layered synthetic diffractor
- ☸ Low E_0: 7 keV to minimize X-ray path length and absorption correction; no C-coating
- ☸ Anticontamination (airjet, cold finger, baffle)
- ☸ Pure metal standards: Boron standard is arc melted (no orientation/crystallographic issues)

Modeling curved background – T_2, Mo_5SiB_2 (91 wt% Mo, 5 wt% Si, 4 wt% B)



Pulse height depression



– Calibrate on B with low current (1-3 nA), then do acquisition at 30 nA)

Data analysis and matrix correction

- Background modeling with exponential curve
- Multiple interference corrections within matrix correction (Donovan, Snyder and Rivers 1993; Donovan 1998)
- Detailed reports include negative k-ratios, showing closeness of fit for B-free phases
- Armstrong's phi-rho-z, modified from Brown and Bastin (Armstrong, 1988)
- Evaluated with various MACs:
  - Henke et al (1982)
  - Better Bastin & Heijligers (1992)
  - Better Pouchou & Pichoir (1991)

Absorber	Henke et al 1982	Pouchou & Pichoir '91	Bastin & Heijligers '92
B	3350	3500	3400
Si	84000	80000	84000
Mo	4717	4600	4550
O		16500	
C	6350	6750	

Results for 4 phases: very accurate

Wt.%

sample	MAC	without interference correction B wt %	Si wt %	Mo wt %	Sum wt %	with interference correction B wt %	Si wt %	Mo wt %	Sum wt %	B k-ratio	Int %
Mo2B	Nominal	5.33	0.00	94.67	100.00	5.33	0.00	94.67	100.00		
Mo2B	Henke	9.71	0.01	95.04	104.75	5.68	0.01	94.16	99.84	0.0667	-41.2
Mo2B	Bastin	8.92	0.01	94.87	103.80	5.23	0.01	94.05	99.29		
Mo2B	Pouchou	8.91	0.01	94.86	103.78	5.21	0.00	95.83	99.27		
Mo5SiB2	Nominal	4.08	5.31	90.61	100.00	4.08	5.31	90.61	100.00		
Mo5SiB2	Henke	8.68	4.94	92.67	106.29	4.38	4.91	91.83	101.12	0.0388	-49.6
Mo5SiB2	Bastin	8.10	4.93	92.56	105.60	4.12	4.91	91.78	100.81		
Mo5SiB2	Pouchou	7.98	4.93	92.54	105.45	4.03	4.91	91.76	100.70		
Mo5Si3	Nominal	0.00	14.95	85.05	100.00	0.00	14.95	85.05	100.00		
Mo5Si3	Henke	4.02	15.44	84.64	104.09	0.00	15.36	84.03	99.39	-0.0049	-123
Mo5Si3	Bastin	3.83	15.43	84.61	103.88	0.00	15.36	84.03	99.39		
Mo5Si3	Pouchou					0.00	15.36	84.03	99.39		
Mo	Nominal	0.00	0.00	100.00	100.00	0.00	0.00	100.00	100.00		
Mo	Henke	4.21	0.01	101.38	105.60	0.00	0.01	100.40	100.40	-0.0005	-101

At.%

sample	MAC	without interference correction B at %	Si at %	Mo at %	Sum at %	with interference correction B at %	Si at %	Mo at %	Sum at %	B k-ratio	Int %
Mo2B	Nominal	33.30	0.00	66.67	100.00	33.30	0.00	66.67	100.00		
Mo2B	Henke	47.49	0.02	52.39	100.00	34.84	0.02	65.13	100.00	0.0667	-41.2
Mo2B	Bastin	45.49	0.02	54.50	100.00	33.00	0.02	66.97	100.00		
Mo2B	Pouchou	45.44	0.02	54.54	100.00	32.97	0.02	67.01	100.00		
Mo5SiB2	Nominal	25.00	12.50	62.50	100.00	25.00	12.50	62.50	100.00		
Mo5SiB2	Henke	41.28	9.04	49.58	100.00	26.35	11.37	62.28	100.00	0.0388	-49.6
Mo5SiB2	Bastin	39.66	9.29	51.05	100.00	25.21	11.55	63.24	100.00		
Mo5SiB2	Pouchou	39.29	9.35	51.36	100.00	24.78	11.62	63.60	100.00		
Mo5Si3	Nominal	0.00	37.50	62.50	100.00	0.00	37.50	62.50	100.00		
Mo5Si3	Henke	20.60	30.47	48.91	100.00	0.00	38.45	61.57	100.00	-0.0049	-123
Mo5Si3	Bastin	19.83	30.77	49.16	100.00	0.00	38.45	61.57	100.00		
Mo5Si3	Pouchou	19.29	30.84	49.49	100.00	0.00	38.45	61.57	100.00		
Mo	Nominal	0.00	0.00	100.00	100.00	0.00	0.00	100.00	100.00		
Mo	Henke	26.90	0.03	73.07	100.00	0.04	0.05	99.91	100.00	-0.0005	-101

THE NEW YORK TIMES **NATIONAL** MONDAY, JUNE 11, 2001

Researchers Turn Compound Into Superconducting Wires

By KENNETH CHANG

Less than half a year after a metallic compound was discovered to be a superconductor, scientists have developed a practical technique for making wires out of it.

Other researchers have also produced thin films of the compound, magnesium diboride, and markedly increased how much electrical current it can carry.

