Control over Connectivity and Magnetism of Tetrahedral $FeSe_2$ Chains through Coordination Fe-Amine Complexes

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Supporting Information

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Table SI 1. Parameters for single crystal data collection and structure refinement for $Fe_3Se_4(dien)_2$ and $Fe_3Se_4(tren)$

Compound	$Fe_3Se_4(dien)_2$	$Fe_3Se_4(tren)$
λ (Å)	Mo-K$_\alpha$, 0.71073	
Temp. (K)	90(2)	
Space Group	$C222_1$ (No. 20)	$P2_1/c$ (No. 14)
a (Å)	9.140(2)	9.039(2)
b (Å)	18.122(3)	10.630(2)
c (Å)	11.544(2)	16.641(3)
β (°)		102.652(3)
V (Å^3)	1912.0(5)	1560.2(5)
Z	4	4
ρ (g·cm^{-3})	2.396	2.681
μ (mm^{-1})	9.861	12.067
θ range (°)	2.25-33.11	2.29-32.00
Data/param.	3541/97	5391/155
R_1	0.055	0.036
wR_2	0.088	0.068
Goodness-of-Fit	1.01	1.04
Diff. peak and hole (e/Å^3)	1.29 and –1.35	1.42 and –1.19
Flack parameter	0.37(2)	N/A

