Dynamics of Disordered Materials*

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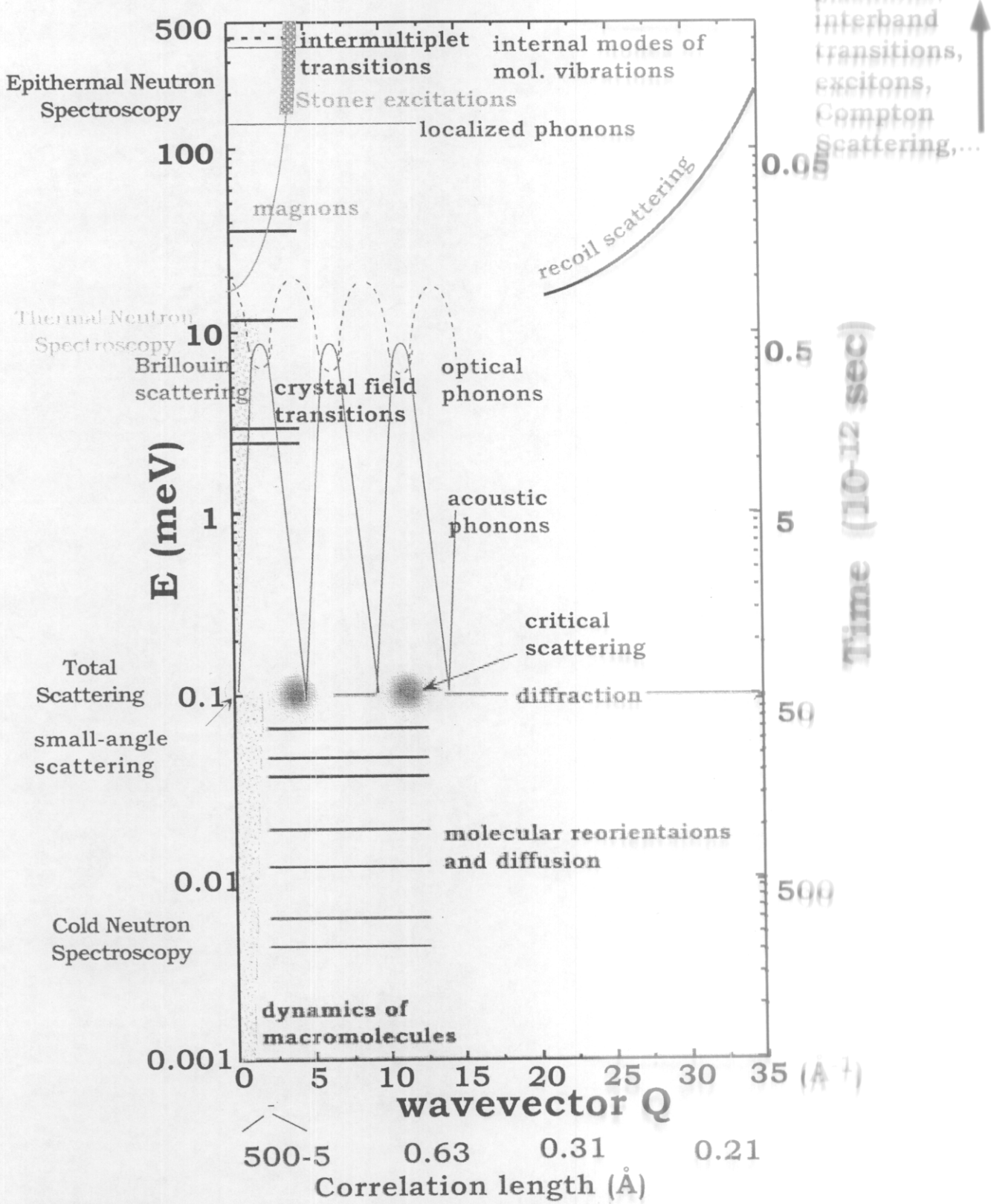