In January, researchers in Japan announced their discovery that magnesium diboride turns into a superconductor — a material where electricity flows with virtually no resistance — at temperatures below minus 389 degrees Fahrenheit. Magnesium diboride has been known since the 1950's, but no one had tested it for superconductivity.

While other materials known as high-temperature superconductors work at higher temperatures, up to minus 240 degrees, m… boride is much cheape…

To make the wires, … Agere Systems, a spin… Technologies, in Murr… filled iron tubes with m… boride powder, then s… flattened the tubes in… fraction of an inch wi… feet long. The wires we… at 1,600 degrees Fahr… fused the magnesium … der solid.

The technique is si… used commercially to … wires out of high-tempe… conductors. Supercond… could find uses in pow… sion cables, efficient el… and magnets for magne… imaging machines.

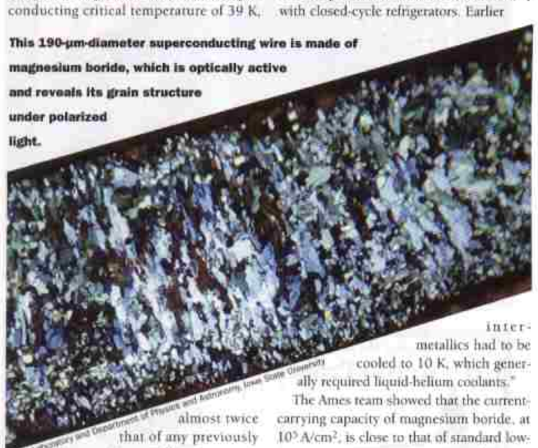
The new wires could find use in motors and power cables.

conductor. Otherwise, forces generated by the electric current in the superconductor push the magnetic fields into the superconductor's atoms. That jostling dissipates energy just as electrons bumping into atoms in ordinary metals produce electrical resistance.

To produce their thin films, the University of Wisconsin and Princeton researchers used ultraviolet lasers to vaporize magnesium diboride, which then settled in a layer about 1-50,000th of an inch thick. The oxygen-tainted magnesium diboride

Intermetallic superconductor

In a dramatic announcement at the Symposium on Transition Elements meeting on January 10 in Sendai, Japan, Jun Akimitsu and colleagues at the Aoyama Gakuin University (Tokyo) reported that the bimetallic compound magnesium boride had a superconducting critical temperature of 39 K, almost twice that of any previously known intermetallic compound. Within weeks, a group at the U.S. Department of Energy's Ames Laboratory at Iowa State University proved that magnesium boride had slightly different transition temperatures, which depended on whether the



This 190-µm-diameter superconducting wire is made of magnesium boride, which is optically active and reveals its grain structure under polarized light.

easier to cool. "Superconductors have to operate at about half their critical temperature to get good current-carrying capacity," explains Ames researcher Paul Canfield. "So magnesium boride could operate at 20 K, a temperature that can be reached easily with closed-cycle refrigerators. Earlier intermetallics had to be cooled to 10 K, which generally required liquid-helium coolants."

The Ames team showed that the current-carrying capacity of magnesium boride, at 10^5 A/cm^2, is close to that of standard low-temperature superconductors such as niobium-tin. However, magnesium boride is a much lighter material, having one-third the density of niobium-tin, so it can carry three times as much current on a weight-for-weight basis.

Boron, Take 2: MgB_2

In early 2001, MgB_2 gained attention as a "high" T_c (39 K) superconductor.

Groups at UW-Madison approached me for assistance in evaluating their MgB_2 films and solids.

With our 200Å LDE, I thought there should be "no problem".

But the problems soon became evident:

(1) E_0?: They had films of 4000-5000-6000Å and 1.4 μm. I had two options: run at high keV (7-10 keV) and then worry later about trying to evaluate the k-ratios with thin film software*— or run at a very low 3-4 keV and try to constrain primary X-ray production to the film. I chose the second.

(2) Standard?: What to use for a Mg standard? This was complicated by my desire not to apply an additional film (carbon), so I couldn't use C-coated oxide or silicates. I had 2 choices: some bulk MgB_2 from the researchers, or some Mg-rich alloy (e.g., $Mg_{93}Al_6Zn_1$). I tried both.

* I have been using Waldo's shareware GMRFilm, somewhat cumbersome; I had access to commercial Strata, but it was not easy to use despite its price ($8K).