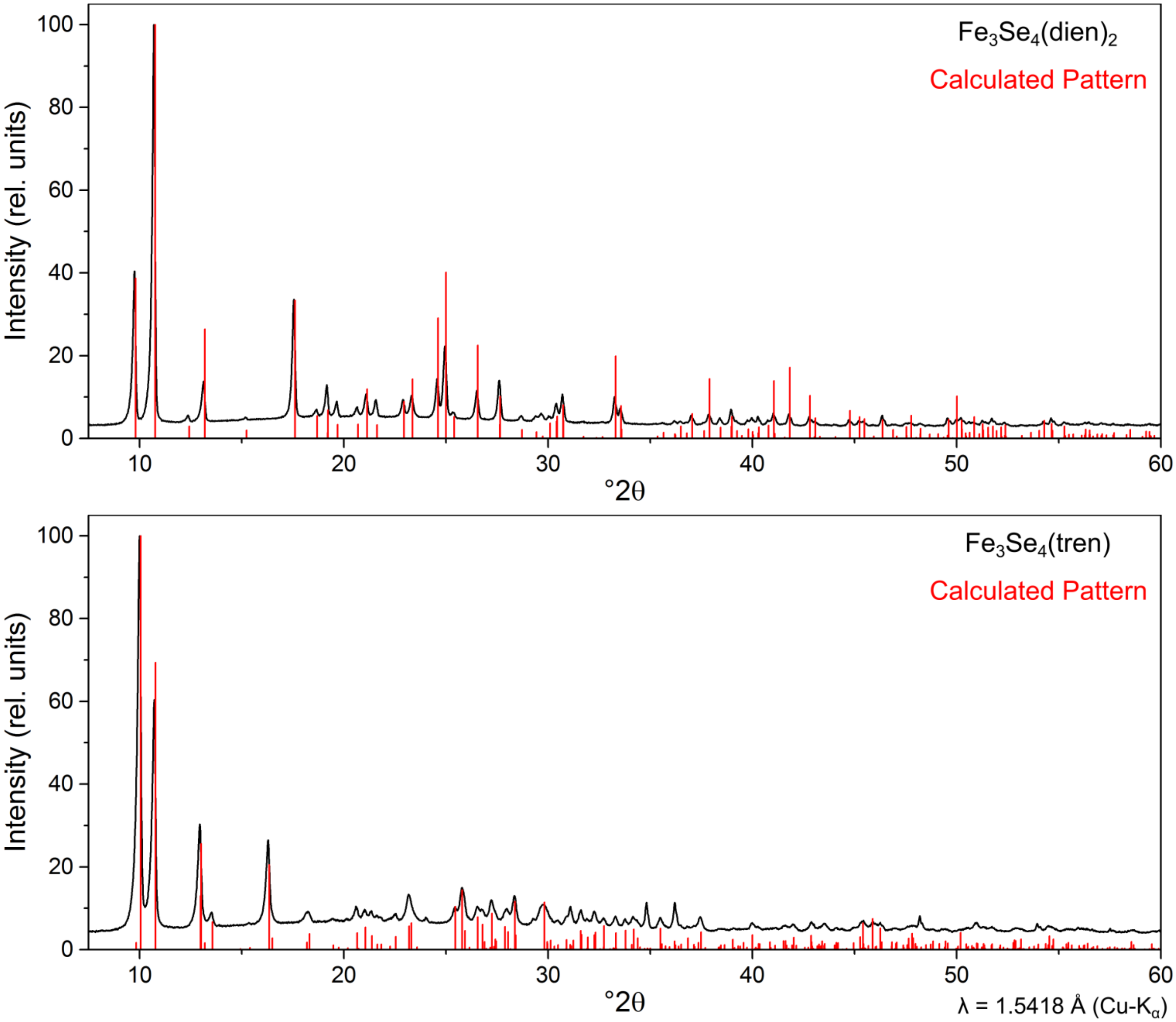


Figure SI 1. Experimental (black) and calculated (red) powder X-ray diffraction patterns for Fe$_3$Se$_4$(dien)$_2$ (top) and Fe$_3$Se$_4$(tren) (bottom). The samples were prepared on single-crystal Si(510) zero-background holders, and the patterns were collected with a D/teX Ultra high-speed silicon strip detector in continuous sweep mode from 5-60° 2θ at a rate of 1°/min with the sample spinning at 60 rpm. The energy window of the detector was narrowed to reduce fluorescence from iron. Least-squares refinement (Le Bail method) was performed in the software Jana2006[1] to determine the room-temperature unit cell parameters; Fe$_3$Se$_4$(dien)$_2$: a = 9.229(1) Å, b = 18.014(2) Å, c = 11.620(1) Å; Fe$_3$Se$_4$(tren): a = 9.019(2) Å, b = 10.734(3) Å, c = 16.840(4) Å, β = 102.99(2)°. These parameters were used with the 90 K atomic coordinates to calculate the theoretical powder diffraction patterns shown above.