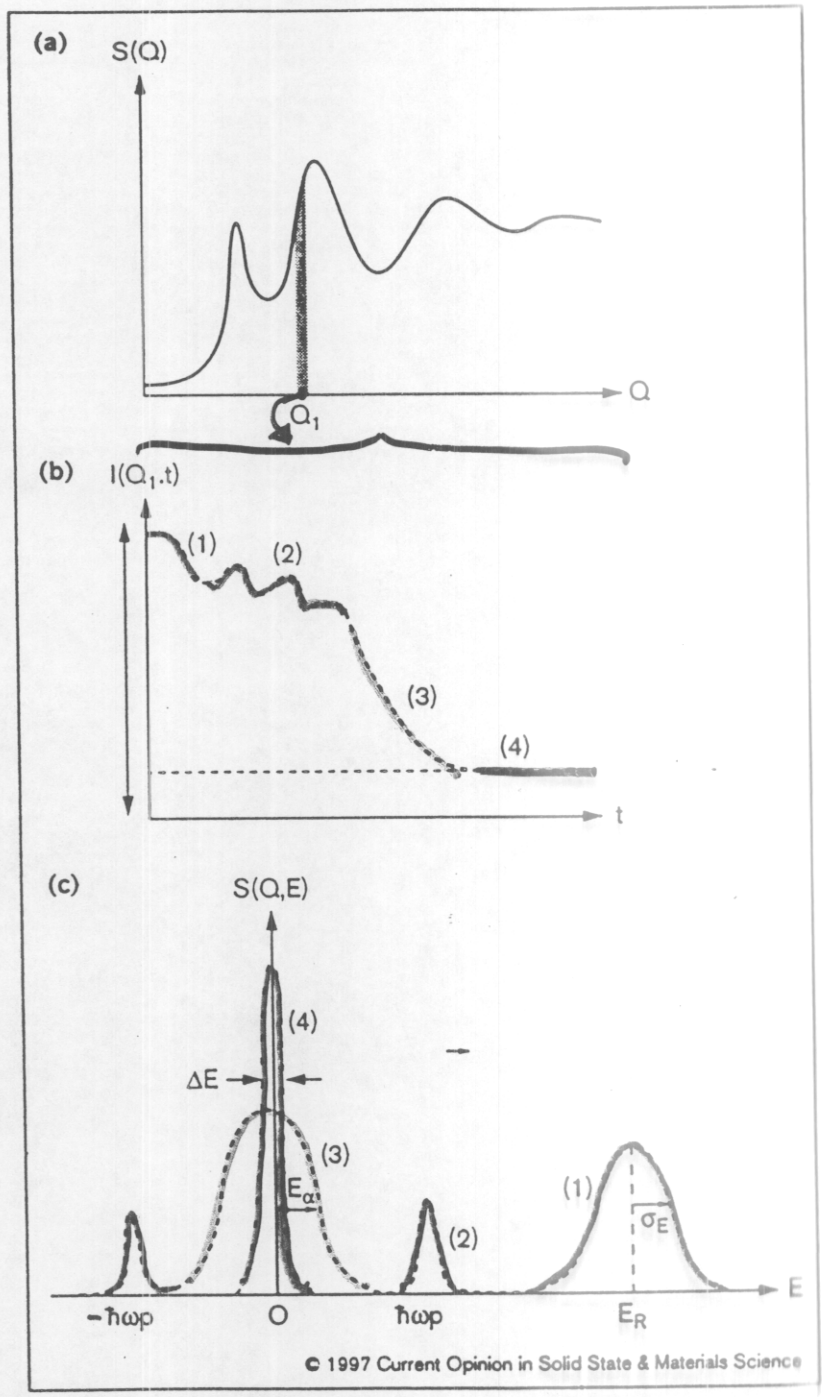
Talk at Symposium on Fundamental Studies of Materials Phenomena Using Neutrons
Oak Ridge, TN, October 2-3, 2001

