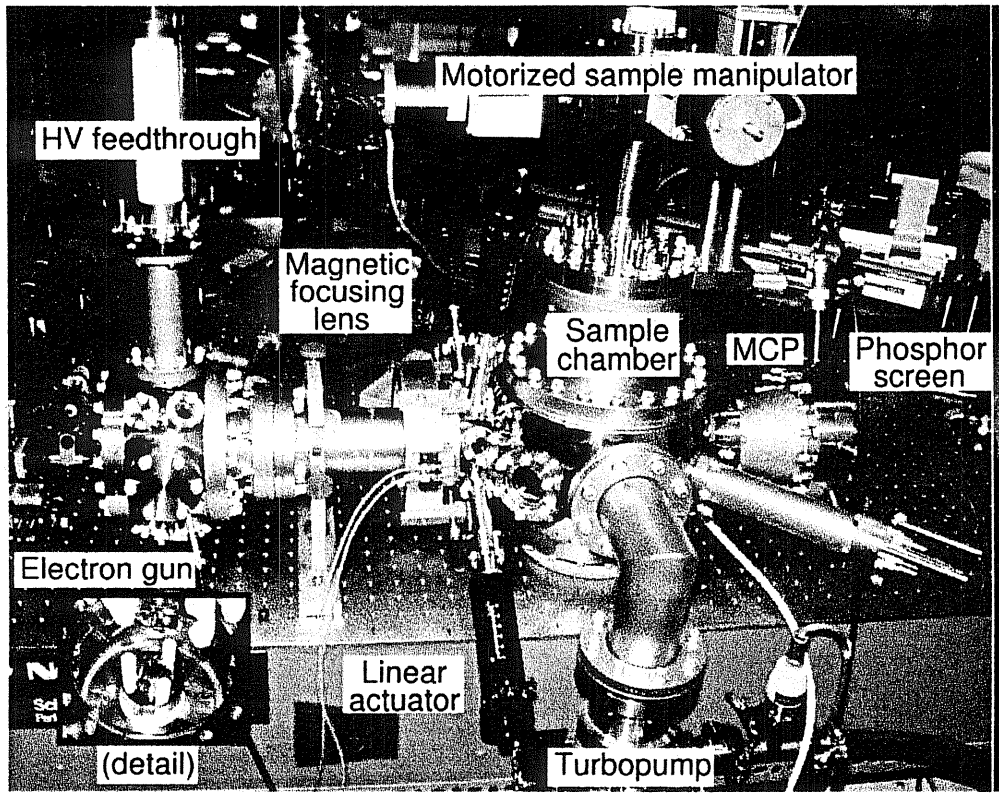
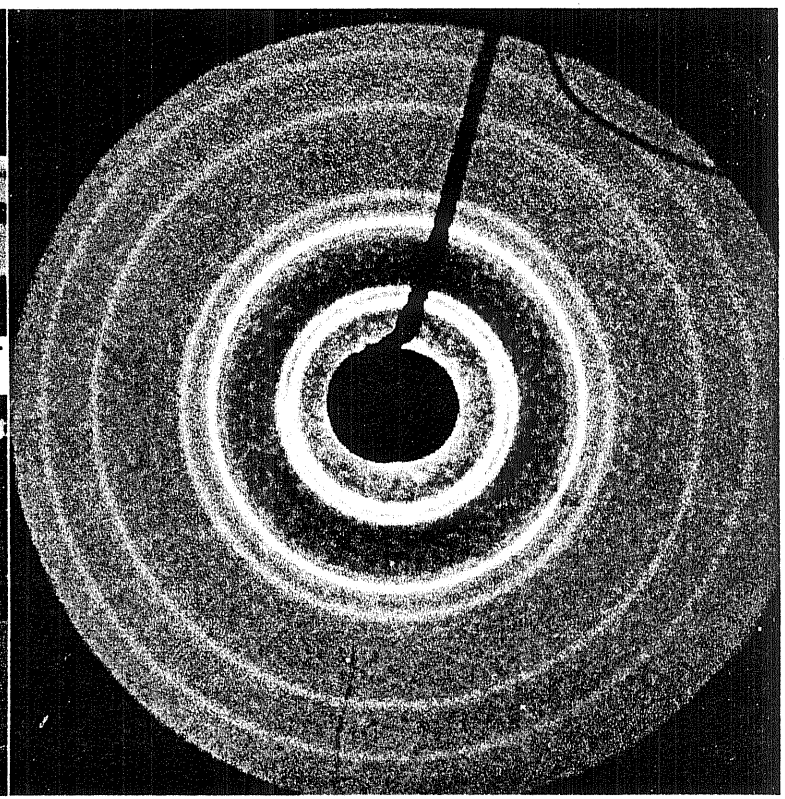
Femtosecond Electron Diffraction: Making the Molecular Movie





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Acknowledgements

- Bradley J. Siwick
- Jason R. Dwyer
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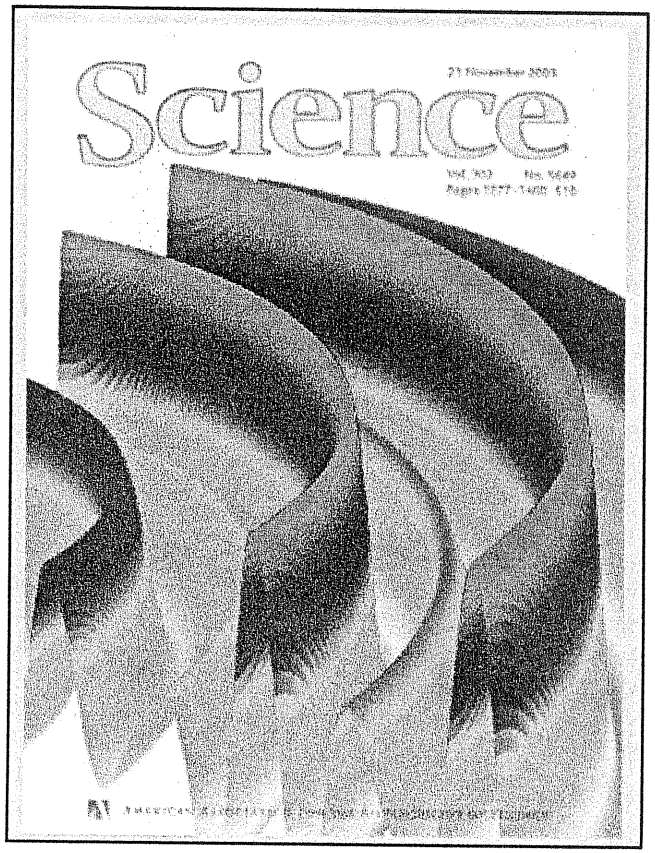
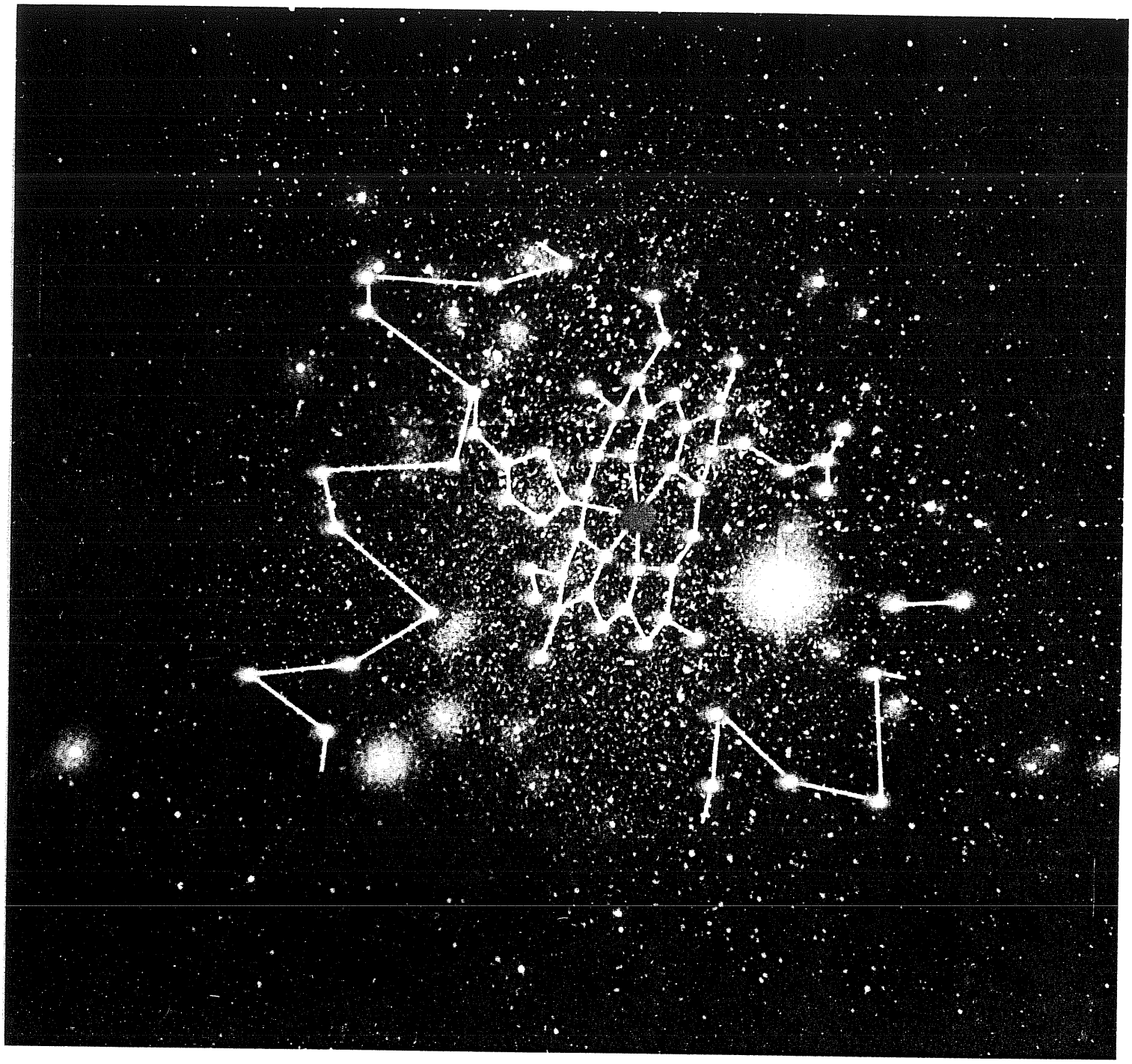
Canada Foundation for Innovation
Fondation canadienne pour l'innovation

Making the Molecular Movie ...First Frames



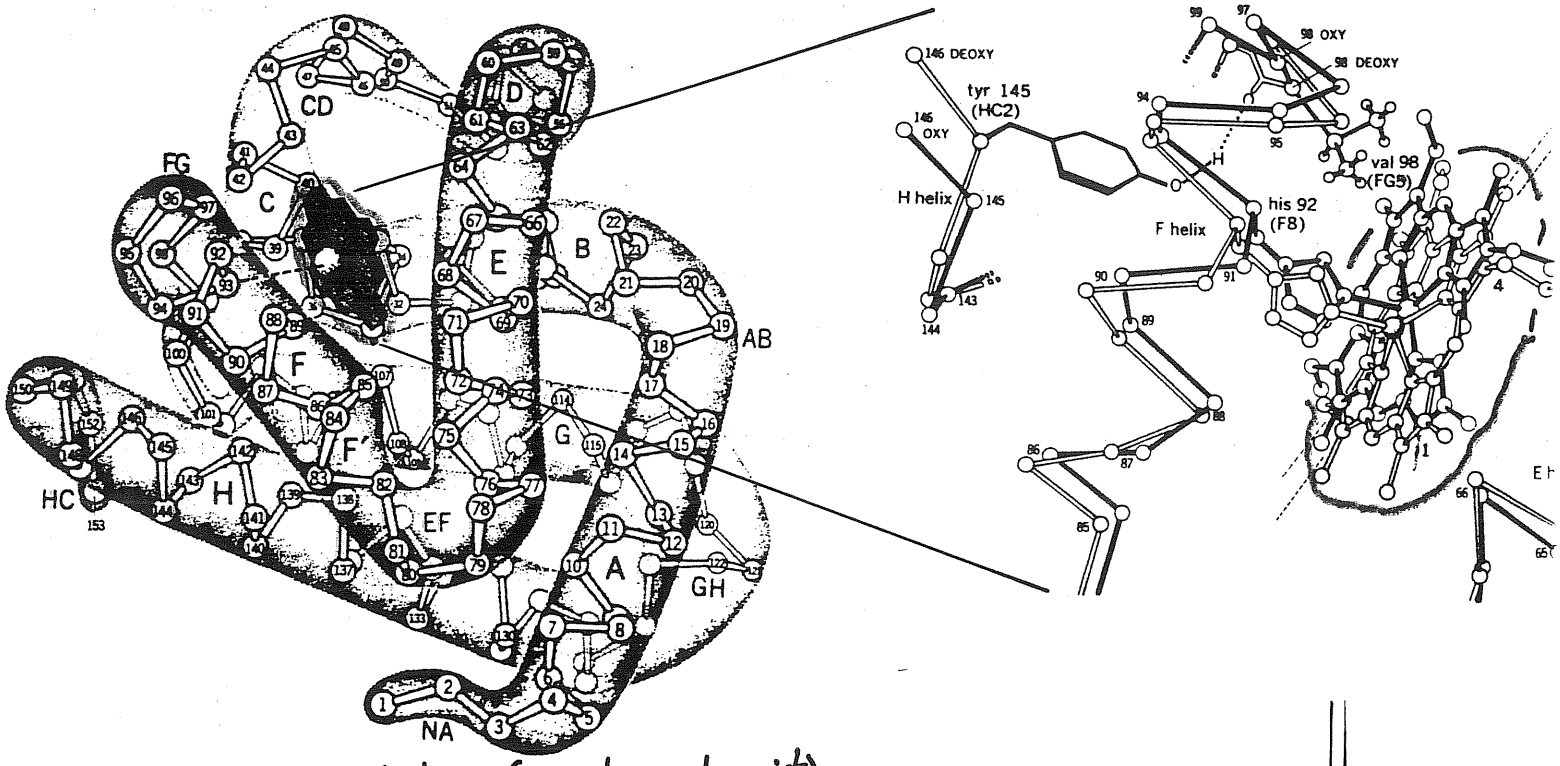
B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. D. Miller, "An Atomic-Level View of Melting Using Femtosecond Electron Diffraction," *Science* 2003 November 21; 302: 1382-1385.