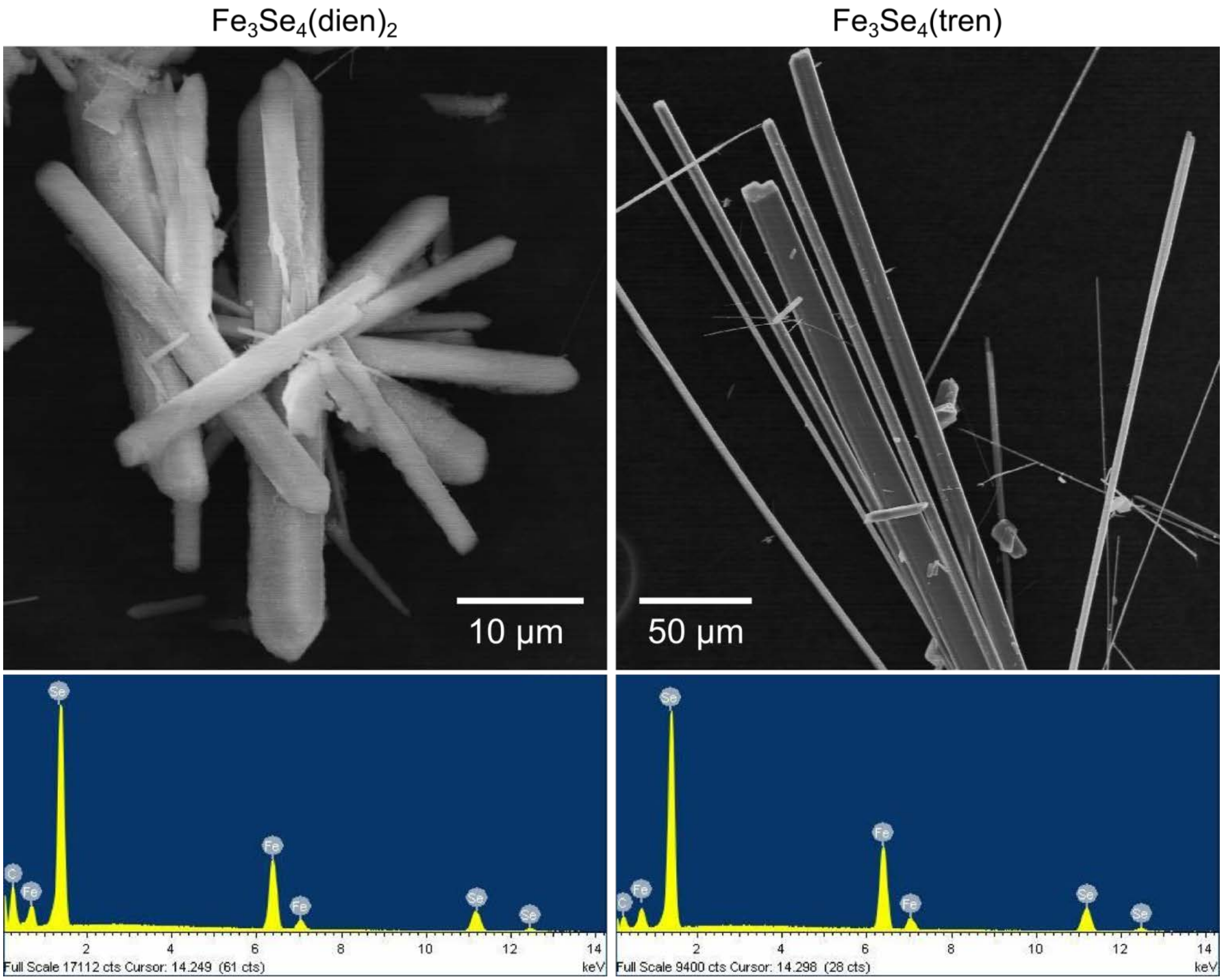
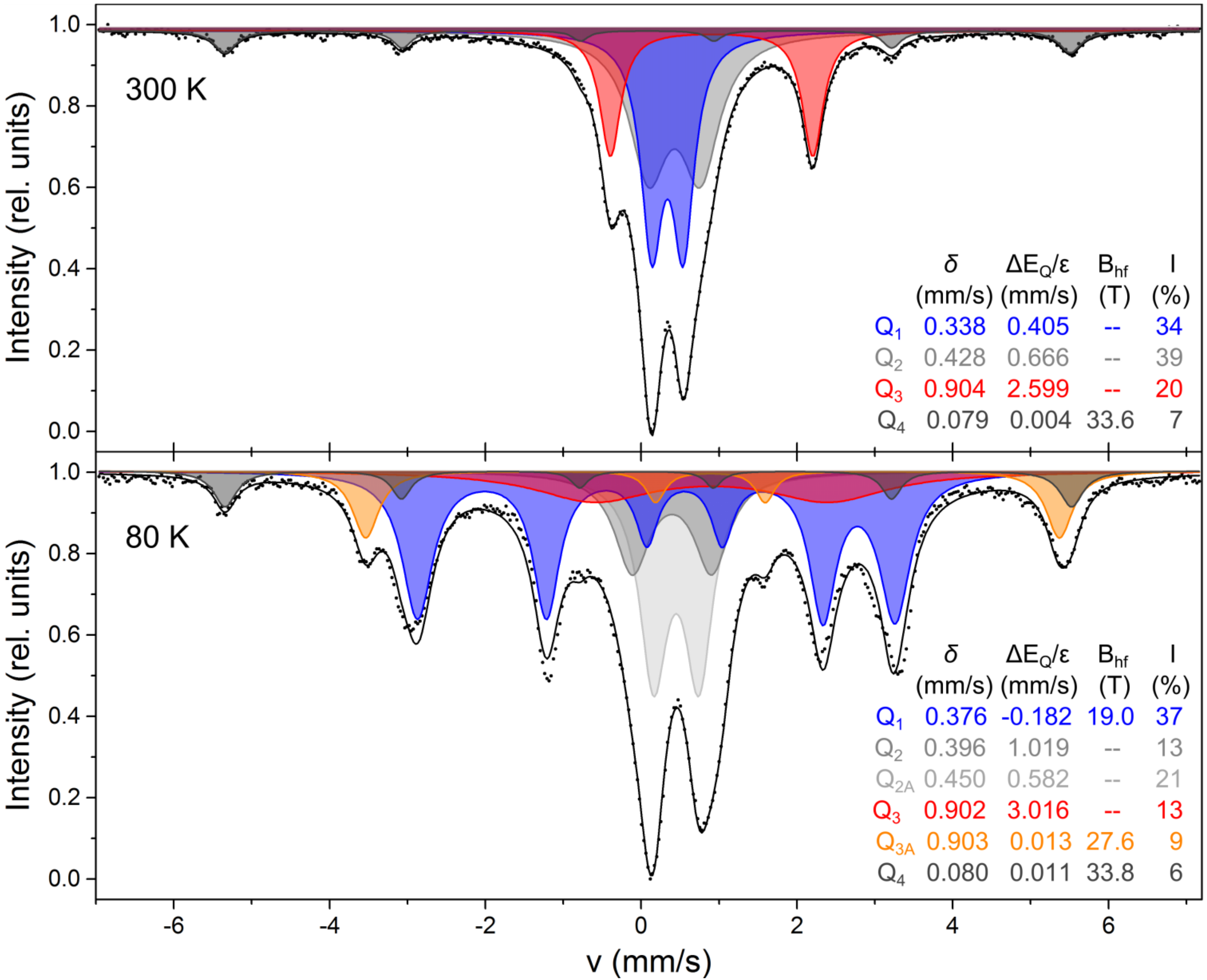