*Work supported by the Office of Science, USDOE, under Contract W-31-109-ENG-38

Elementary Excitations in Condensed Matter



Dynamical Regimes probed by Inelastic Neutron Scattering

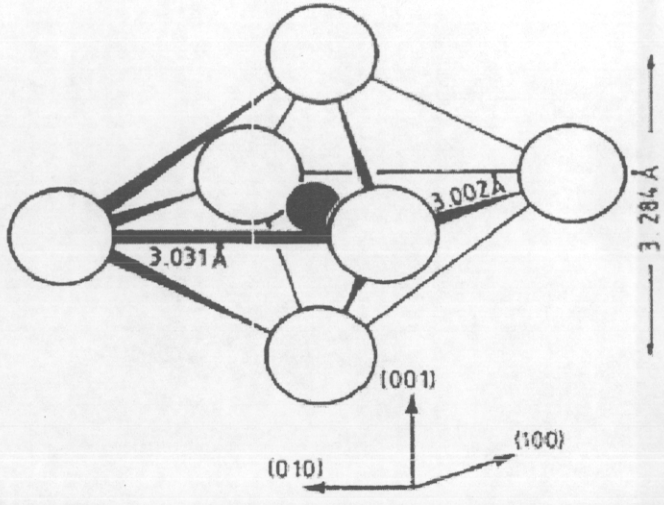


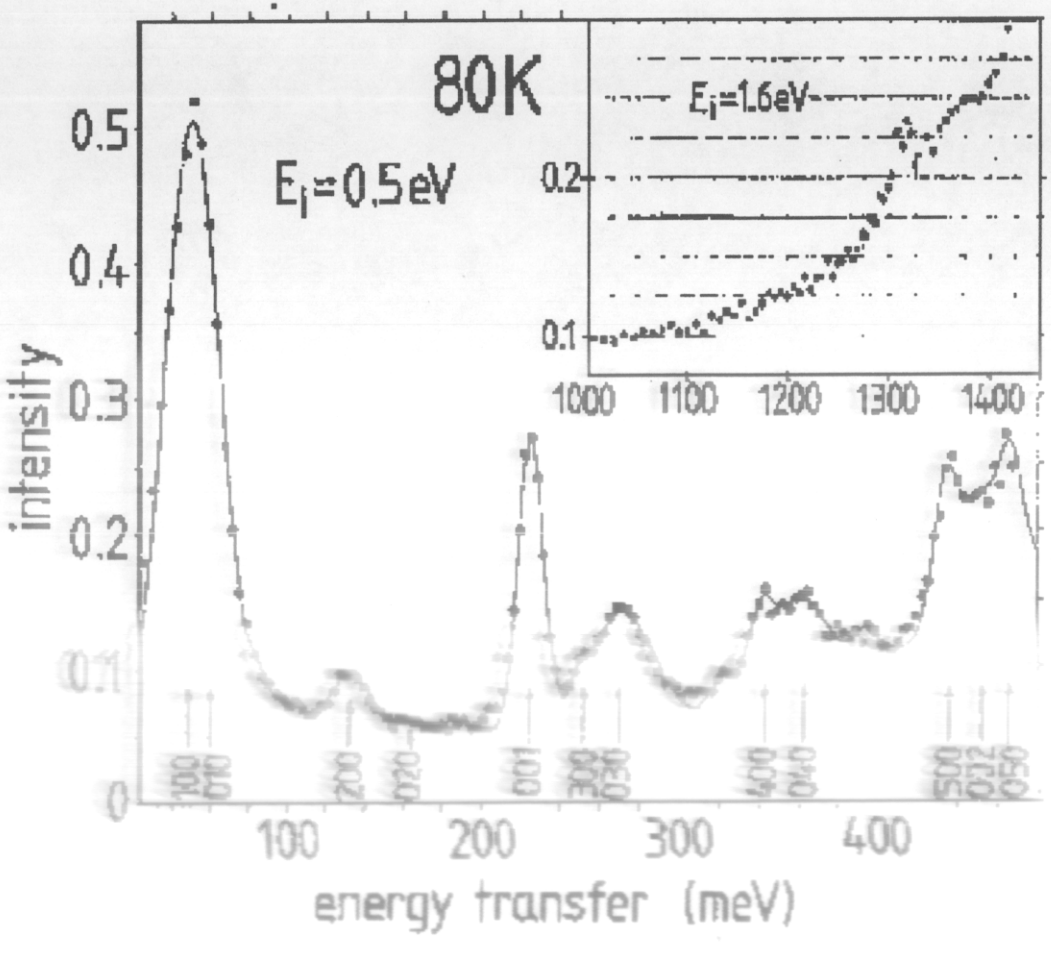
① Recoil; (2) one-phonon; (3) quasielastic; (4) elastic.

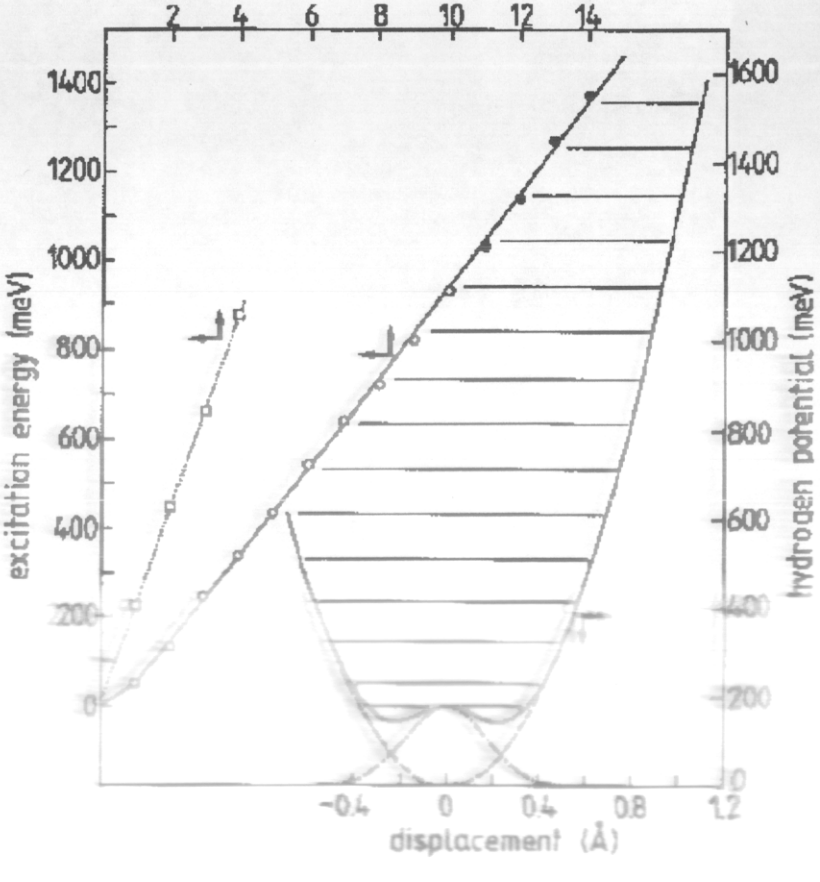
High-energy neutron vibrational spectroscopy on β-V_2H