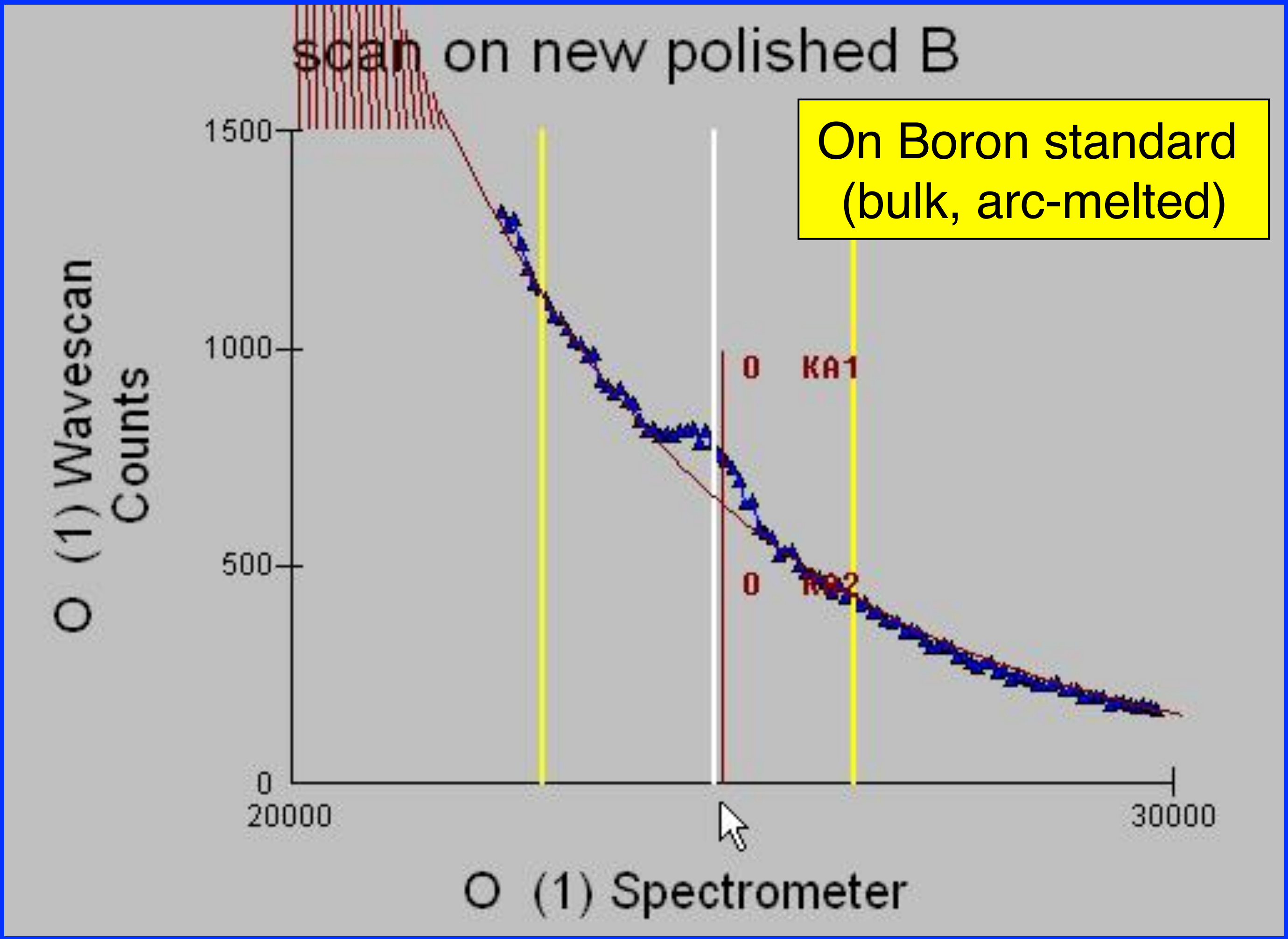
Problem with my easy standard?

Even before we got to the unknowns, a possible problem arose with what I thought was my problem-free Boron standard.

Because the substrate had oxygen in it, and it would always be an acquired element, we acquired O Ka counts on our Boron standard … and found apparent Oxygen, when I had been assured by the main PI that that was impossible

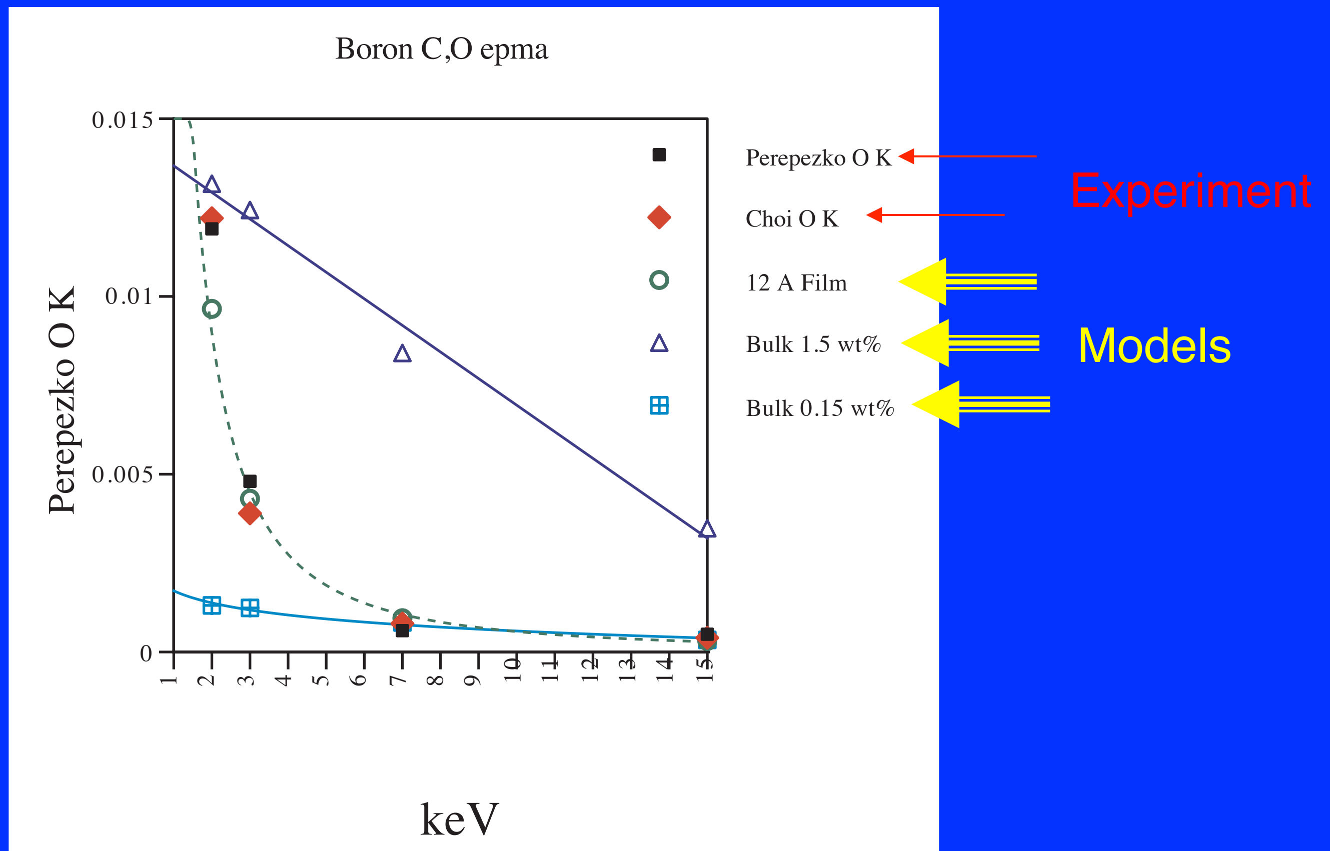
The alternative was that there was a thin skin of oxide on the standard.