Figure SI 2. Scanning electron microscope (SEM) images (top) and energy-dispersive X-ray (EDX) spectra (bottom) of $Fe_3Se_4(dien)_2$ (left) and $Fe_3Se_4(tren)$ (right), collected with an accelerating voltage of 20 kV. Only Fe, Se, and C were visible by EDX, though the precise elemental compositions could not be accurately determined due to sample degradation caused by the electron beam.



	δ (mm/s)	$\Delta E_Q/\varepsilon$ (mm/s)	B_{hf} (T)	I (%)
Q_1	0.338	0.405	--	34
Q_2	0.428	0.666	--	39
Q_3	0.904	2.599	--	20
Q_4	0.079	0.004	33.6	7

	δ (mm/s)	$\Delta E_Q/\varepsilon$ (mm/s)	B_{hf} (T)	I (%)
Q_1	0.376	-0.182	19.0	37
Q_2	0.396	1.019	--	13
Q_{2A}	0.450	0.582	--	21
Q_3	0.902	3.016	--	13
Q_{3A}	0.903	0.013	27.6	9
Q_4	0.080	0.011	33.8	6

Figure SI 3. ^{57}Fe Mössbauer spectra for Fe_3Se_4(tren) collected at 300 K (top) and 80 K (bottom). Experimental data: black circles; calculated spectra: black lines; Fe_3Se_4(tren) component spectra: blue, red, and orange lines; impurity phases: gray lines. Spectra were collected using a conventional constant-acceleration spectrometer employing a ^{57}Co/Rh source held at room temperature. Least-squares refinement was performed using the software Recoil.[2] The room-temperature spectrum can be described by four components, including three doublets and one sextet: Q_1 and Q_2 have centroid shifts (δ) characteristic of Fe^{3+}, Q_3 corresponds to Fe^{2+}, and Q_4 is a magnetically-split signal from an elemental iron impurity with an intensity of 7%. Q_2 had a much higher linewindth compared to Q_1 and Q_3. Based on the ratio of the intensities of Q_1 to Q_3 we can assign Q_1 to the Fe^{3+} in the $FeSe_2$ chains and Q_3 to the Fe^{2+} in the Fe(tren) complexes, while Q_2 corresponds to the Fe^{3+} in an unidentified impurity phase that remains non-magnetic at low temperature. The 80 K spectrum is more complex, and must be described by six components, including three doublets and three sextets. The signal from elemental iron (Q_4) remained unchanged, while Q_2 split into two similar doublets, Q_2 and Q_{2A}. The Fe^{3+} in the $FeSe_2$ chains (Q_1) underwent complete magnetic ordering, appearing as a sextet with a hyperfine field (B_{hf}) of 19.0 T. The Fe^{2+} in the Fe(tren) complex underwent partial magnetic ordering, evidenced by the decrease in intensity and broadening of Q_3 and the formation of the sextet Q_{3A} with B_{hf} = 27.6 T. As none of the impurity phases ordered between 300 K and 80 K, these spectra confirm that the magnetic ordering observed by SQUID magnetometry occurs entirely in the Fe_3Se_4(tren) phase, and that the strongest interactions are between the Fe^{3+} in the $FeSe_2$ chains, with weaker interactions observed in the Fe^{2+} in the Fe(tren) complexes.