R. Hempelmann, D. Richter and D. L. Price

Phys. Rev. Letters 58, 1016 (1987)







Kinetic energy of β-V_2H studied by deep inelastic neutron scattering

R. Hempelmann, D. Richter and D. L. Price

J. Less-Common Metals 172-174, 301-306 (1991)

Vibrational spectroscopy:

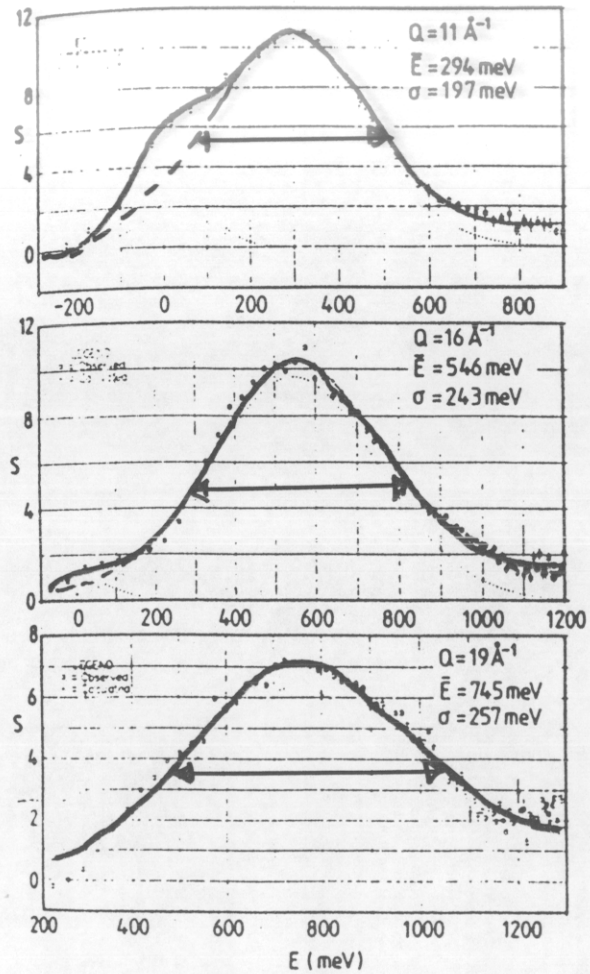
$E_{kin}(x) = 15.4$ meV
$E_{kin}(y) = 16.2$ meV
$E_{kin}(z) = 55.8$ meV

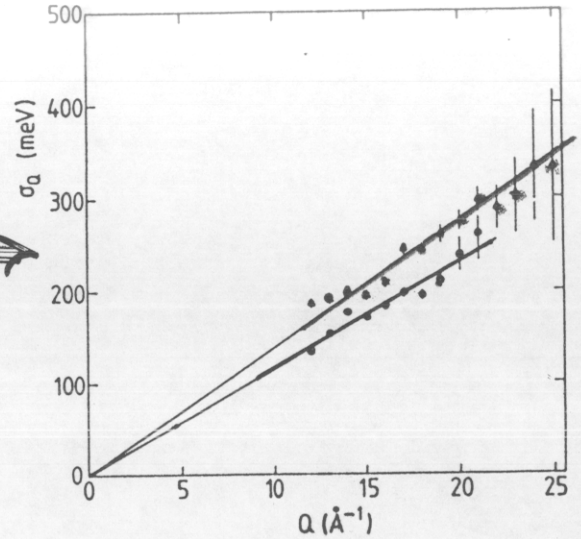
⇓

$E_{kin}(xy) = 15.8$ meV

$E_{kin}(xz) = 35.6$ meV

Compton profiles:





⇓

$E_{kin}(xy) = 16.0 \pm 0.4$ meV

$E_{kin}(xz) = 25.5 \pm 0.8$ meV

Discrepancy in z direction may be due to invalidity of impulse approximation in this direction.

Correlated Motions in Glasses Studied by Coherent Inelastic Neutron Scattering

J. M. Carpenter and D. L. Price
Materials Science and Technology Division and Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois 60439
(Received 24 September 1984)

Coherent inelastic neutron scattering provides detailed information about the correlated atomic displacements in the vibrational modes of a glass. As an example, we show the wave-vector dependence of the scattering function of vitreous SiO_2 corresponding to different peaks in the one-phonon density of states. Pending the availability of results from computer simulations, we give a qualitative comparison with the Sen-Thorpe model.