… Always do a wavescan
(here at the very low end of the LSM 100Å)



... But is the Oxygen in the bulk or in a surface film?

Oxygen on Boron metal (2 stds)



Not bulk, but ~12 Å film B_2O_3 (2 different Boron standards)

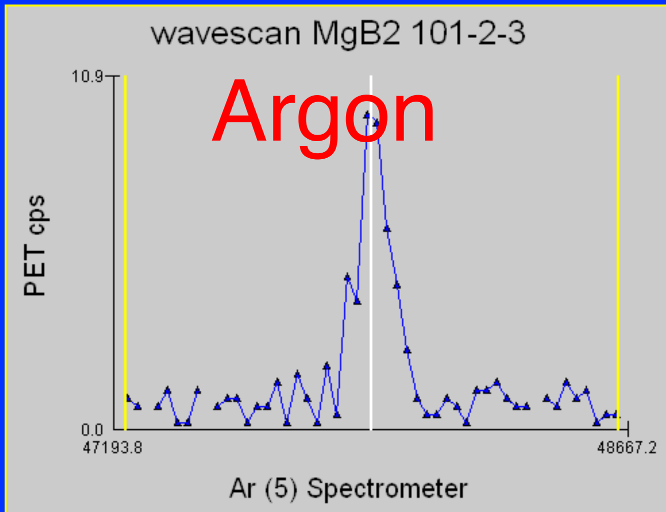
Thin film modeled with GMRfilm (R. Waldo)

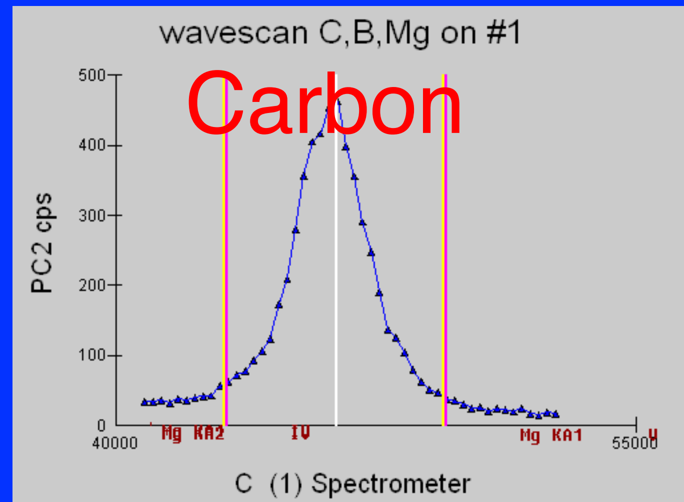
And then they gave me the MgB_2 specimens

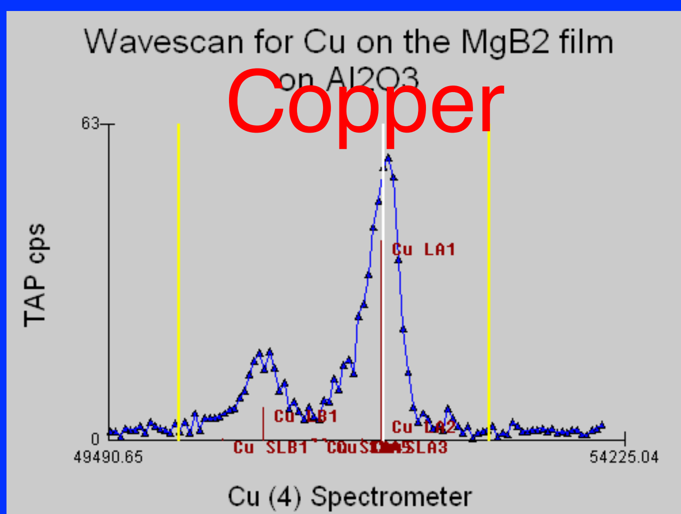
Upon examination of the very first specimens, other problems became apparent. Many surfaces were <u>not mirror smooth</u>. Analytical totals were low (~90 wt%) even on those films with fairly smooth surfaces.

This wasn't the first time that I had to question the grad students — "just exactly how did you make this film" and "please check the stated composition of your sputtering target".