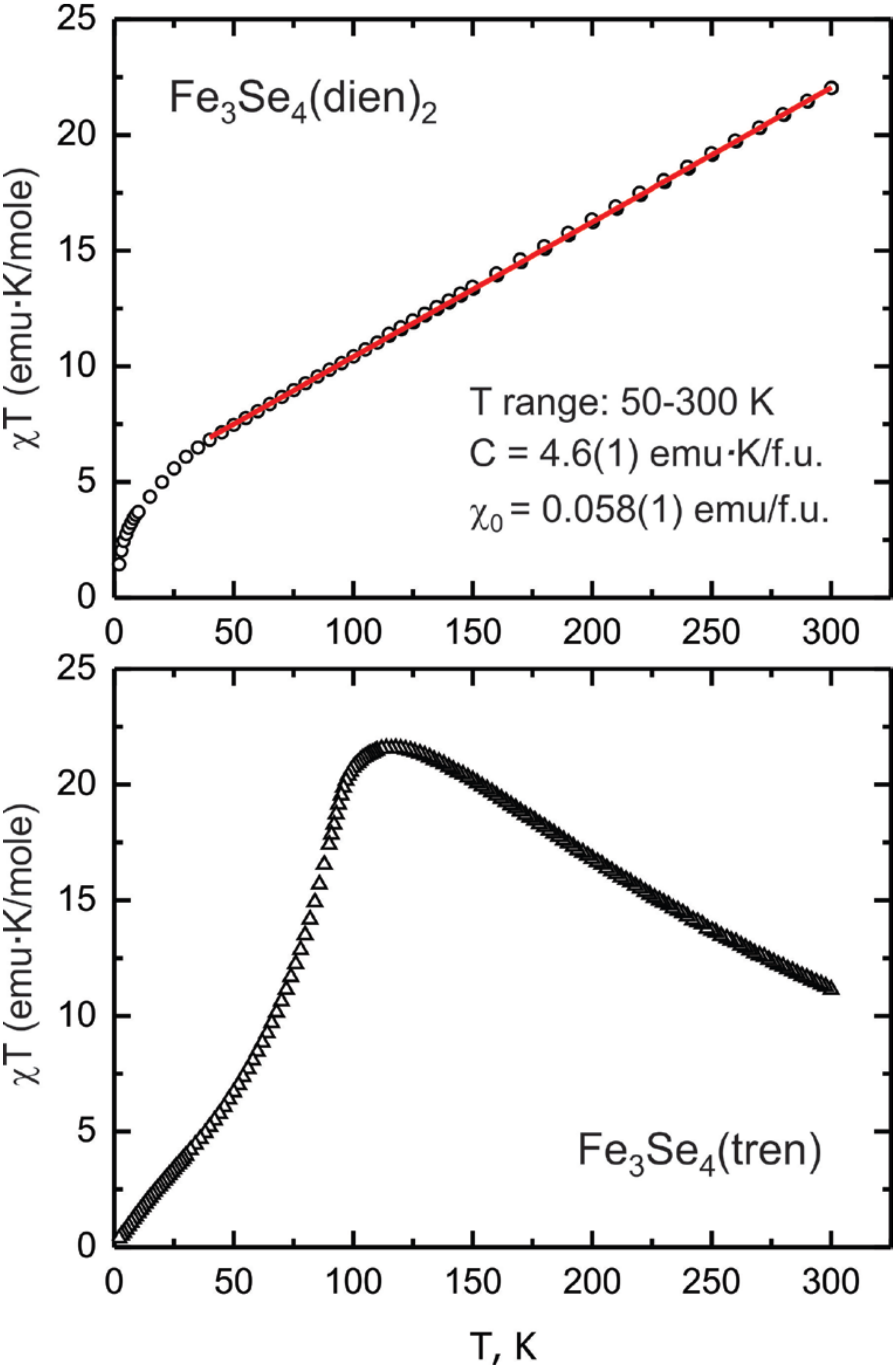


Figure SI 4. Temperature dependences of χT for $Fe_3Se_4(dien)_2$ (top) and $Fe_3Se_4(tren)$ (bottom) in an applied field of 10 mT. A temperature-independent contribution, χ_0, for $Fe_3Se_4(dien)_2$ was estimated from the linear fit shown by the red line.

References

1. V. Petricek; M. Dusek; L. Palatinus. *Z. Kristallogr.* **2014**, *229*, 345.
2. K. Lagarec; D. C. Rancourt. *Recoil, Mössbauer Spectral Analysis Software for Windows, Version 1.0;* Department of Physics, University of Ottawa: Canada, **1998**.