Mother Nature and the Molecular Big Bang

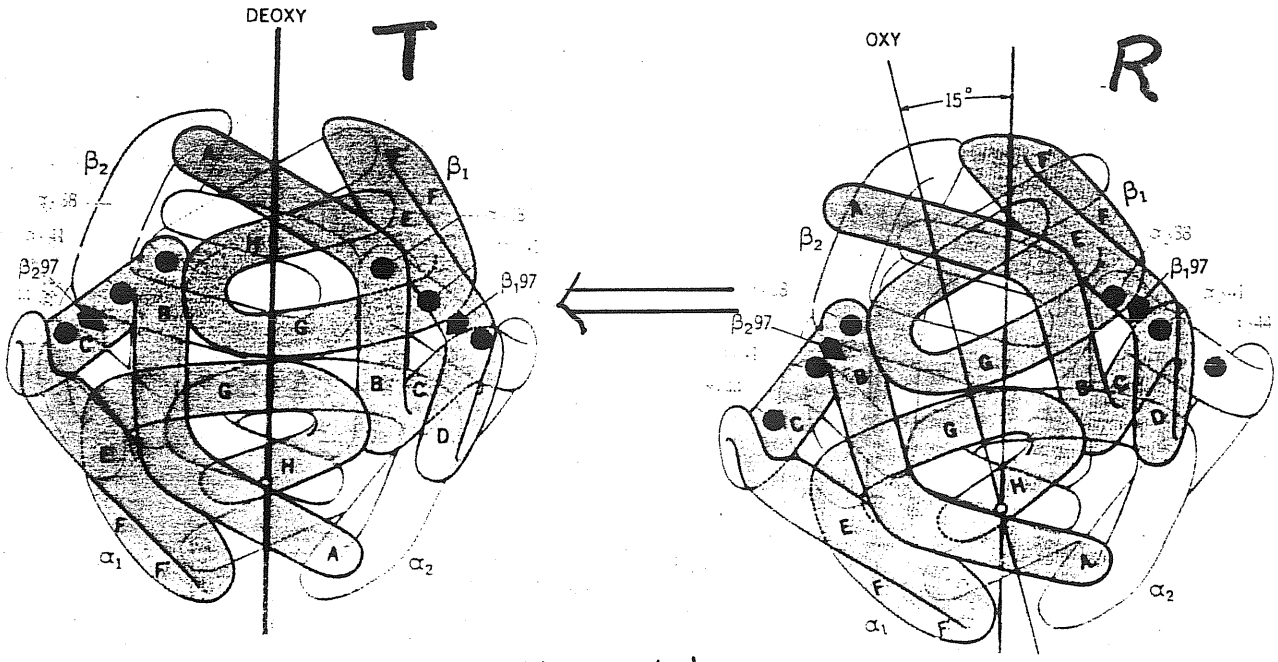


The "Molecular Dance":

Functionally Important Protein Motions



Myoglobin (single subunit)



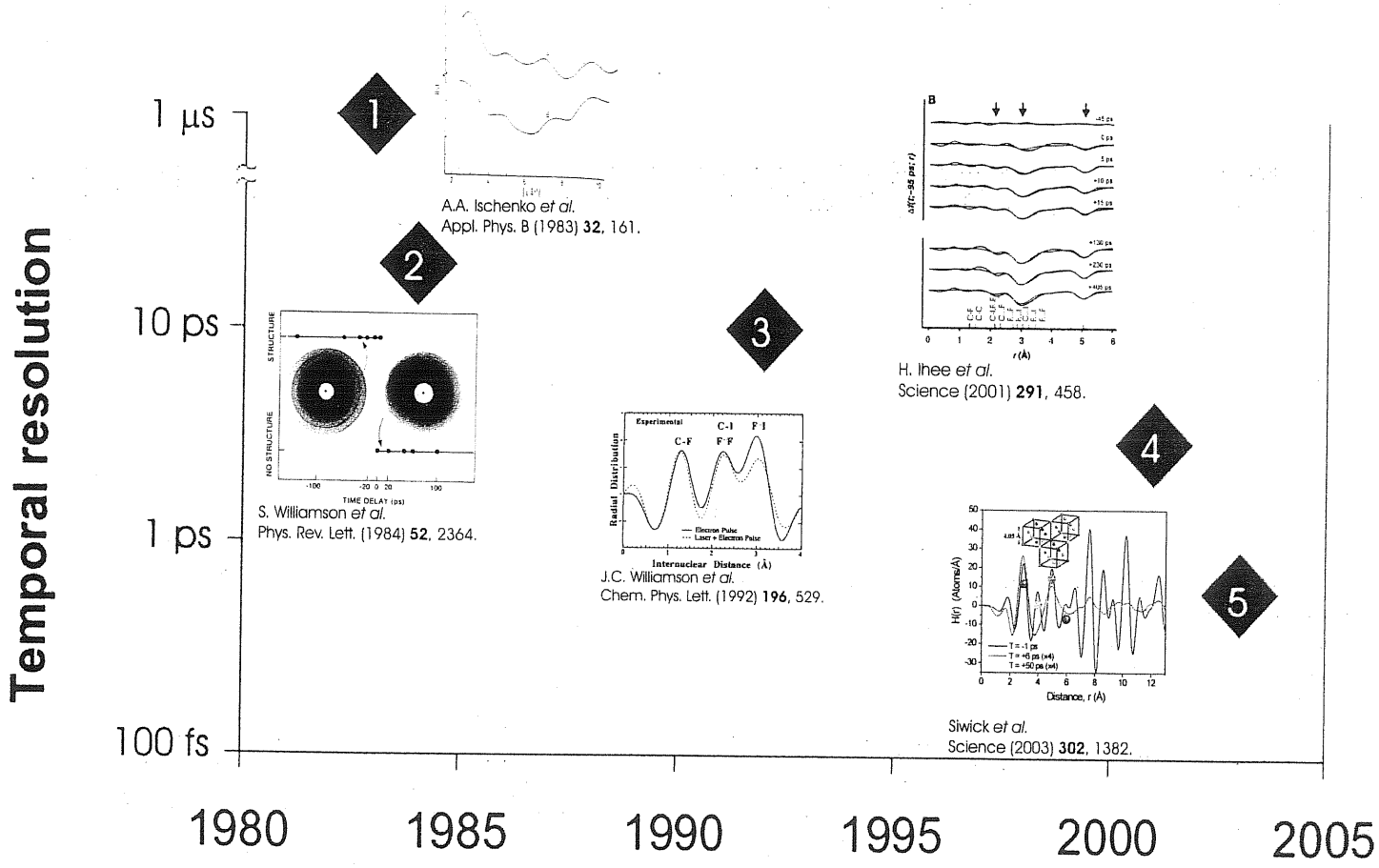
Hemoglobin

What is the mechanism of correlated atomic displacements?

Introduction and Motivation

- Time-resolved electron diffraction harbours great promise for resolving the fastest chemical processes with atomic level structural detail (i.e. molecular movies).
- The main obstacles hindering femtosecond (fs) temporal resolution in these experiments are associated with delivering fs electron pulses with sufficient current density (100 mA/mm^2 or more) to the sample. Space-charge effects (Coulomb repulsion) act to broaden the electron pulse as it propagates.
- To determine an optimal configuration for femtosecond electron sources it is necessary to have a complete quantitative understanding of the propagation dynamics of fs photoelectron pulses, so models were developed.
- The results of the modeling were used to design a photo-activated electron gun capable of generating sub-500 fs electron pulses containing number densities sufficient for structure determinations with ~100 shots. Studies with this new instrument have focused on strongly driven solid-liquid phase transitions in polycrystalline aluminum as a model problem.

Progression of time-resolved electron diffraction



Electrons vs. X-rays

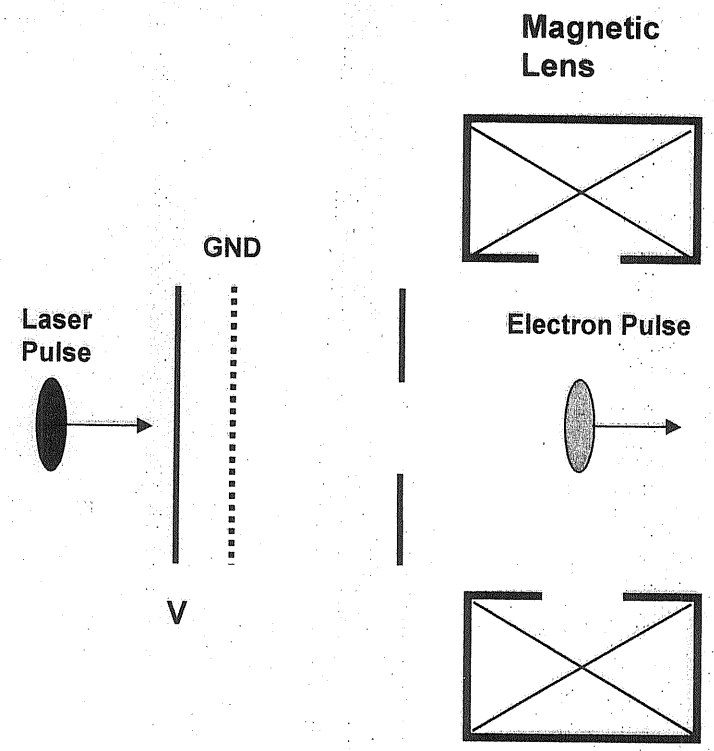
Electrons	X-rays
• Strongly scattered	• Weakly scattered
• Table top experiment	• Synchrotron based
• Pumped volume better matches scattering length	• Pulse duration independent of photon number
• Energy deposited in sample per scattering event 400-1000 times less (1.5 A x-rays)	• Potential for Laue diffraction
* • Incoherent	• Coherent

* Coherent e-wavepackets possible
Watche Dormisian, J. Sipe + R.D. Mille ..... in progres

Modeling of Propagation Dynamics

The influence of space-charge on the propagation dynamics of fs electron packets through a photoactivated electron gun (right) was investigated with:

- Classical N-body simulation
  - Numerical simulation of the full N-electron equations of motion using a Barnes-Hut tree algorithm.
- Mean Field Model
  - Approximate potential of electron packet as a disk of charge to generate the pulse length equation:



$$\frac{d^2 l}{dt^2} = \frac{Ne^2}{m\varepsilon_o \pi r^2}\left[1 - \frac{l}{\sqrt{l^2 + 4r^2}}\right]$$

l = pulse length, t = propagation time, N = number of electrons, r = electron beam radius,

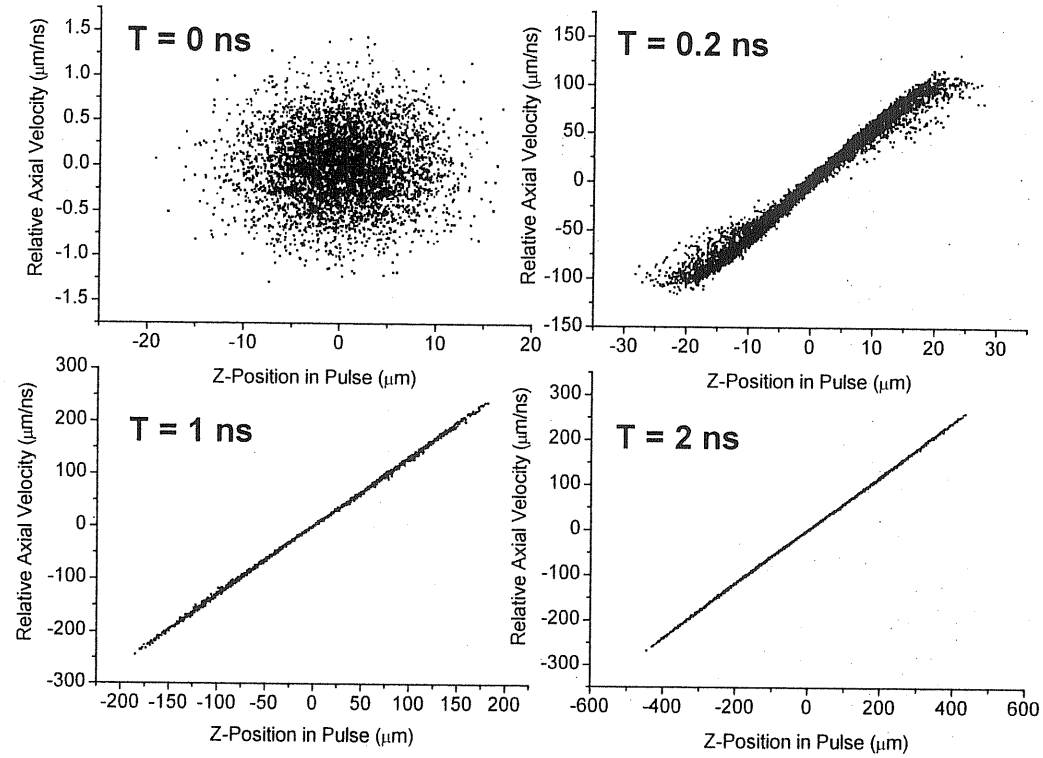
B. Siwick et al. J. Appl. Phys. 2002

Velocity (or Kinetic Energy) Chirp

- Vacuum is dispersive for electrons:

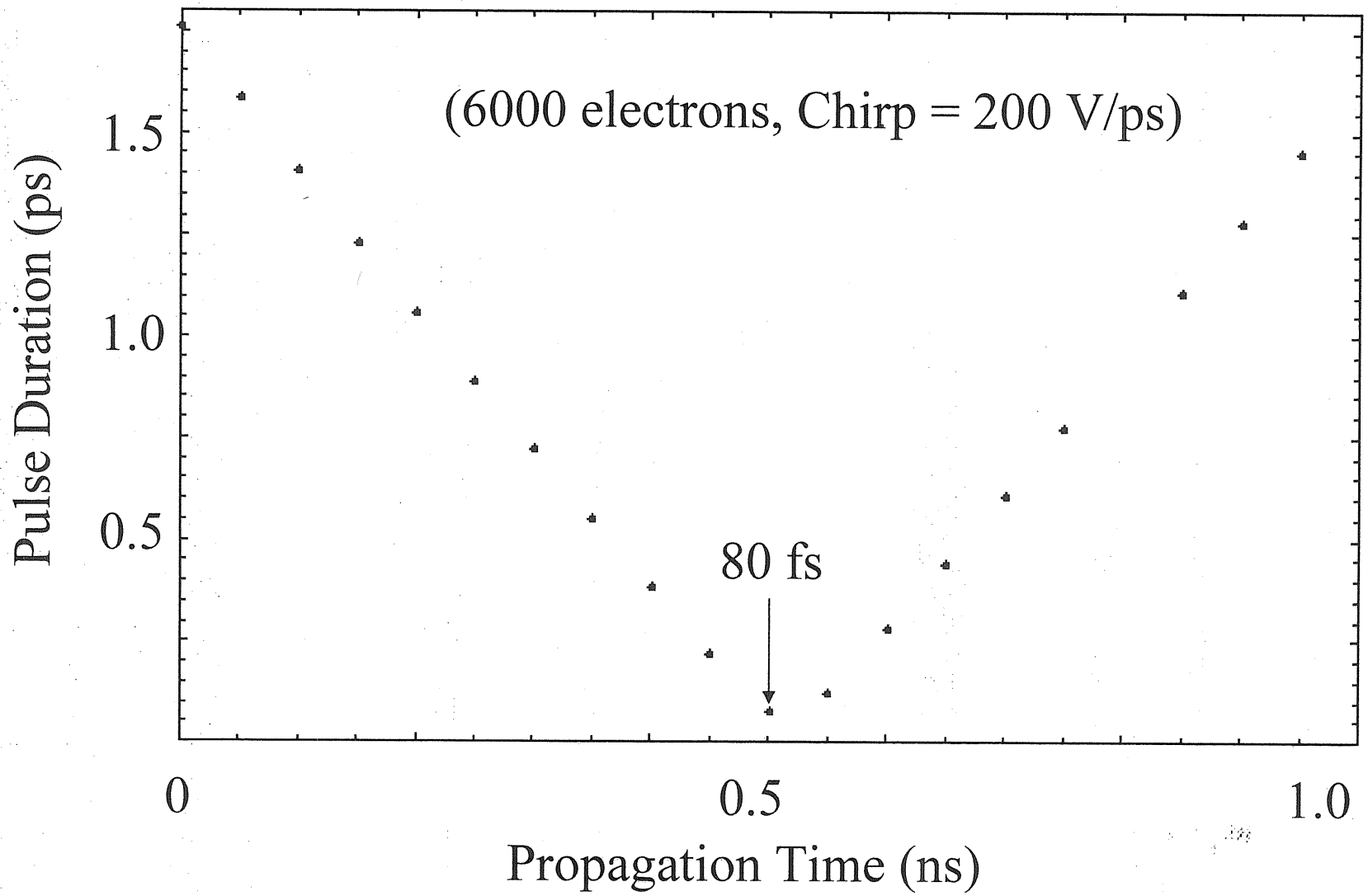
$$v = \sqrt{2E_k / m}$$

- The spatial distribution of velocities evolves as the pulse lengthens.
- Electrons redistribute inside the packet to produce a linear velocity chirp.
- The dynamical time-scale is related to the potential energy of the initial charge distribution (pulse).



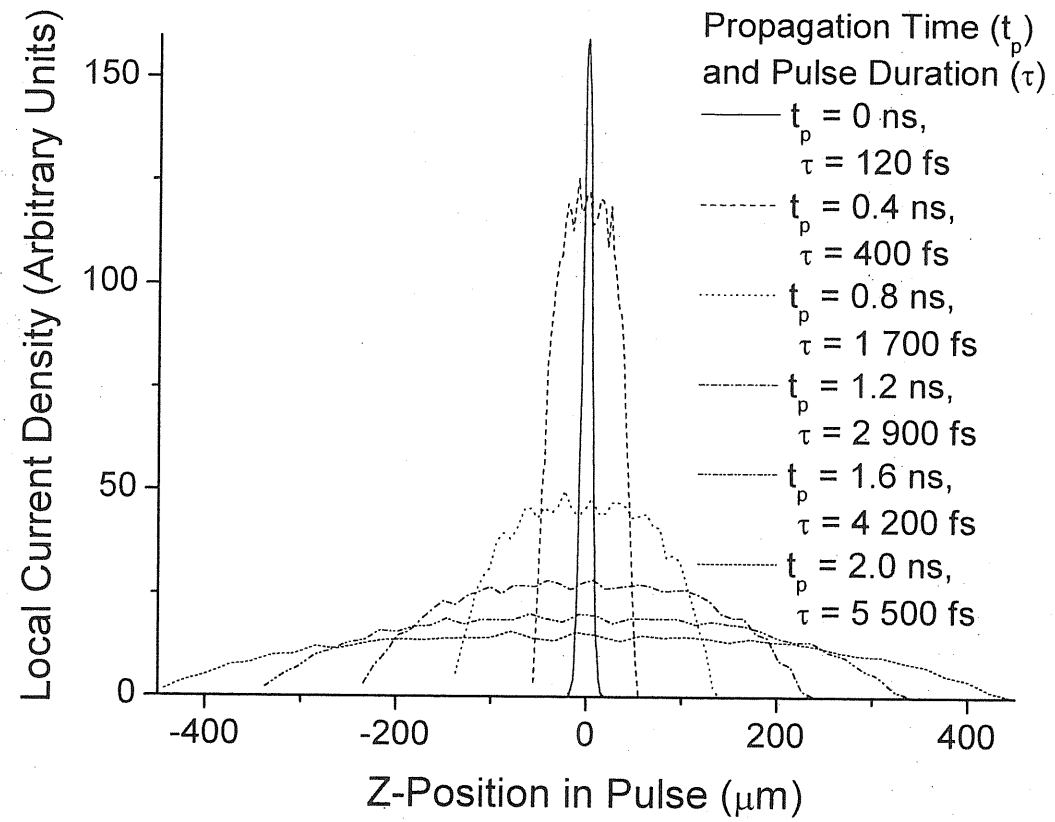
Axial velocity (Vz) vs. axial position (Z) for all electrons in the pulse at four times (T) during its propagation (N = 10 000, τo = 150 fs, r(0) = 75 μm, 1.5 mrad initial beam divergence).

Electron Pulse Compression via Pre-Chirping



Pulse Envelope Dynamics

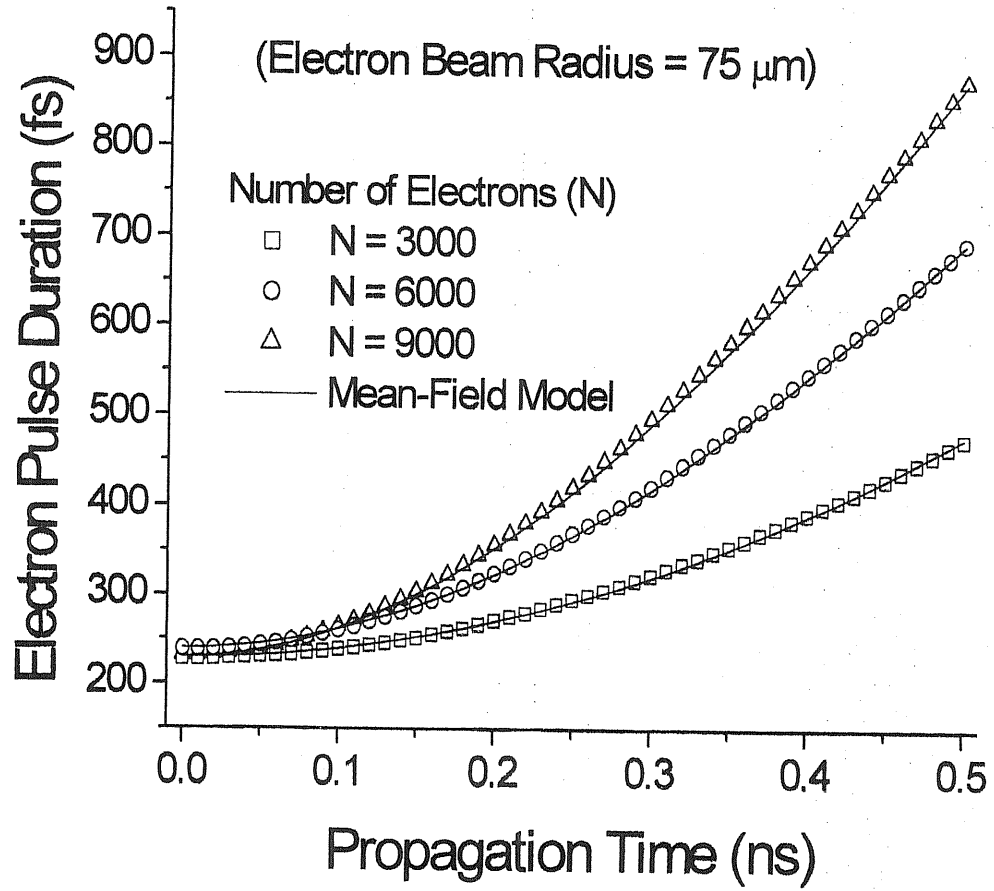
- The N-body simulation shows that the initial Gaussian profile becomes more "flat-topped" as the temporal duration of the pulse increases with propagation time.



Dynamics of the axial pulse envelope during 2 ns of propagation (N = 10 000, τo = 120 fs, r(0) = 75 μm, 1.5 mrad initial beam divergence. 100 μm = 1ps for 28.4 keV electrons). The initial envelope (τp = 0) has been divided by 5 to fit on this scale. The peak of this envelope is actually 797 in these units.

Temporal Broadening

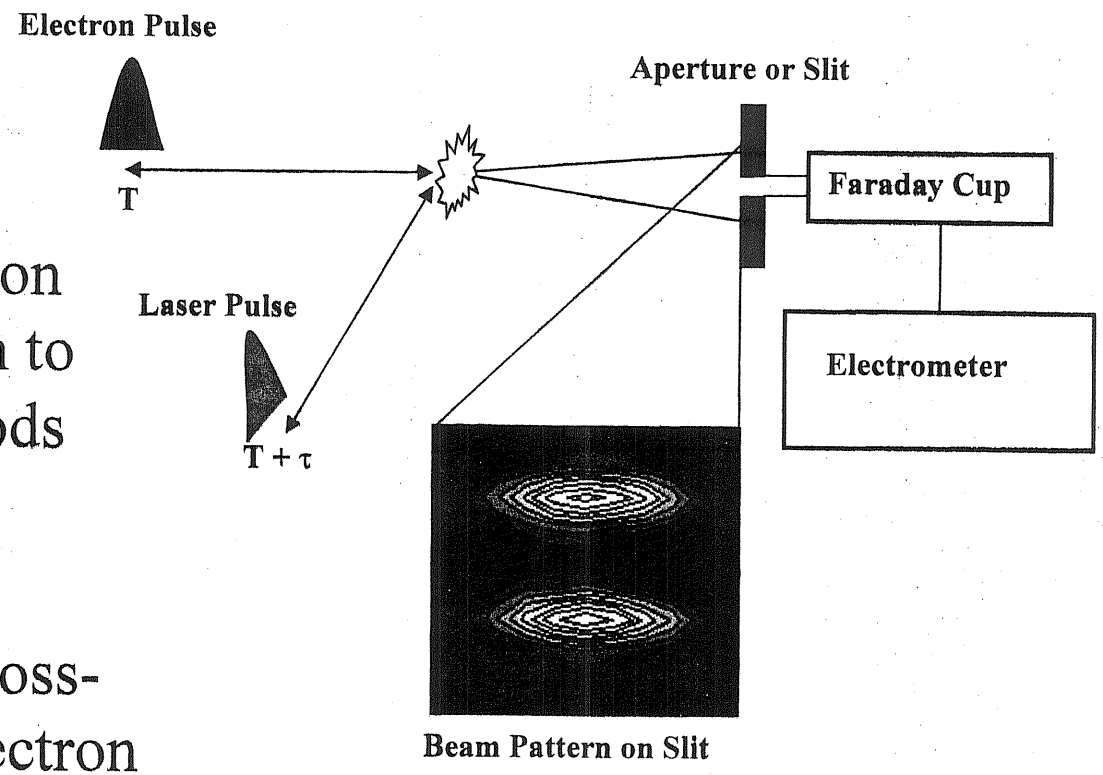
- Approximately quadratic time-dependent pulse broadening at early times.
- Rate of pulse broadening levels off as the charge distribution spreads out in time.
- If propagation time is kept below 0.5 ns, sub-picosecond electron pulses containing 10^4-10^5 electrons and beam diameters of several hundred microns are possible.



Electron pulse duration vs. propagation time and its dependence on N. The results of the N-body simulation are presented along with the predictions of the mean-field theory. These electron beam parameters match those used in the strongly-driven solid-liquid phase transition studies.

All-Optical Electron Pulse Duration Measurement I

- New approaches for electron pulse characterization, akin to the nonlinear optical methods used for laser pulses, are desirable.
- We propose a method to cross-correlate a femtosecond electron pulse with an intense laser pulse using the ponderomotive potential.



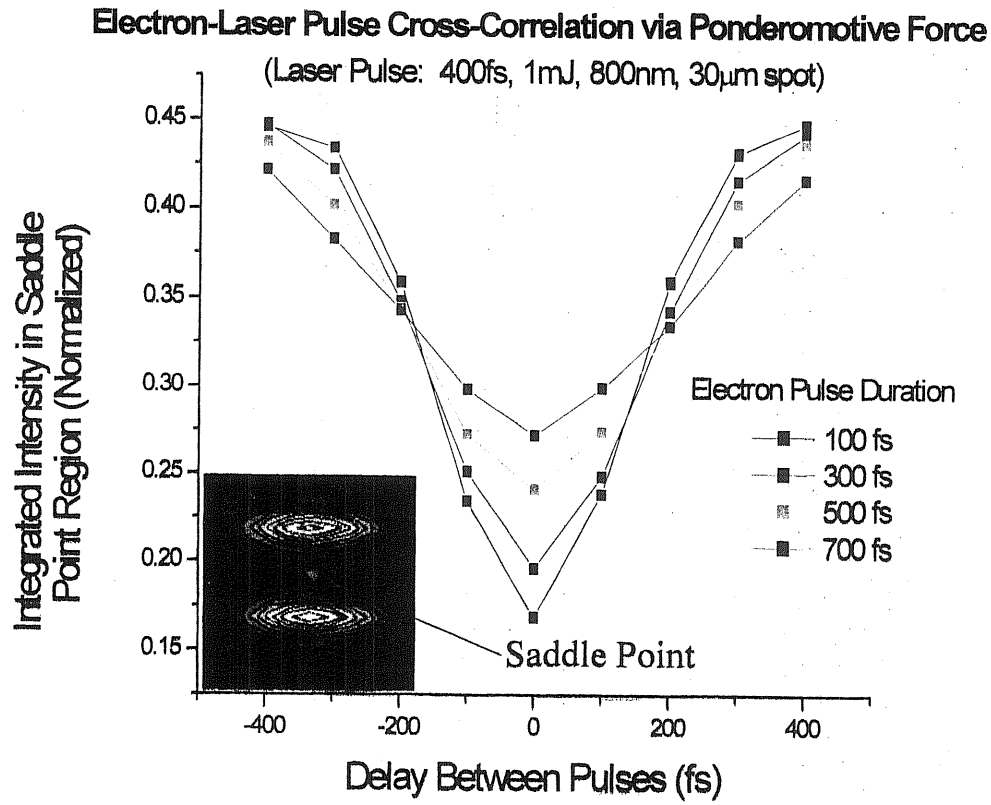
$$\vec{F}_{pond} = -\nabla U_{pond}$$

$$U_{pond} = (e^2\lambda^2 I)/(2\pi m c^3)$$

I = intensity , λ = wavelength, c = speed of light, e = electron charge, and m = electron rest mass.