MgB_2 …plus

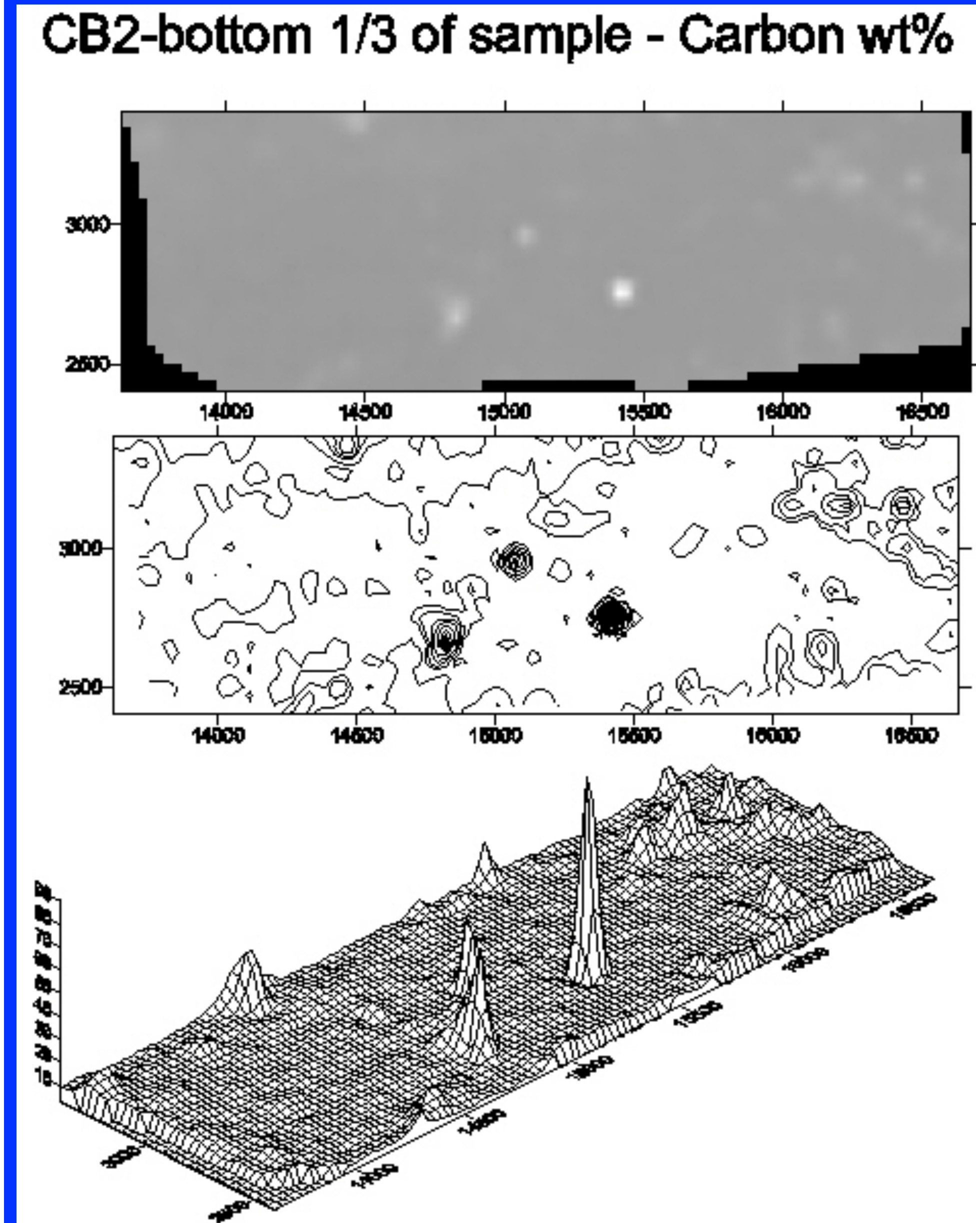


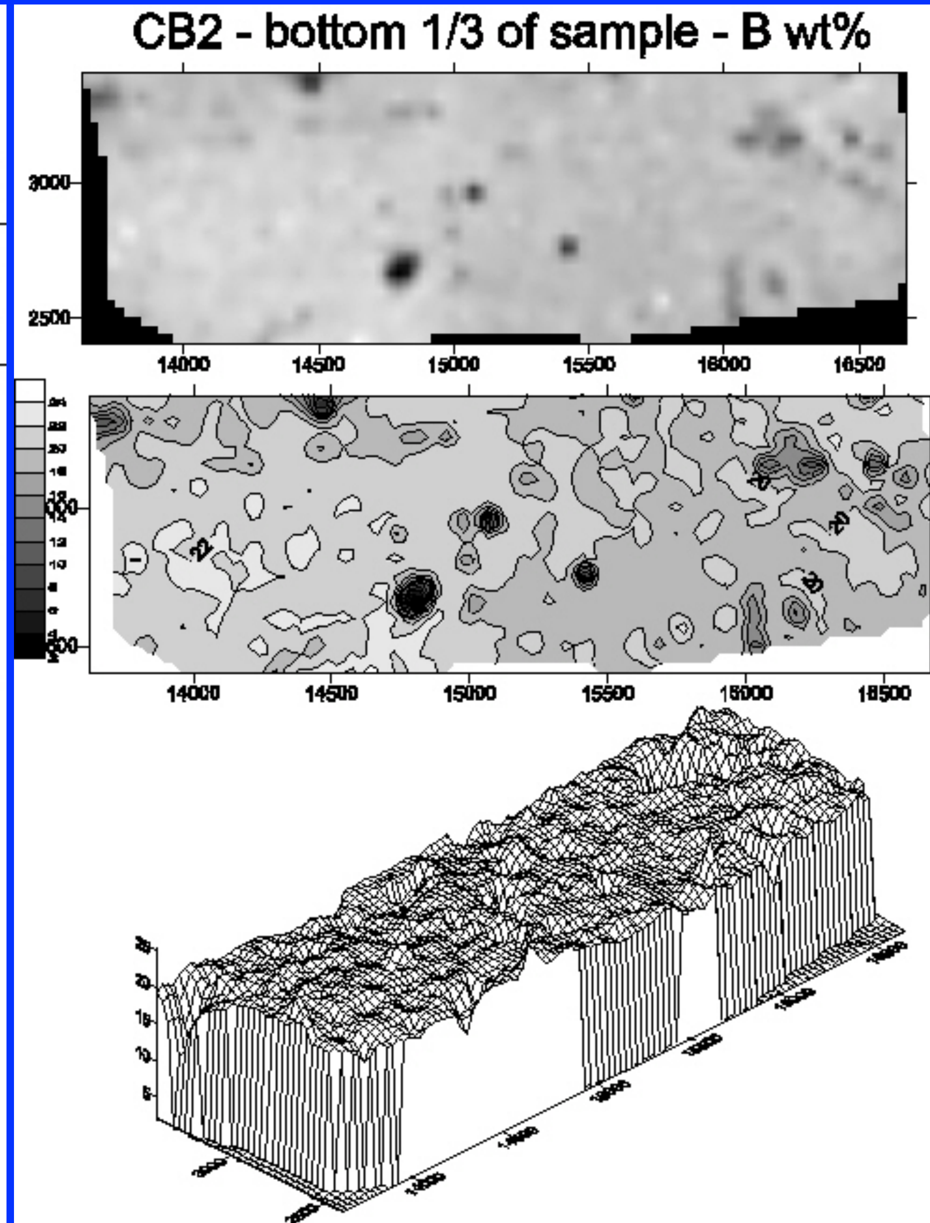




Over months of study, many unexpected elements turned up, generally from the sputtering process: the Ar atmosphere, Cu