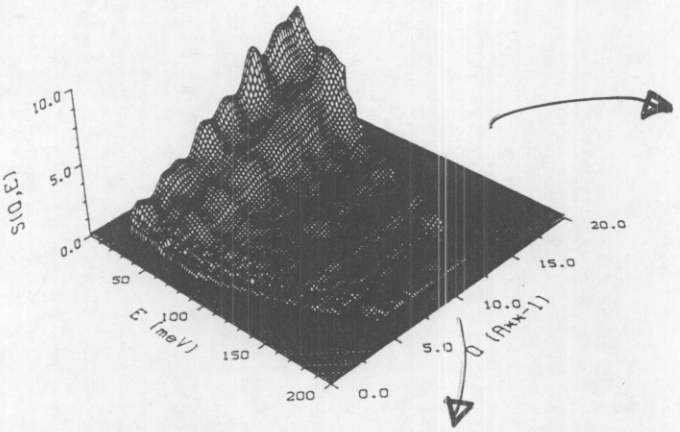


FIG. 1. Scattering function of a-SiO_2 at 33 K.

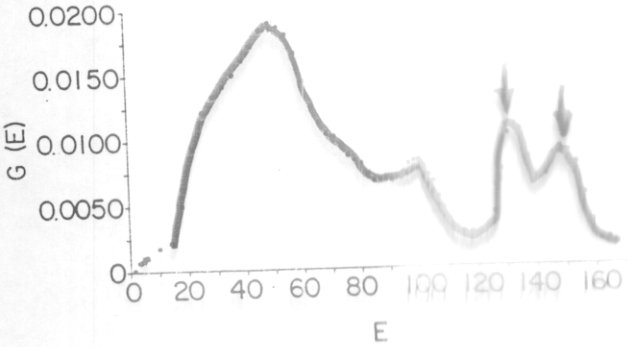


FIG. 2. One-phonon density of states $g(E/\hbar)$ for a-SiO_2.

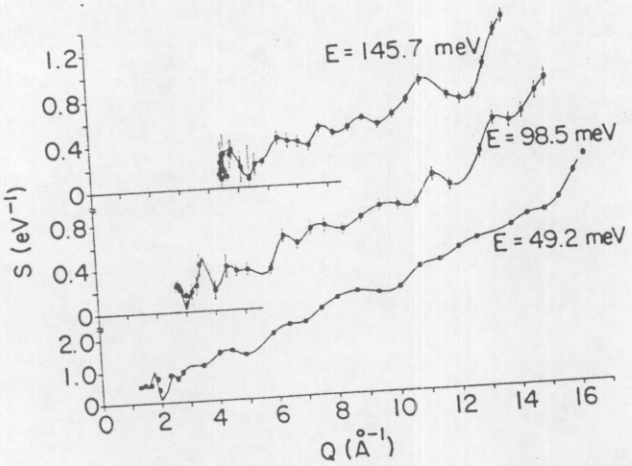


FIG. 3. Q variation of $S(Q,E)$ for a-SiO_2 at $E=49.2$, 98.5, and 145.7 meV. The solid curves represent cubic spline fits through the data, taking account of the statistical errors indicated by the bars on each data point.

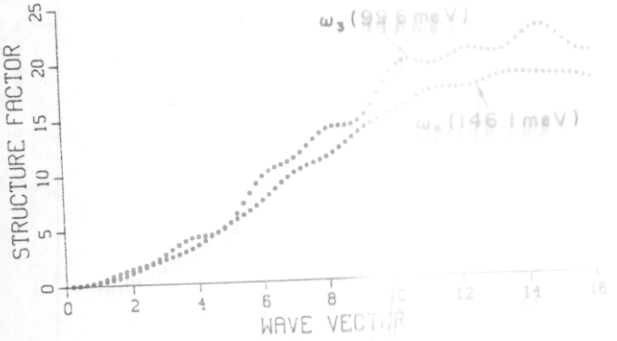


FIG. 4. $S^{(1)}(Q,E)$ for the ω_3 and ω_4 modes of the Sen-Thorpe model (Ref. 10).