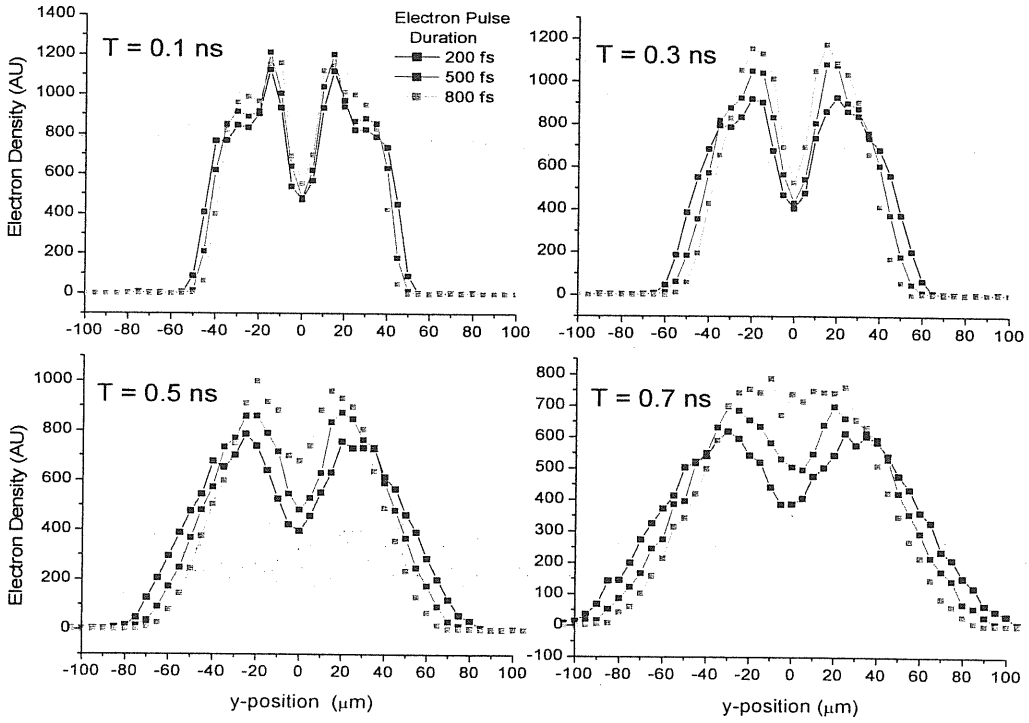
All-Optical Electron Pulse Duration Measurement II

- Monte-Carlo Simulation of ponderomotive interaction
- If a Gaussian electron pulse is intersected at 90° with a high intensity laser pulse the "far-field" beam pattern is no longer Gaussian.
- The height of the saddle point in the "far-field" pattern is sensitive to the delay between the laser and electron pulses and to the temporal duration of the two pulses.
- Transverse electron velocities (after the interaction) can be as high as 10 000 m/s for the simulated pulse parameters.



Using the ponderomotive interaction to perform an electron-laser pulse cross-correlation. By measuring the electron beam current through a slit (30 μm wide in the above simulation) centered on the unperturbed beam maximum, one has a sensitive measure of the pulse overlap. This can also be used to determine T = 0 in a femtosecond electron diffraction experiment.

All-optical electron pulse duration measurement



Electron beam profile perpendicular to the plane of interaction at four times, T, after the interaction with the laser pulse ponderomotive potential (N = 3000).

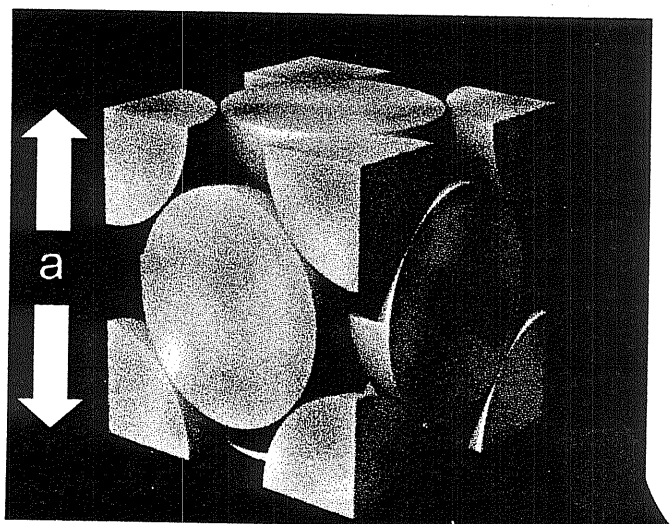
How does a solid melt on the ultrafast timescale?

Solid equilibrium structure

Monatomic fcc lattice, a=4.05Å

Liquid equilibrium structure

Radial density function shows liquid structure



http://www-solidstate.physik.uni-bremen.de/~ischnell/fcc/

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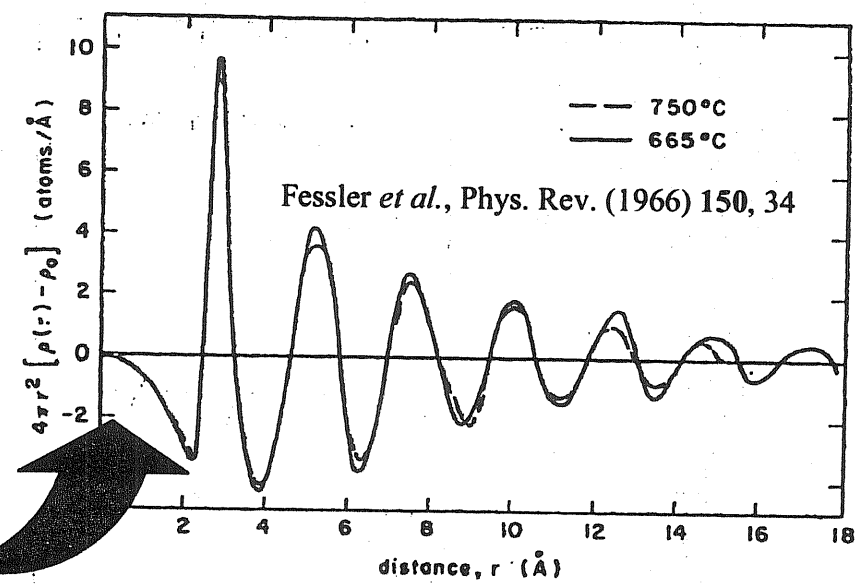
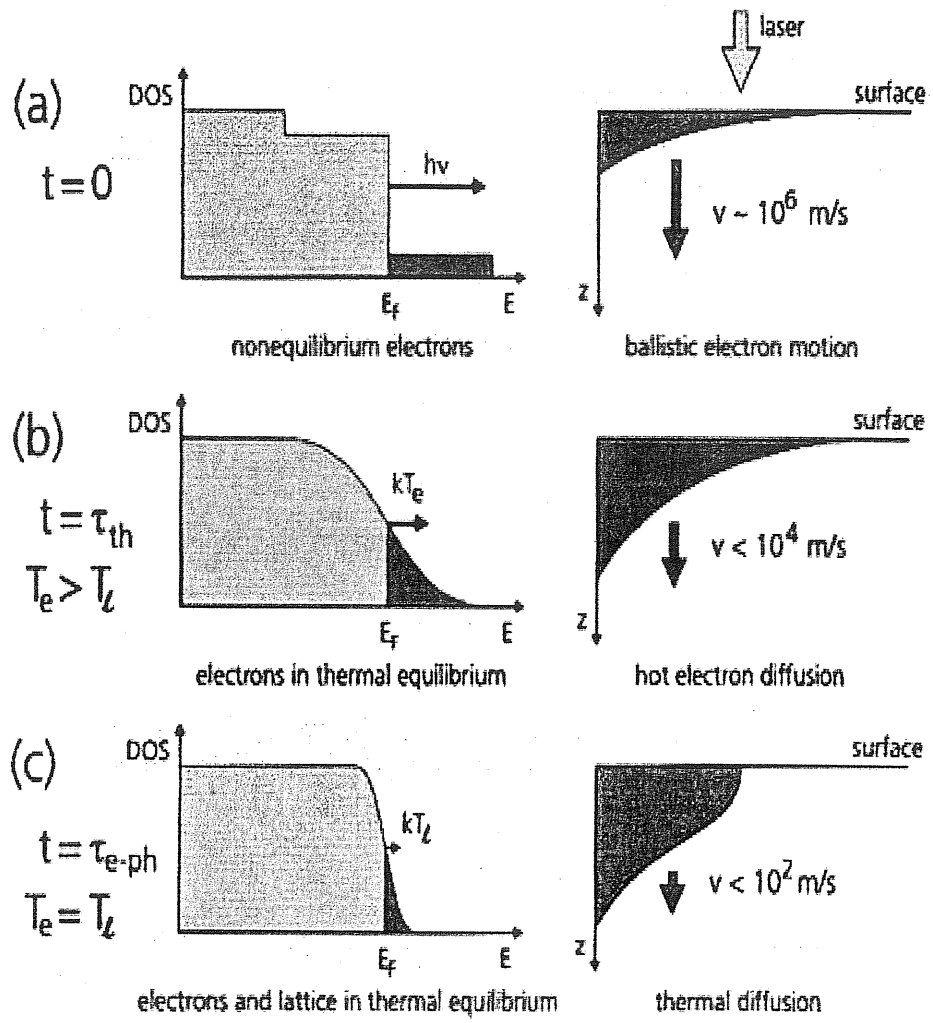


Need time-resolution!

Solid-Liquid Phase Transitions

Nonthermal Melting

Traditional Electron Relaxation (small perturbation limit) *

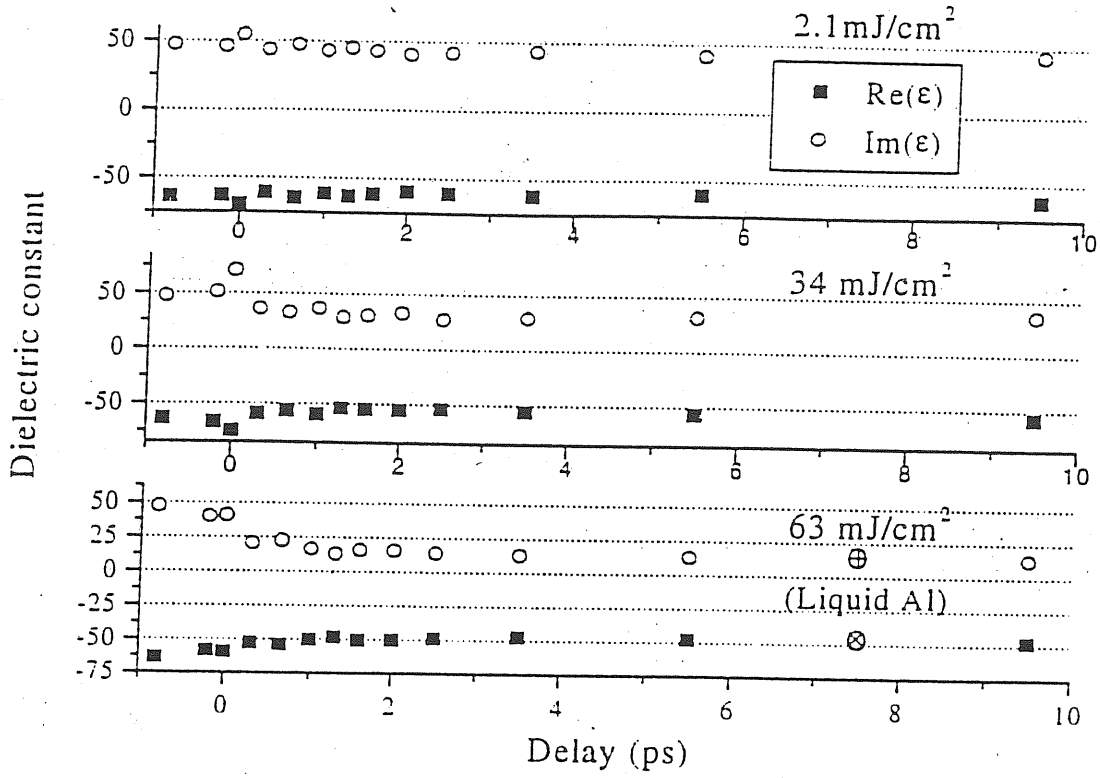


At high excited carrier densities the band structure is affected. More electrons are in anti/bonding orbitals and the lattice becomes "unbound".