from sputtering holder, C from "pure B sputtering target" (B_4C, manufacturer didn't think C counted as an element!).

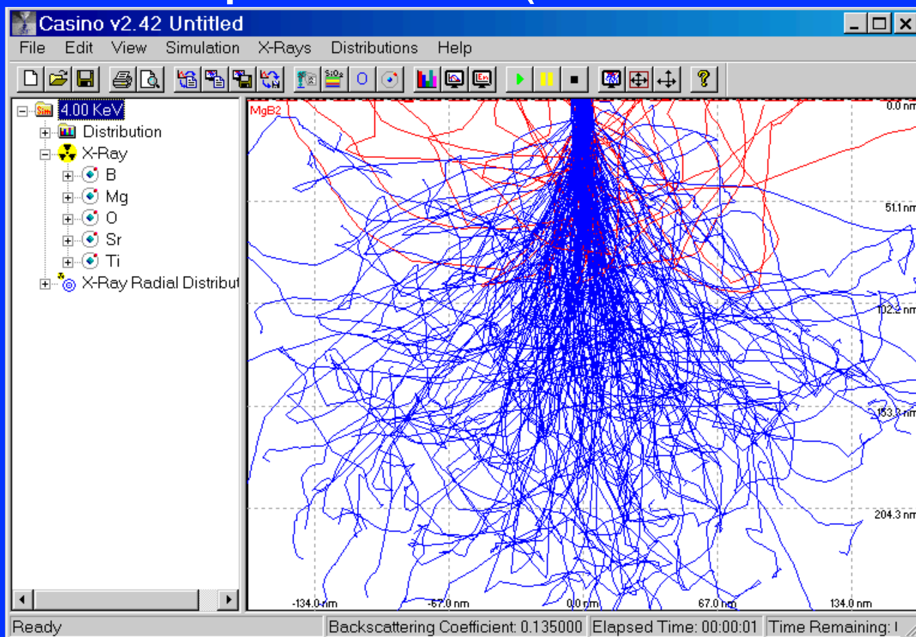
X-ray Map of MgB_2 film — to see just how bad the inpurity is