Normal modes of vibration of vitreous SiO_2

M. Arai et al., Trans. ACA 27, 114 (1991)

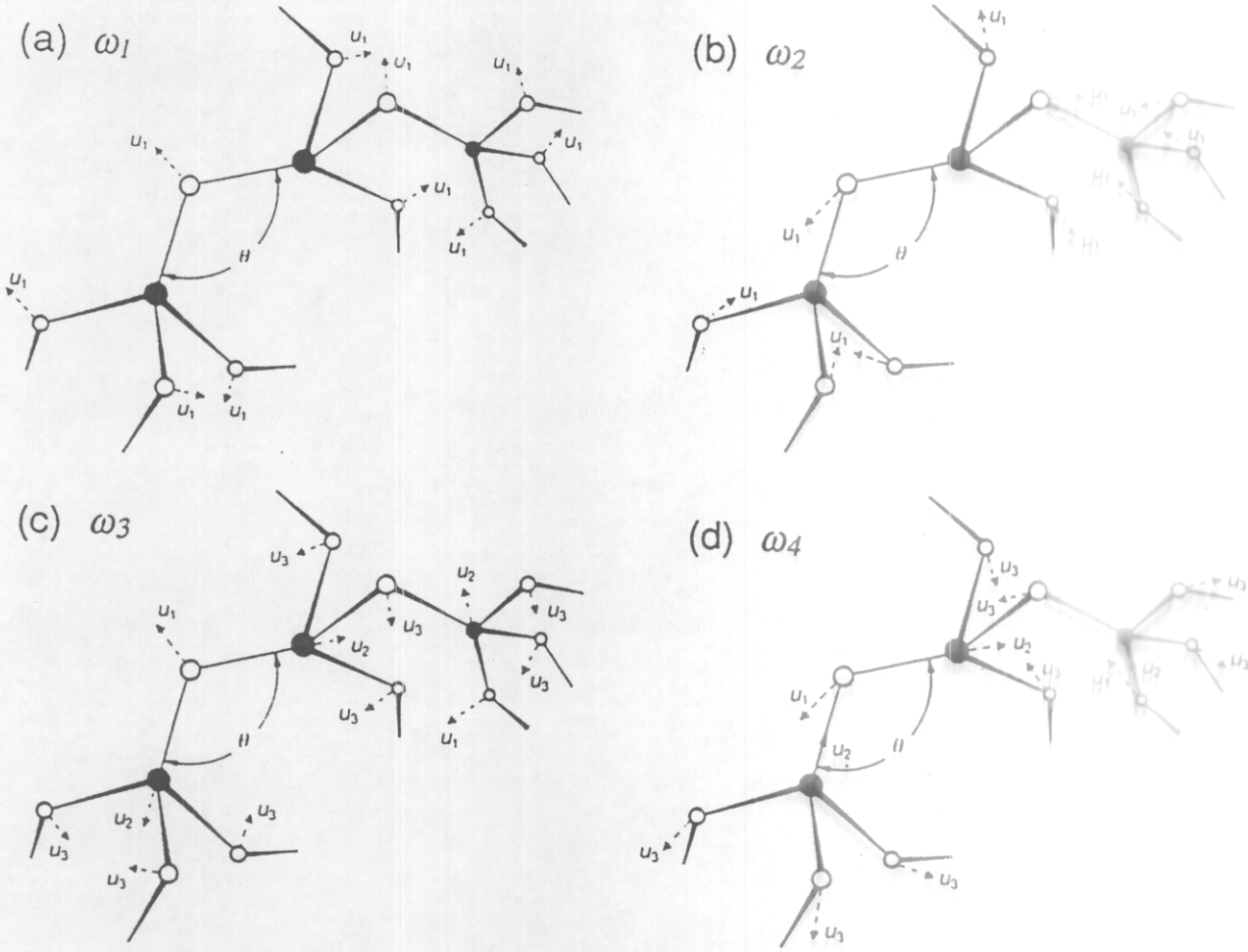
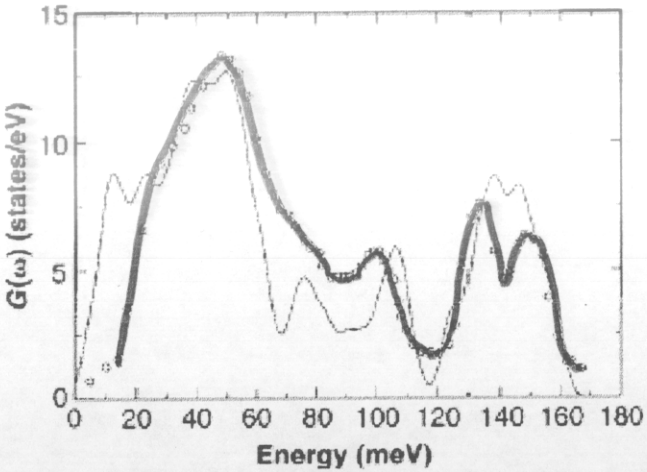


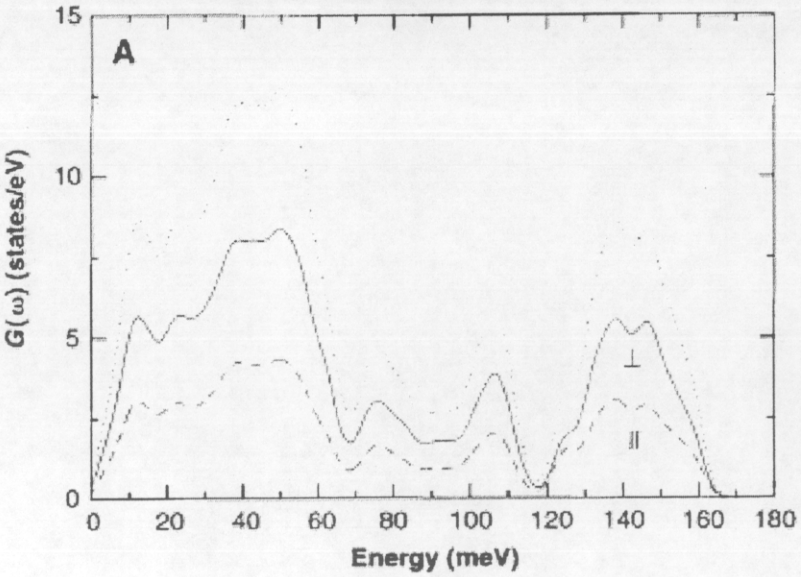
Figure 3. Normal modes ω_1, ω_2, ω_3 and ω_4 for the central-force-only calculation. (a) ω_1; Oxygen atoms execute bending motion with the Si atom sitting still. (b) ω_2; Oxygen atoms execute stretching motion without Si atomic motion. (c) ω_3; Oxygen motion is bending while the Si atom moves along the Si-O bond direction. The amplitude of the displacement vector has the ratio shown in section 2.2.3. (d) ω_4; Oxygen motion is stretching while the Si atom moves along the Si-O bond direction. The amplitudes of U_1, U_2 and U_3 are shown in section 2.2.4. (cited from ref. 6)