Examples: Mazur et al. For GaAs (e(w,t)); Guo et al. For Al (e(w,t)); Wilson et al for Ge (laser x-ray diffraction)

*Hohlfield et al. Chem Phys., 251 237-258,(2000)

Evidence for Nonthermal Solid to Liquid Phase Transitions

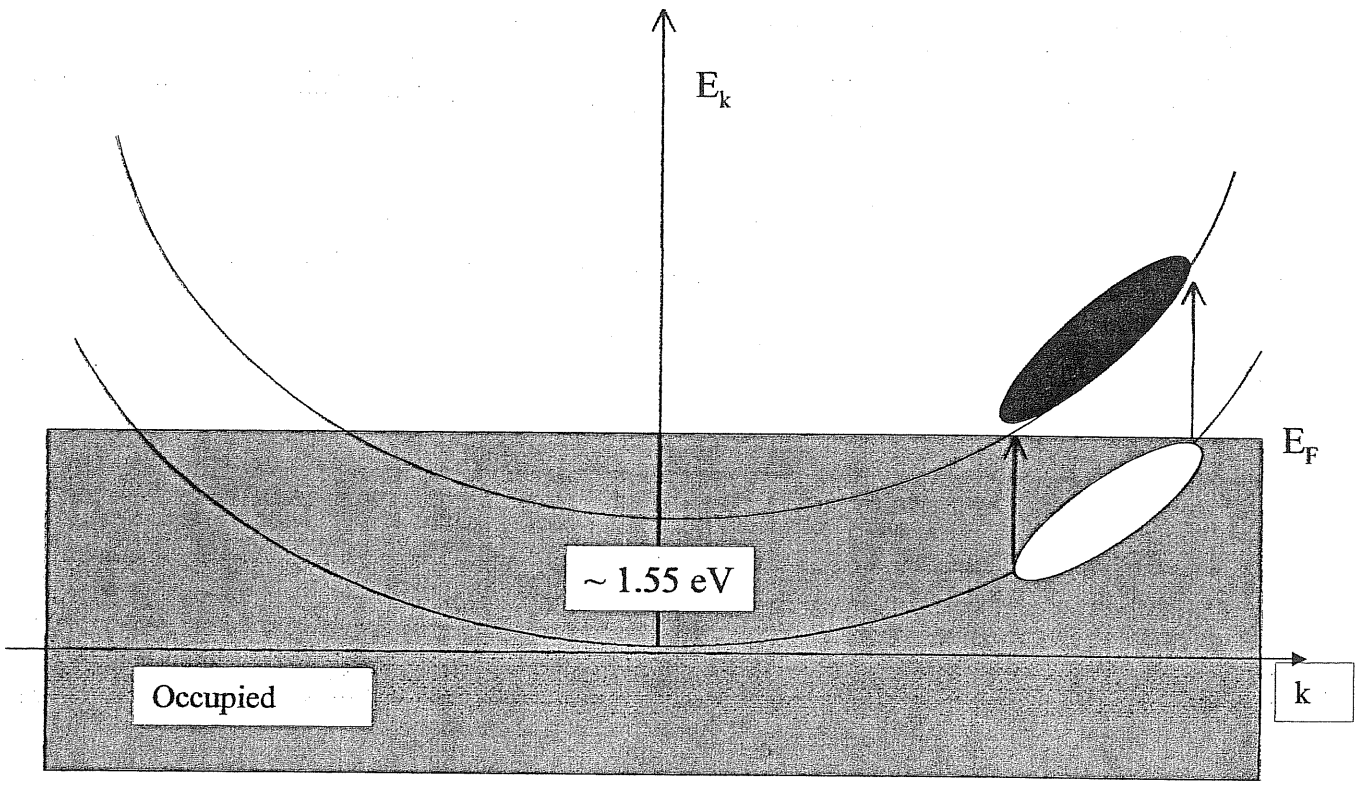


- Apparent melting (re: Im(ε) and Re(ε)) in less than 1 ps ⇒ too fast to be thermal (C. Guo *et al.* PRL 84(19) 4493, **2000**)

primary evidence from change in optical properties that correlated to liquid state (Al only one example of general phenomena) in less than thermalization time ….Approaching single period of optical phonon

Q: How does a solid undergo disorder transition and radial distribution function of liquid within ½ to 1 collisional period?

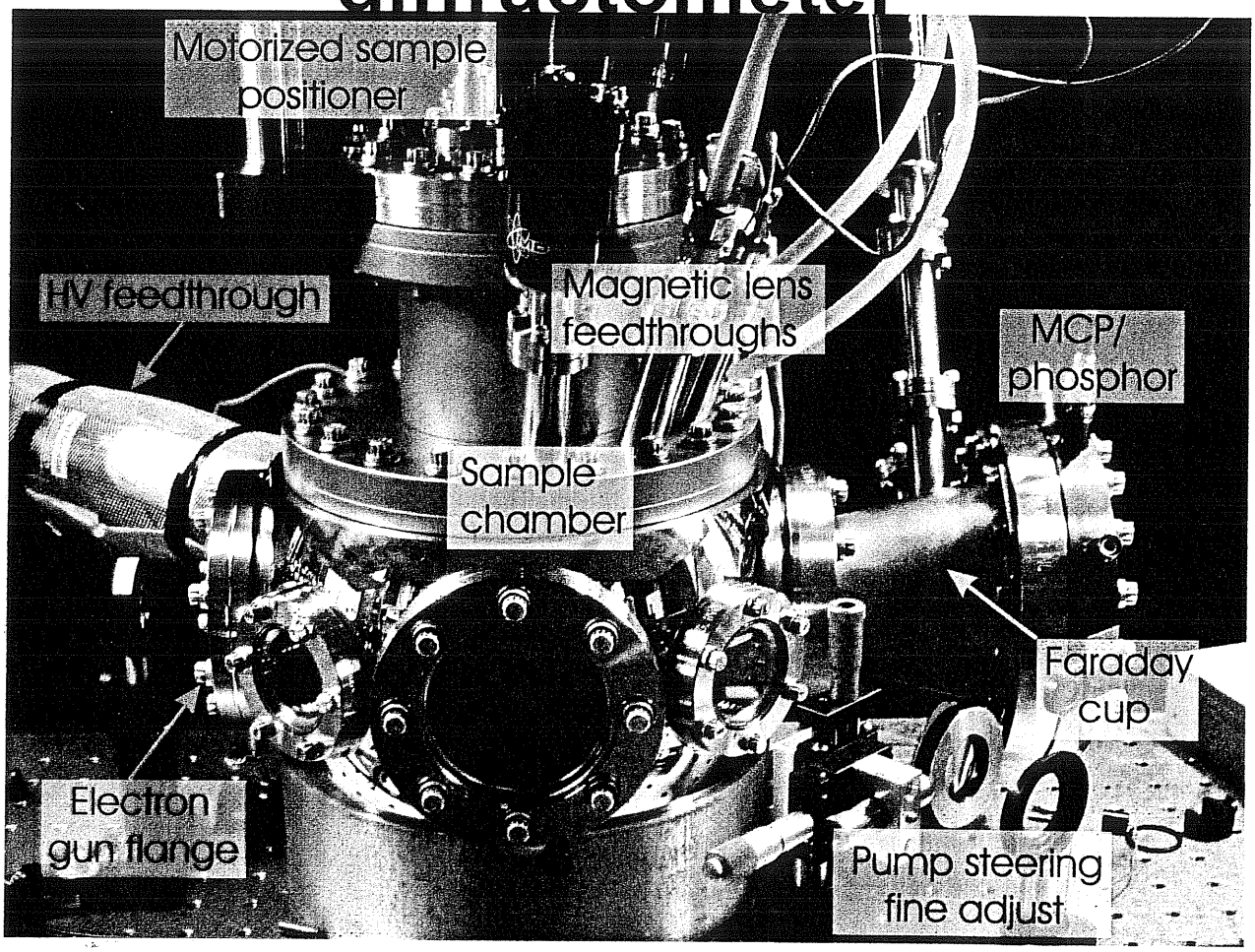
Interband excitation in Al



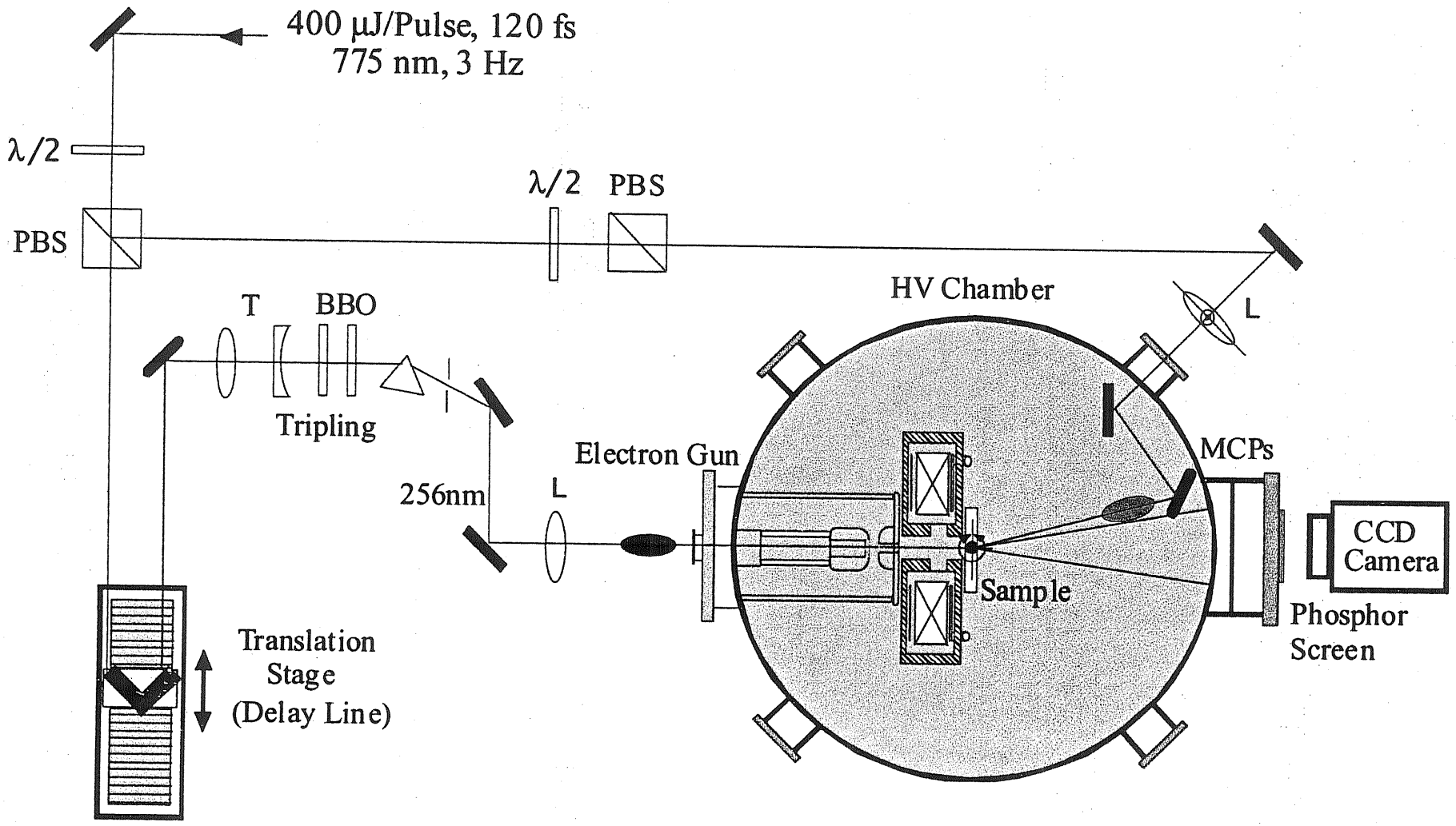
Parallel band structure of Al

Excitation of an estimated 15% of the electrons into the conduction band results in band structure collapse and a structural phase transition.