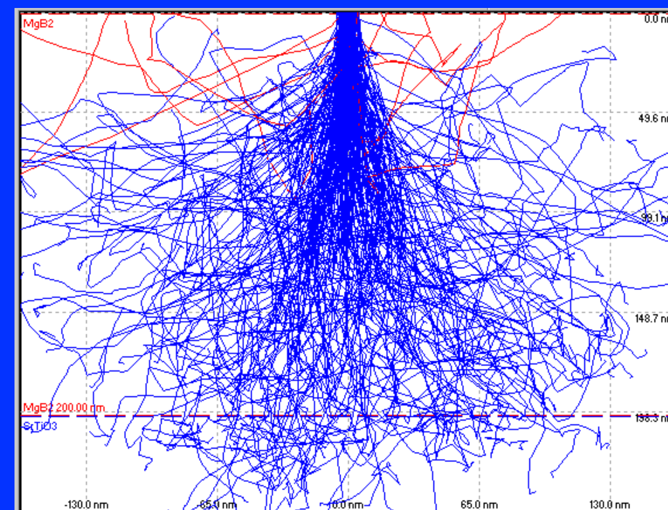


Monte Carlo Simulations — MgB_2 Film

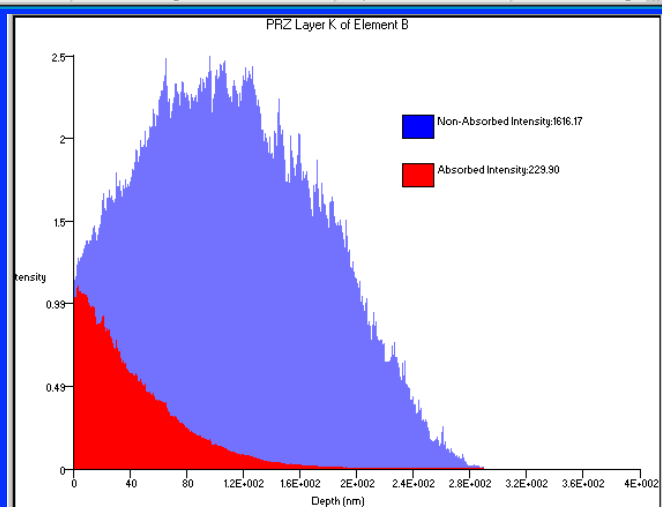
To answer the question: just how thin a film can we treat as a "bulk specimen" (for normal matrix correction) for a given E_0.

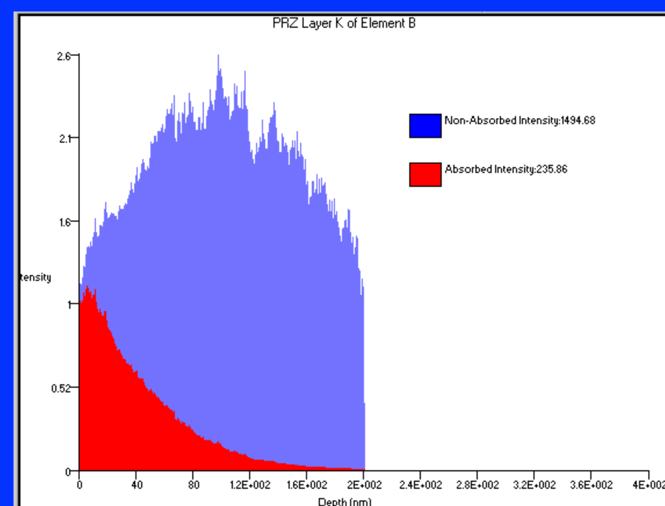


4 keV, LEFT: 500 nm thick, then RIGHT: 200 nm



Here, using the excellent (free) CASINO Monte Carlo program





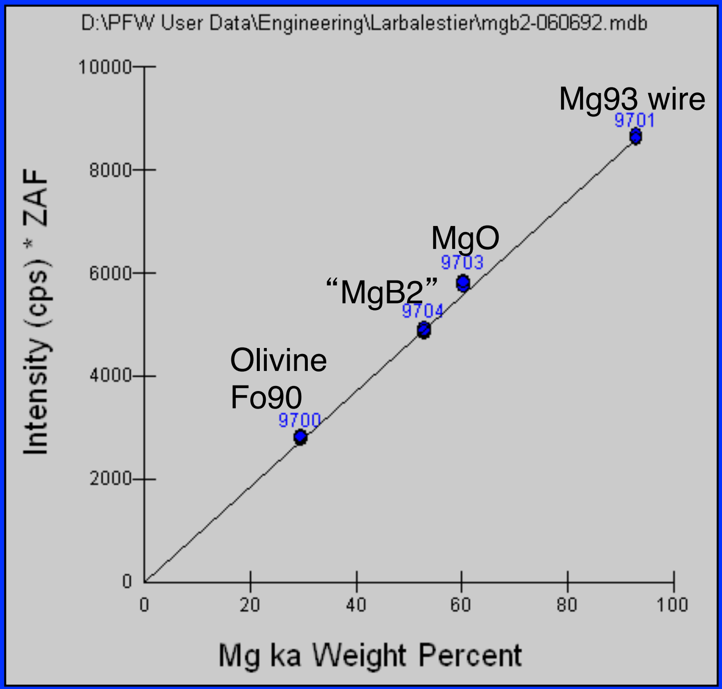
Easier Question – Is there Mg deficiency in <u>Bulk</u> MgB_2 ?

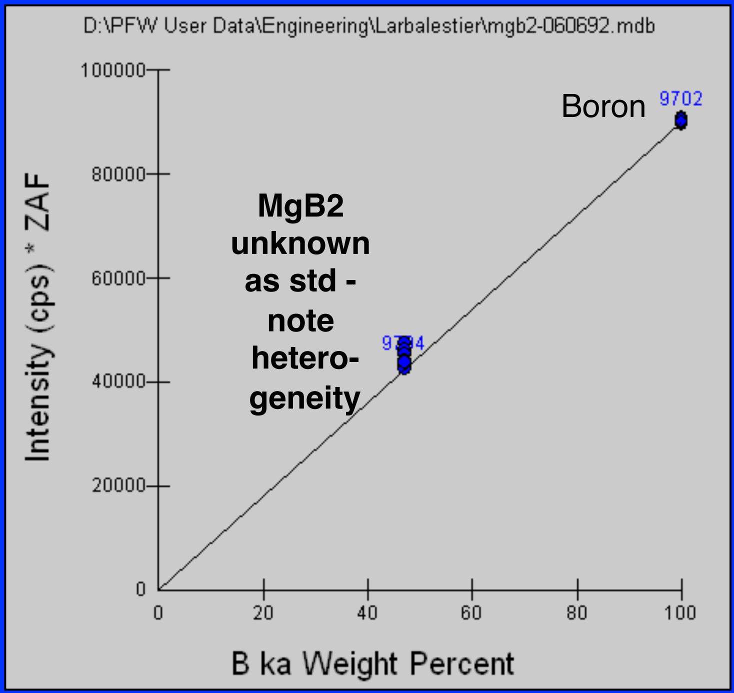
In 2002, I was asked an easier question: please tell us the extent of Mg deficiency in MgB_2 – in solid chucks of it.