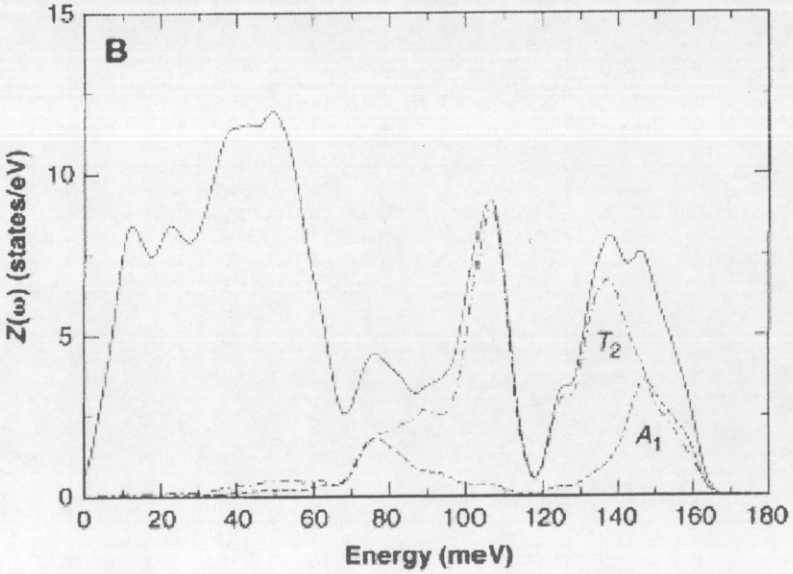
Origin of the High-Frequency Doublet in the Vibrational Spectrum of Vitreous SiO2

J. Sarnthein, A. Pasquarello and R. Car, Science 275, 1925 ((1997)



Double peak around 140 meV is not due to transverse optic / longitudinal optic splitting as previously thought (**A**) but to modes of different symmetry types (**B**)





Polymer Electrolytes are ionically conducting solid phases formed by the dissolution of salts in ion-coordinating macromolecules.

Applications: electric vehicles

storage of solar energy and wind power

portable electronics: laptop computers, cellular phones…

Properties: Good chemical and electrochemical stability

Good mechanical properties

Ease to processing: thin film batteries

Low electronic conductivity

Conductive at 0 ~ 100°C

Problems: low ionic conductivity

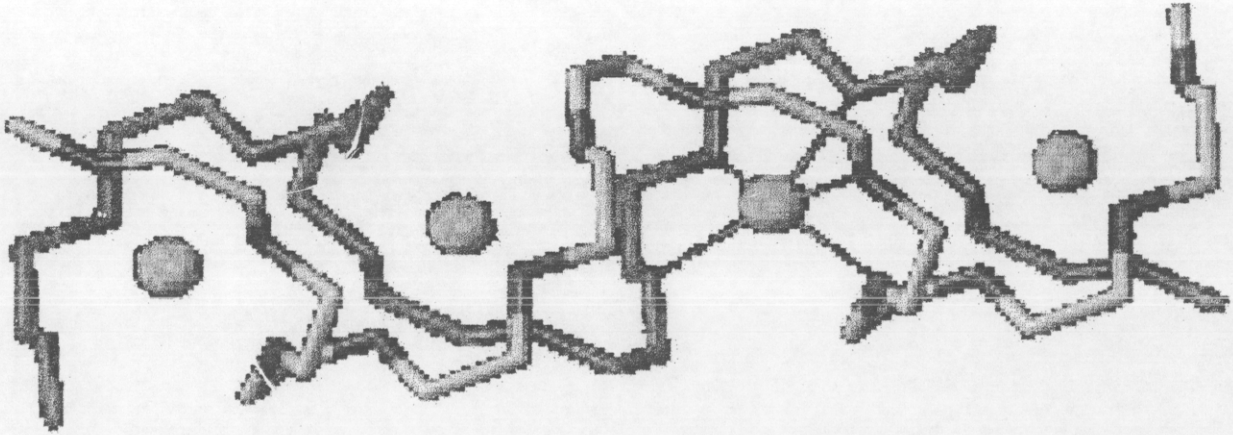
The major subject of this field is to improve the ion conductivity at room temperature and understand the mechanism of ion transport.