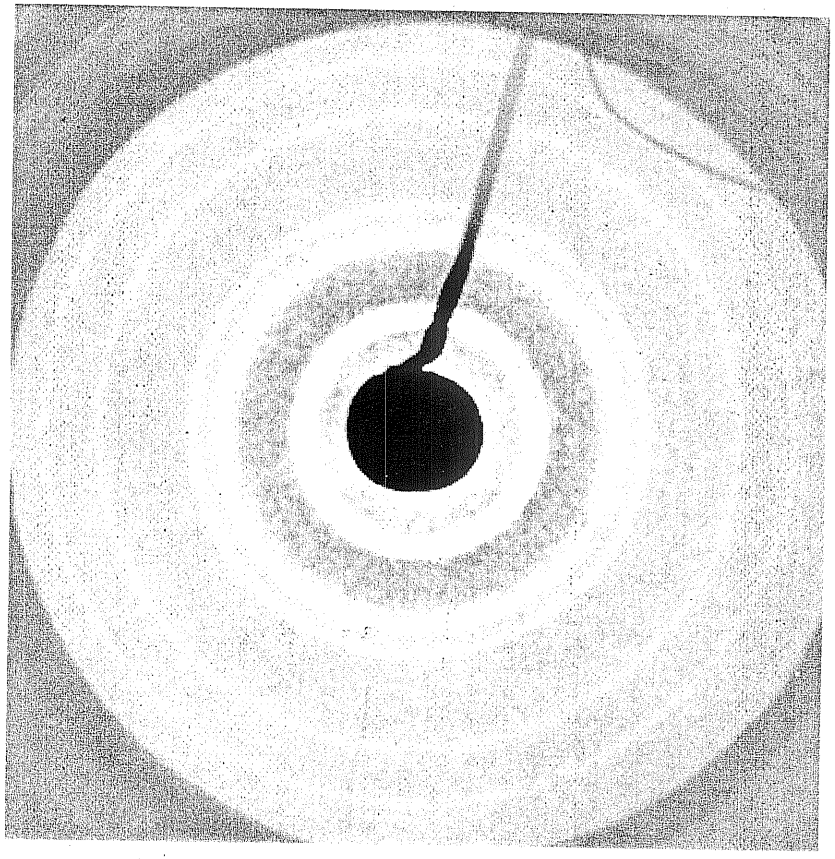
Femtosecond electron diffractometer

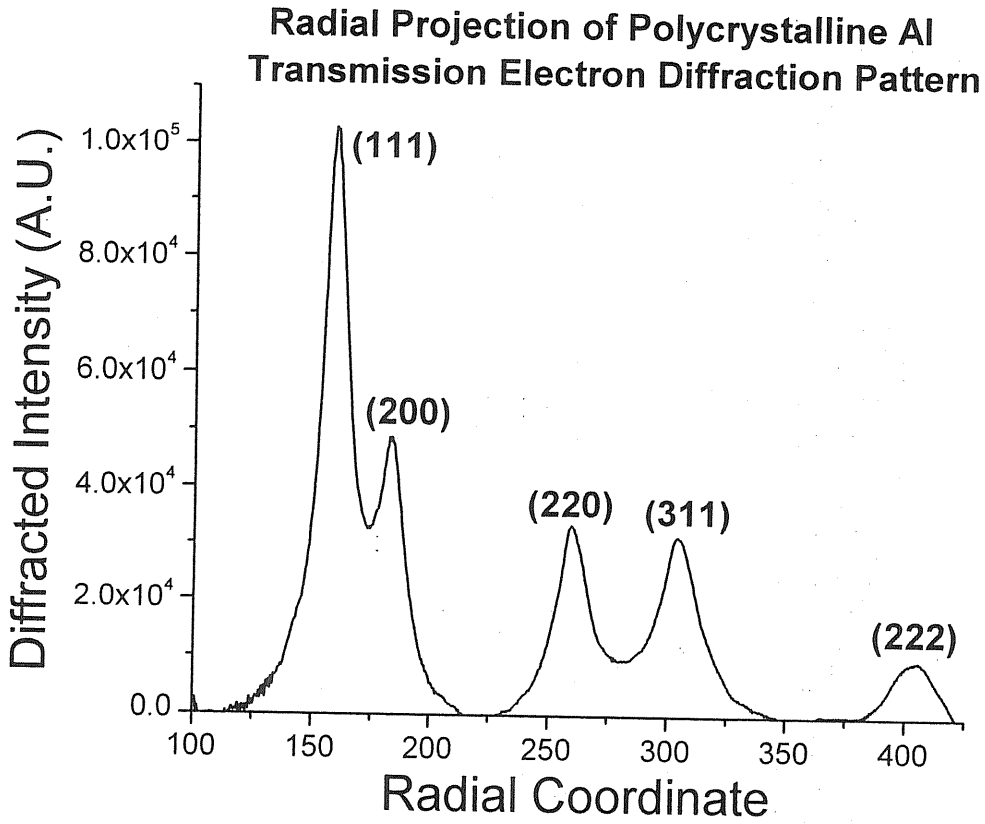


Femtosecond Electron Diffraction: Apparatus Schematic

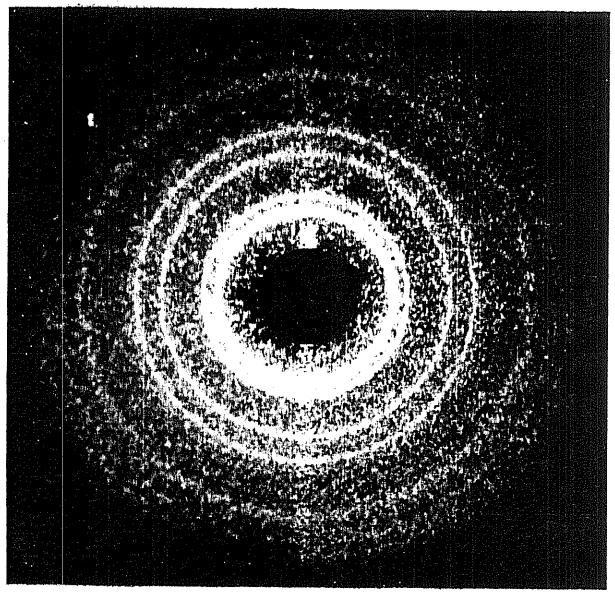


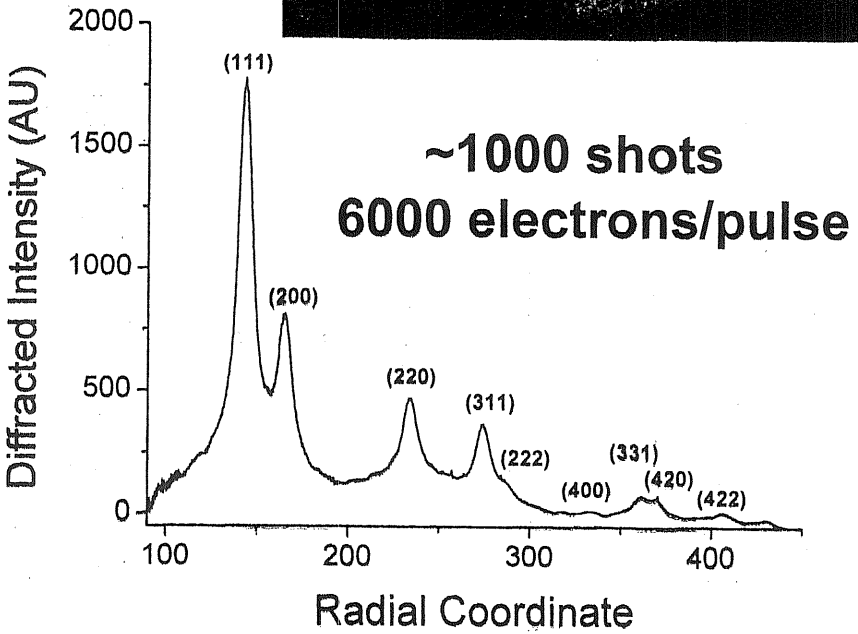
Femtosecond Electron Diffractometer: Polycrystalline Aluminum

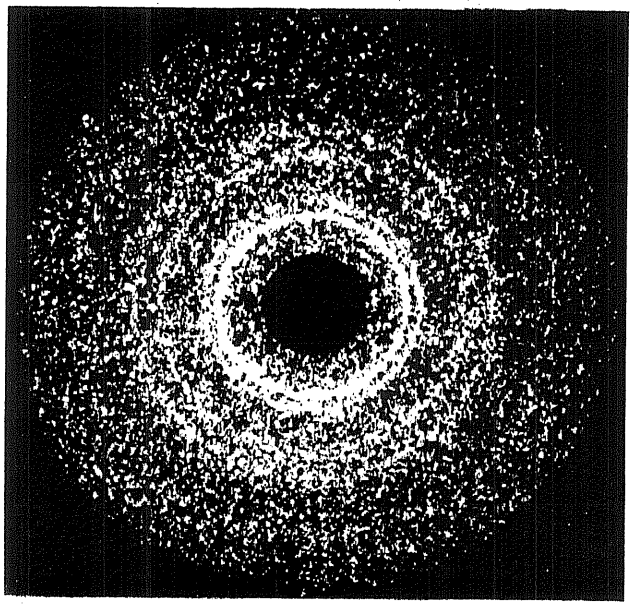


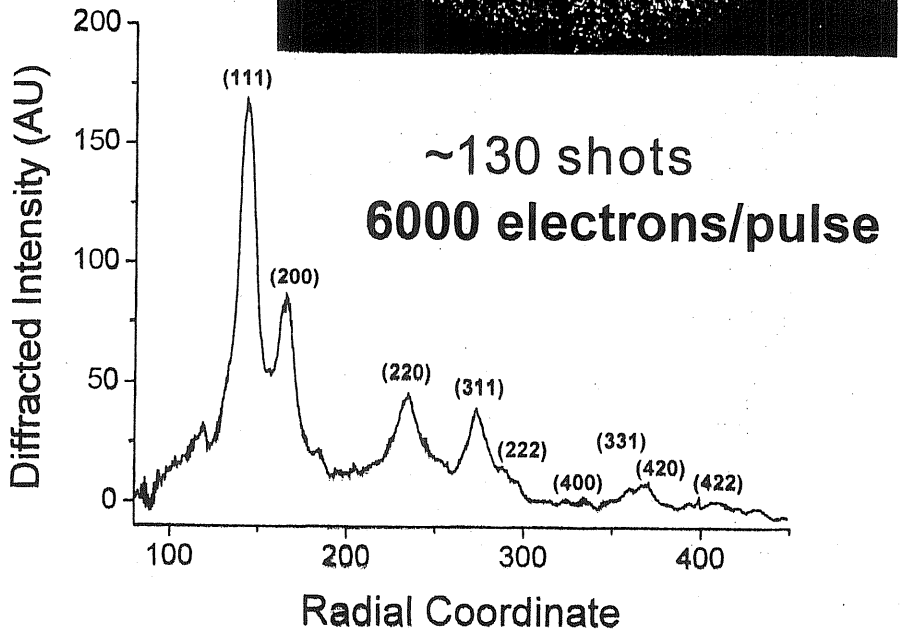


Polycrystalline Aluminum Diffraction Patterns





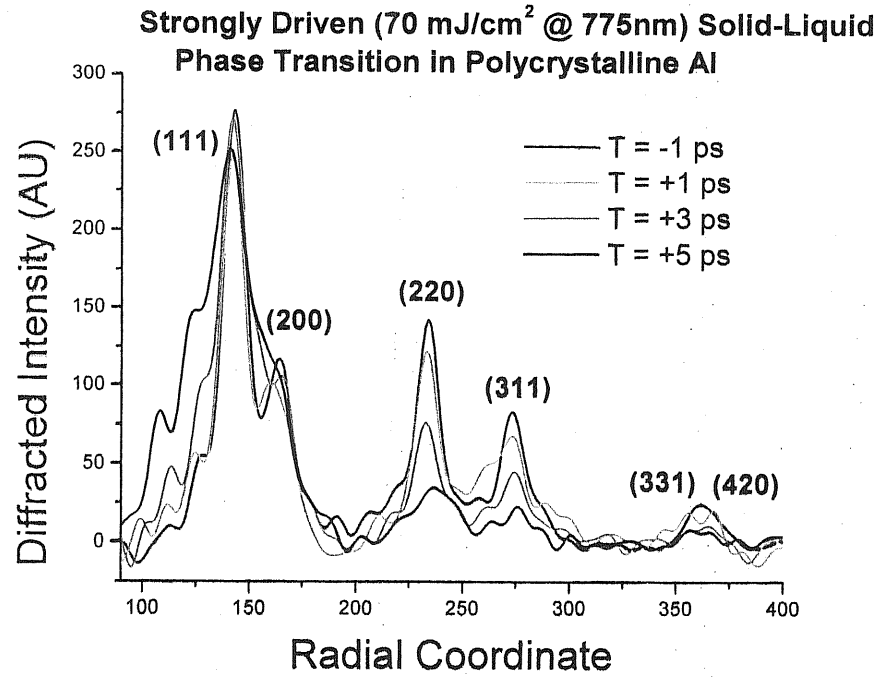


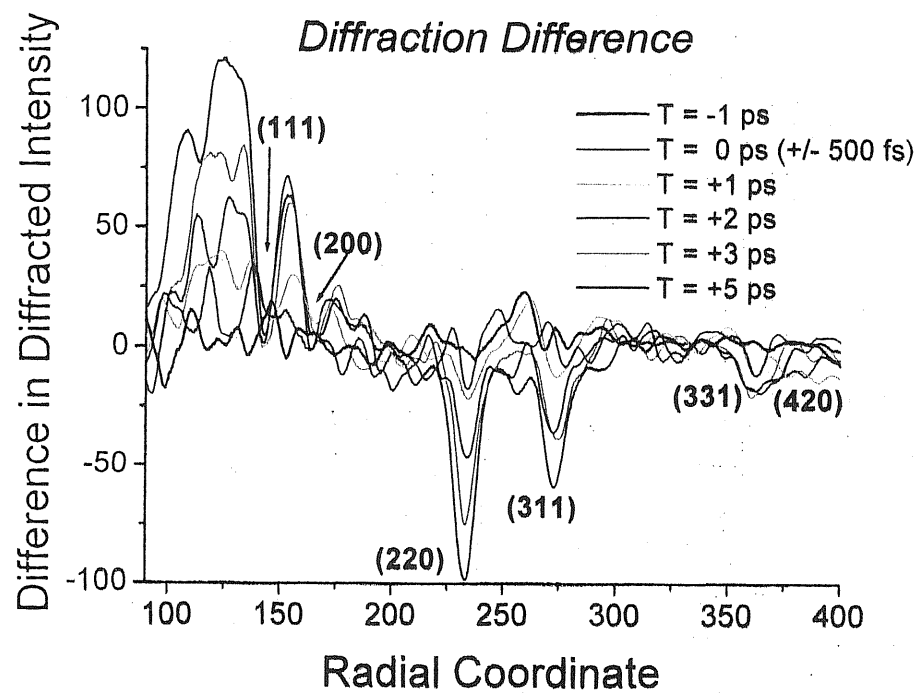


High Fluence I (70mJ/cm2): Non-Thermal 'Melting'

- Long-range order is lost on a non-thermal time-scale*
- Reduction in ring intensity is not accompanied by a significant peak shift due to lattice expansion.
- Significant broadening of the (111) & (200) rings to lower radial coordinate is a pronounced feature of the dynamics.

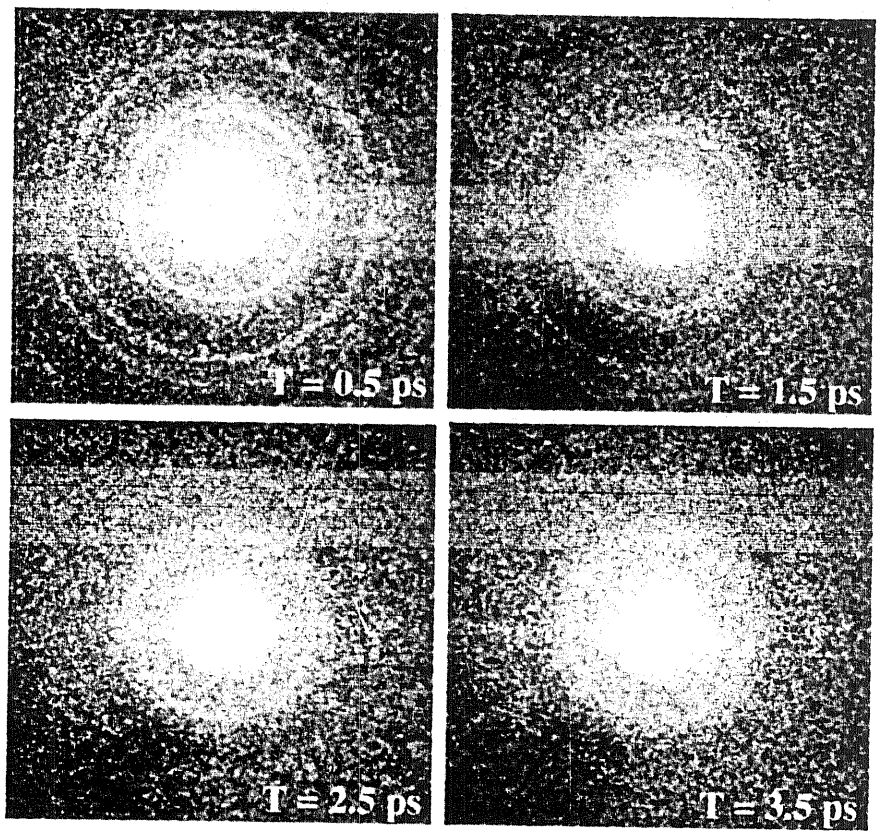
* C. Guo *et al.*, Phys. Rev. Lett. **84**, 4493 (2000).