I could now

- Have polished surfaces
- Use higher keV
- Carbon coat and test the various Mg standards against each other (MgO, Mg-rich olivine Fo90, Mg_{93} wire)

We Can Check Out Several Mg Standards using the PfW "Evaluate" Application





Carbon-coated, 7 keV

(This also is a way to visualize possible issues with standards, e.g., slightly off compositions, peak shifts)

Using MgO as standard

Un 5 MgB2 (Bulk)
TakeOff = 40 KiloVolts = 7 Beam Current = 20 Beam Size = 0
Number of Data Lines: 21 Number of 'Good' Data Lines: 17
First/Last Date-Time: 06/06/2002 06:50:46 PM to 06/06/2002 07:14:38 PM
WARNING- Using Exponential Off-Peak correction for B ka
WARNING- Using Exponential Off-Peak correction for O ka
WARNING- Using Empirical Mass Absorption Coefficients

Results in Elemental Weight Percents

ELEM:	Mg	B	O
TYPE:	ANAL	ANAL	ANAL
BGDS:	LIN	EXP	EXP
TIME:	10.00	10.00	10.00

ELEM:	Mg	B	O	SUM
78	52.246	48.427	.218	100.892
79	51.445	47.357	.316	99.118
80	52.077	47.839	.373	100.290
81	51.292	48.350	.394	100.036
84	51.927	48.102	.474	100.503
86	50.569	47.749	1.158	99.476
87	50.984	47.214	.494	98.692
88	50.991	46.732	.354	98.078
89	52.075	46.959	.291	99.324
90	51.281	47.795	.531	99.607
91	51.174	48.786	.600	100.560
92	51.156	48.424	.727	100.306
93	51.697	48.513	.439	100.648
94	50.641	47.904	.607	99.153
95	51.032	49.029	.629	100.690
96	50.988	47.537	.318	98.843
98	51.465	47.372	.223	99.061
AVER:	51.355	47.888	.479	99.722
SDEV:	.501	.647	.229	
SERR:	.121	.157	.055	
%RSD:	1.0	1.4	47.7	
STDS:	9703	9702	9703	

ZCOR:	1.0193	4.4761	1.4791
KRAW:	.9108	.1070	.0095
PKBG:	148.12	56.60	1.18
INT%:	.00	.00	.00

Results Based on 2 Atoms of B

ELEM:	Mg	B	O	SUM
78	.960	2.000	.006	2.966
79	.966	2.000	.009	2.975
80	.968	2.000	.011	2.979
81	.944	2.000	.011	2.955
84	.960	2.000	.013	2.974
86	.942	2.000	.033	2.975
87	.961	2.000	.014	2.975
88	.971	2.000	.010	2.981
89	.987	2.000	.008	2.995
90	.954	2.000	.015	2.970
91	.933	2.000	.017	2.950
92	.940	2.000	.020	2.960
93	.948	2.000	.012	2.960
94	.940	2.000	.017	2.958
95	.926	2.000	.017	2.943
96	.954	2.000	.009	2.963
98	.966	2.000	.006	2.973
AVER:	.954	2.000	.014	2.968
SDEV:	.016	.000	.006	
SERR:	.004	.000	.002	
%RSD:	1.6	.0	47.4	

Using Mg93 wire as standard

Wt % Elemental, using Mg93Al6Zn1 for Mg std

AVER:	52.843	48.307	.479	101.628
SDEV:	.514	.654	.228	
SERR:	.125	.159	.055	
%RSD:	1.0	1.4	47.7	
STDS:	9701	9702	9703	
STKF:	.9287	1.0000	.3402	
STCT:	8618.1	90052.6	14936.4	
UNKF:	.5185	.1070	.0032	
UNCT:	4811.8	9635.5	142.3	
UNBG:	32.8	173.5	787.8	
ZCOR:	1.0191	4.5153	1.4768	
KRAW:	.5583	.1070	.0095	

On 2 atoms of B

AVER:	.973	2.000	.013	2.987
SDEV:	.016	.000	.006	
SERR:	.004	.000	.002	
%RSD:	1.6	.0	47.4	

Despite apparent “good results” it would be useful to try to acquire K-ratios at various E0s to experimentally calculate MAC for B Ka in Mg and compare with the only MAC that exists (Henke)

Conclusions

1. Using low E0 (3-7 keV) is generally beneficial for Boron analysis.
2. Even massive interference like Mo Mz on B Ka can be correctly removed with good interference correction and versatile background modeling capability.
3. We need an reliable electrically conductive Mg standard; maybe the $Mg_{97}Al_6Zn_1$ wire?
4. Any experimental thin film—especially newly synthesized when bugs are not worked out— can be a challenge and should be approached with an open mind for “other” elements.