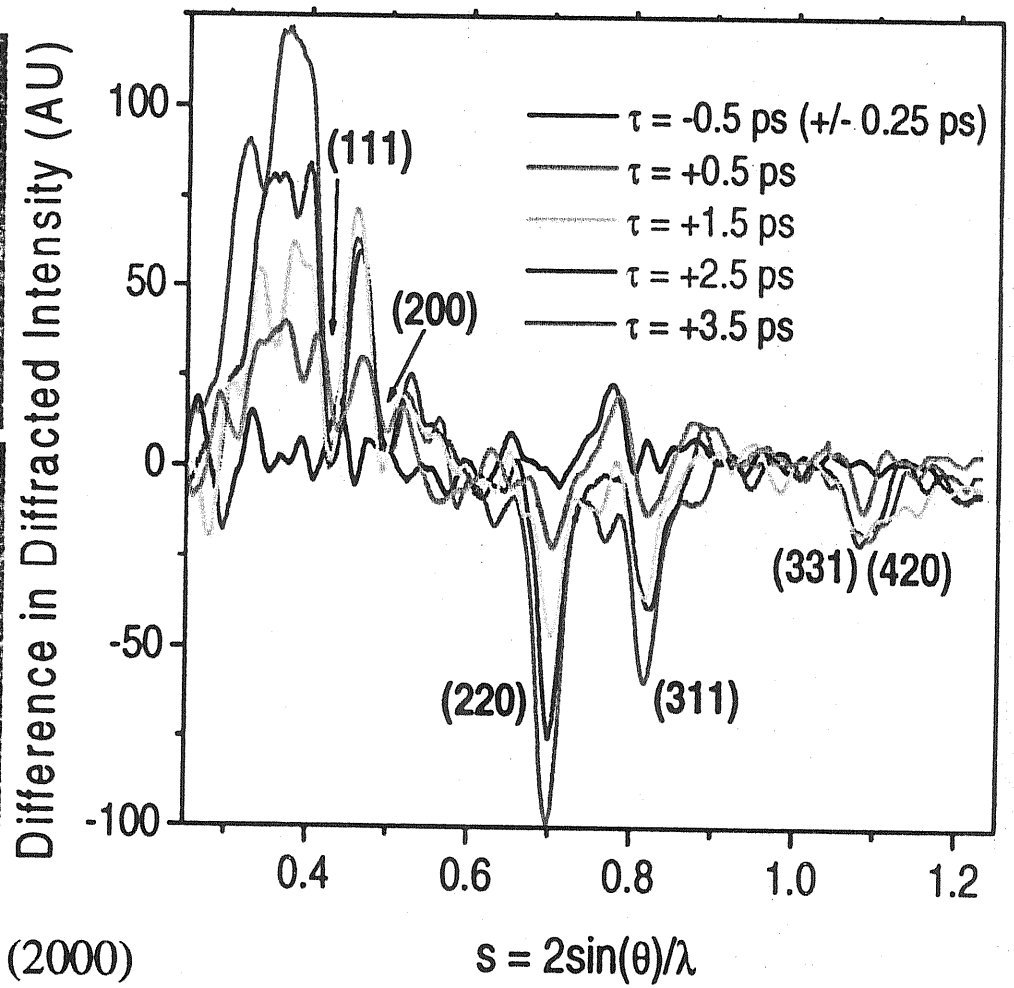




Ultrafast* Solid-Liquid Phase Transition in Aluminum

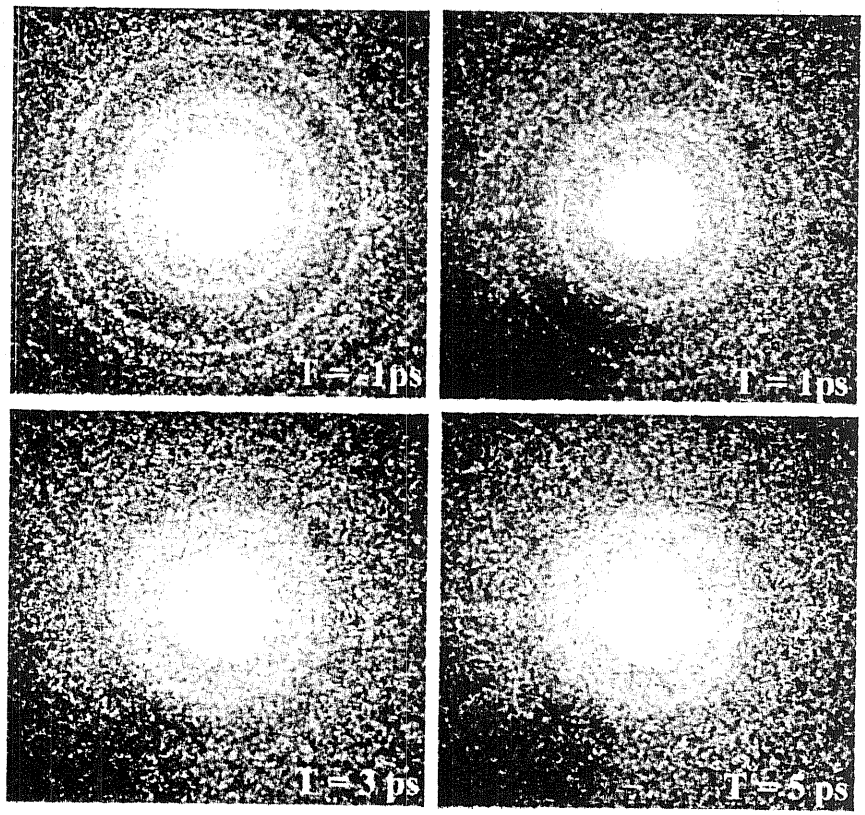
150 shots, ~6000 e/pulse

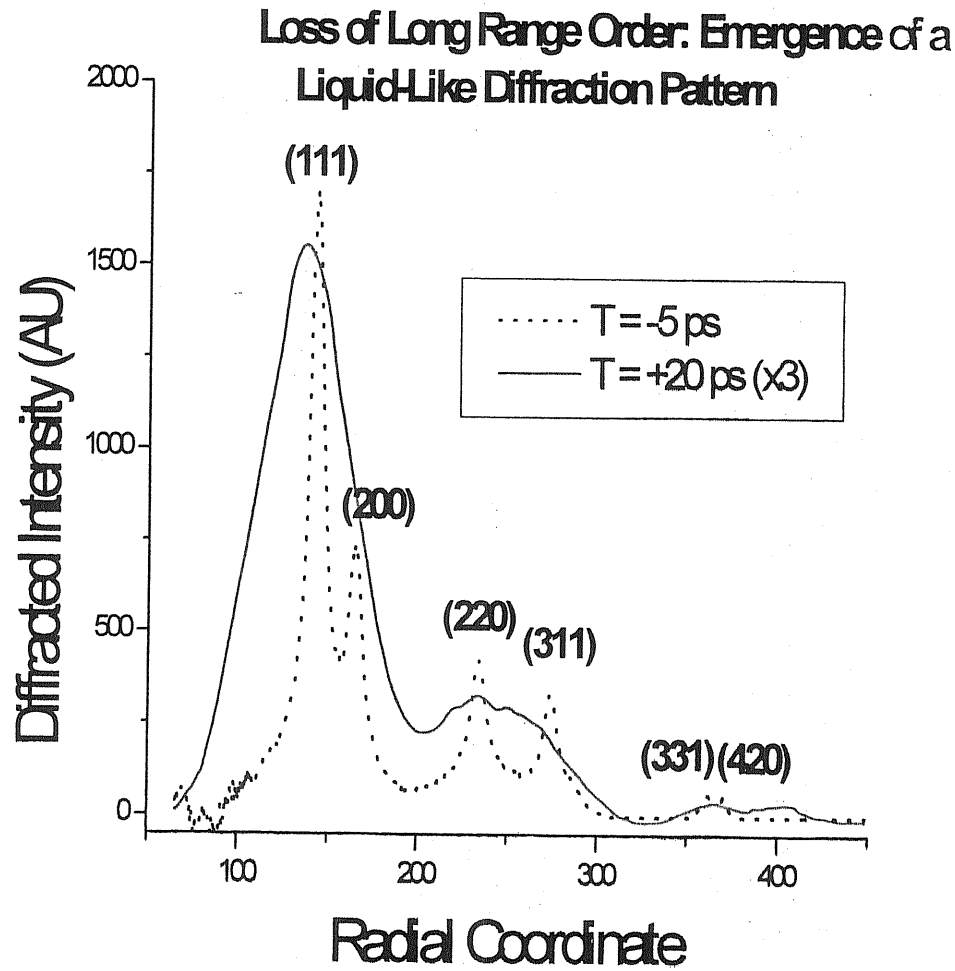




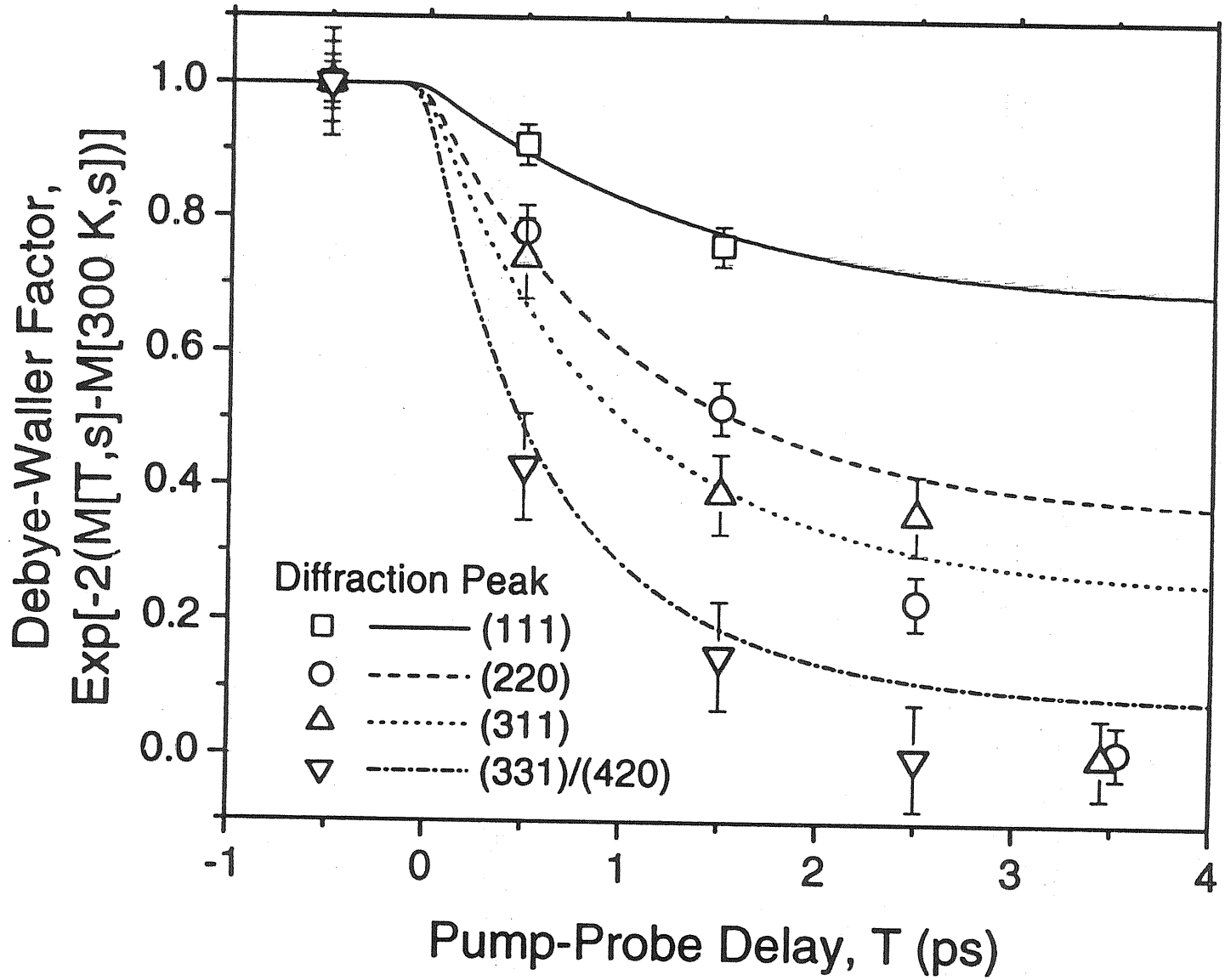
*C. Guo et al., *Phys. Rev. Lett.*, **84**, 4494 (2000)

High Fluence II (70mJ/cm2): Structure of the Disordered State

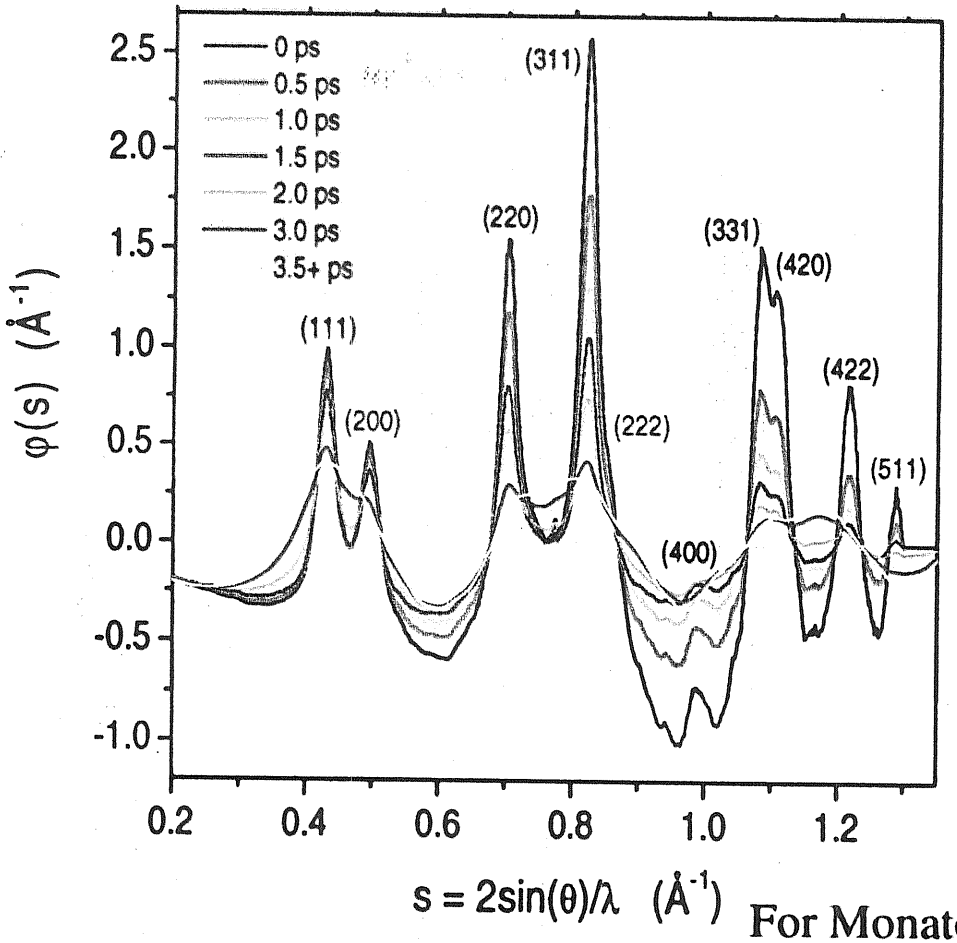


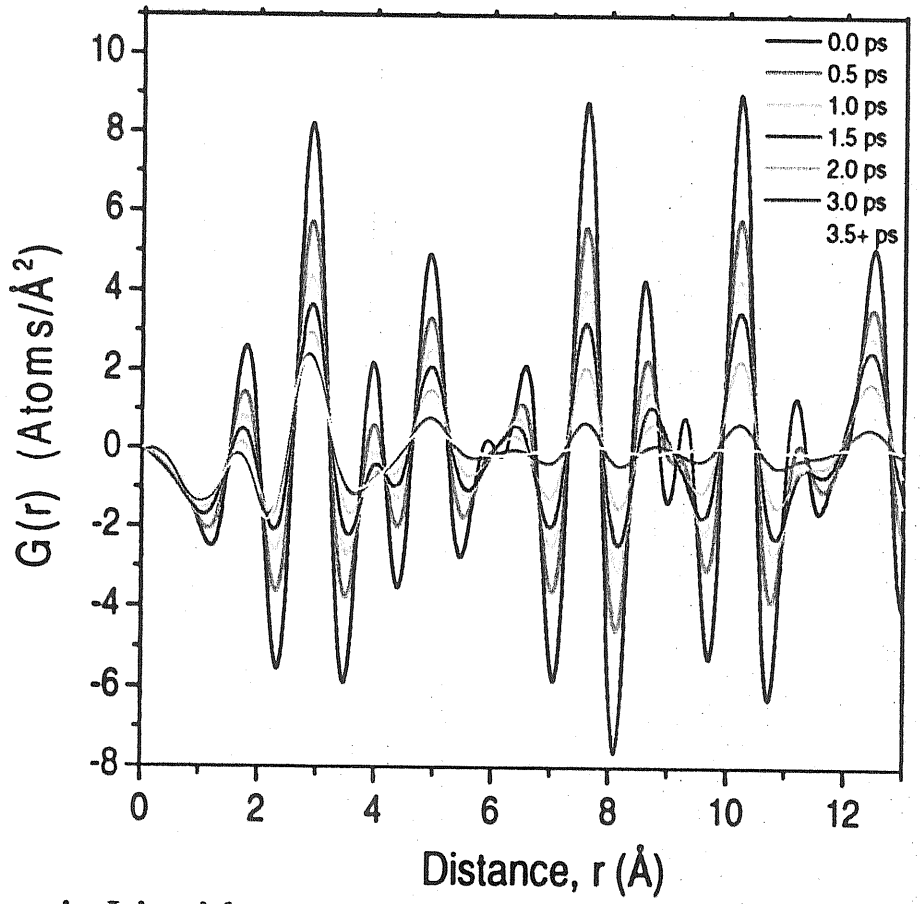


The Effect of Temperature: The Debye-Waller Factor



Ultrafast Melting: An Atomic-Level Perspective





For Monatomic Liquids:

Reduced Density Function

Reduced Intensity Fcn.

$$G(r) = 4\pi r(\rho(r) - \rho_o) = 8\pi \int_0^\infty \varphi(s)\sin(2\pi s r)\,ds$$

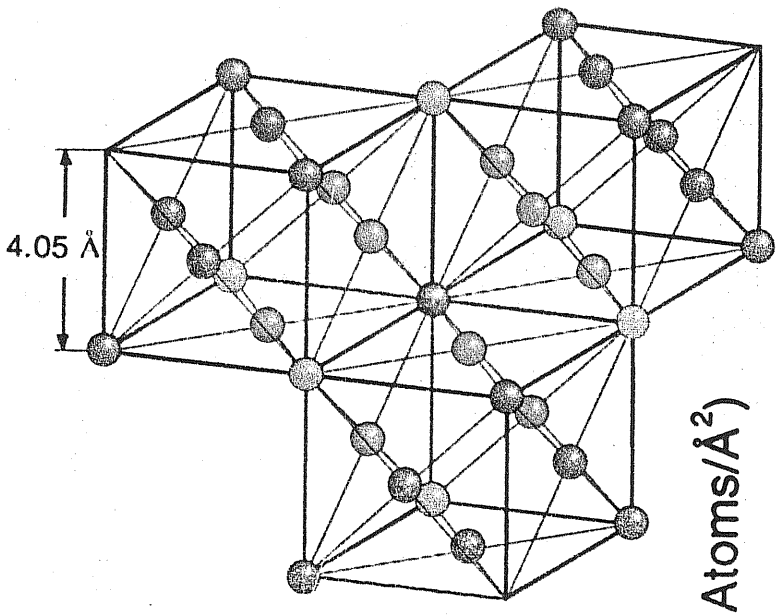
Diffracted Intensity

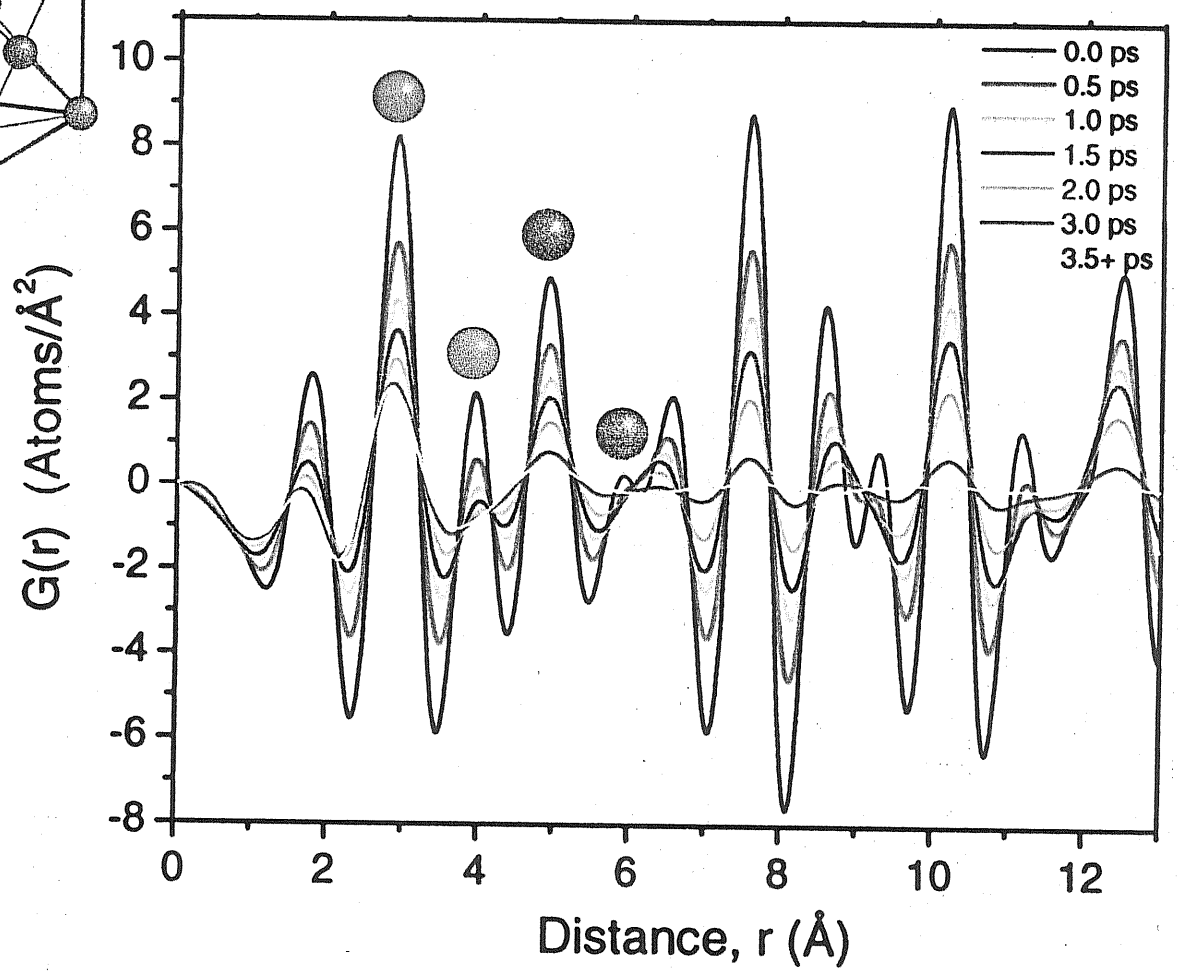
where, $$\varphi(s) = s\left(\frac{I(s)}{Nf^2} - 1\right)$$

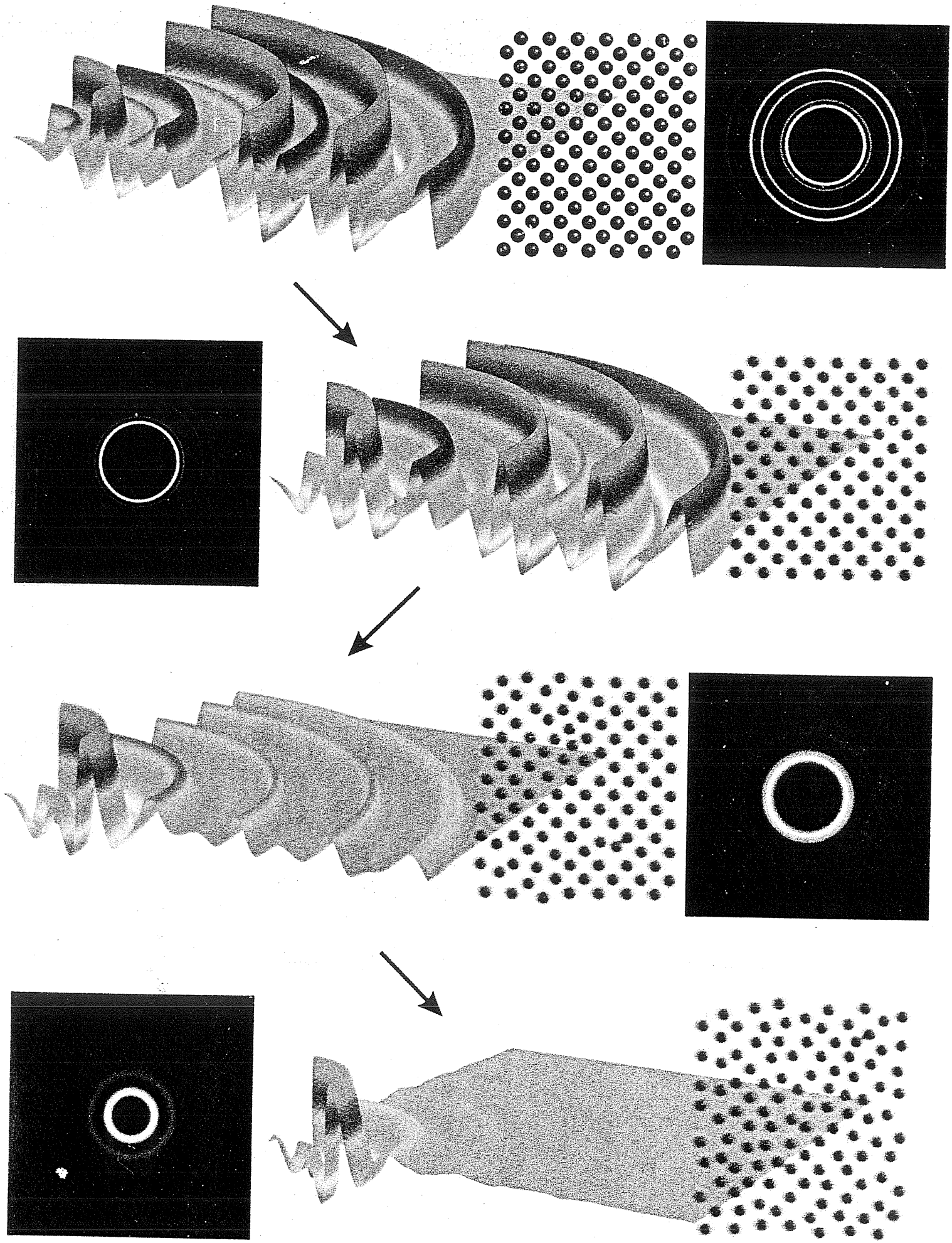
Atomic Form Factor

Normalization Constant

Time-Dependent Pair Correlation Function







Summary

First femtosecond electron diffraction studies (electron pulses < 500 fs …. Approach 200 fs with pulsed fields) ⇒ time resolution now good enough to follow transition state processes with atomic resolution

"Camera for the Molecular Movie" is within reach

Concept of Electron-Optics introduced for electron pulse characterization and manipulation (< 100 fs pulses in high number densities)

Single Shot Diffraction capabilities

First fully resolved Solid to Liquid phase transition ⇒ (tentative) lattice disorder does not seem to occur till thermalization and phonon heating…extremely fast order to disorder transition.