Is the Li^+ ion coordinated by one or by two PEO chains?

1) MD simulations of $P(EO)_8LiI$ show crosslinking of two chains.
[F.Muller-Plathe and W. F. van Gunsteren, JCP 103, 4745(1995)]

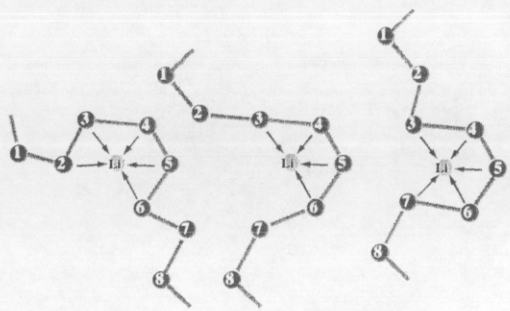
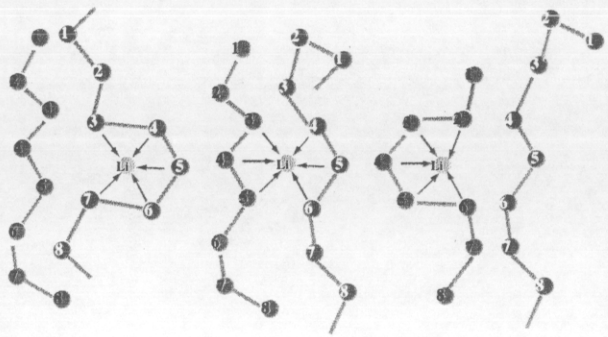
2) QC studies: two chains structure are energetically favored over one chain.
[Baboul et al. JACS, (1999)]

3) In c- $P(EO)_6LiAsF_6$, Li^+ ions are in cylinders formed by two PEO chains.
[P. Bruce et al. Nature, 398, 792(1999)]



Neutron Diffraction : Li^+ ions are coordinated by two neighboring polymer chains. [Mao et al. PRL (2000)]

The ion conducting mechanism of polymer electrolytes

Intrachain conduction	Interchain conduction
	

Thermal motion of polymer segments assists migration of Li^+ ions. The relaxation rates are estimated to be in the range of 0.1 to 5 ns, which can be probed by quasielastic neutron scattering (QENS) and spin echo neutron spectroscopy (SENS).

Neutron Spin-Echo Spectrometer

F. Mezei, Nucl. Instr. Methods 164, 153 (1979); Lecture Notes in Physics, vol. 128 (Springer-Verlag, Heidelberg, 1980)

The spin-echo method is the one quasi-elastic spectrometer in which energy transfers are measured directly instead of a difference between specified incident and scattered energies. It allows very high energy resolution, of order 10^{-6} meV, with good intensity.[49] The method is shown in Fig. 28. Cold neutrons from a neutron guide are roughly monochromated and polarized by a supermirror reflection. The polarization direction is moved horizontally by a $\pi/2$ flipper. The incident neutrons precess some hundreds of rotations along a horizontal precession field shown as a spiral in the figure. The rotation angle θ_0, is inversely proportional to the incident velocity v_0. The neutron polarization is then reversed in a π flipper. Scattered neutrons are "unwound" by θ_1 in a similar precession field so that the net precession angle is

$$\theta = \theta_1 - \theta_0 = \frac{\gamma H l}{v_1} - \frac{\gamma H l}{v_0} = \gamma H l\left(\frac{1}{v_1} - \frac{1}{v_0}\right). \tag{3.10}$$

The polarization of the emerging neutrons gives the projection or cosine of the precession angle. Inserting $Q = 2mv_0 \sin \phi/2$ and $v_0 - v_1 = \hbar\omega/v_0 m$, this may be written

$$P = P_0 \int S(Q, \omega) \cos\left[\left(2 \sin \frac{\phi}{2}\right)^3 \frac{\gamma H l}{\hbar^2 Q^3} m^2 \omega\right] d\omega.$$

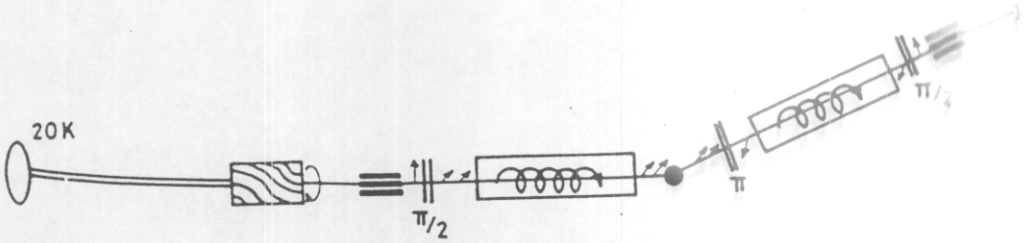
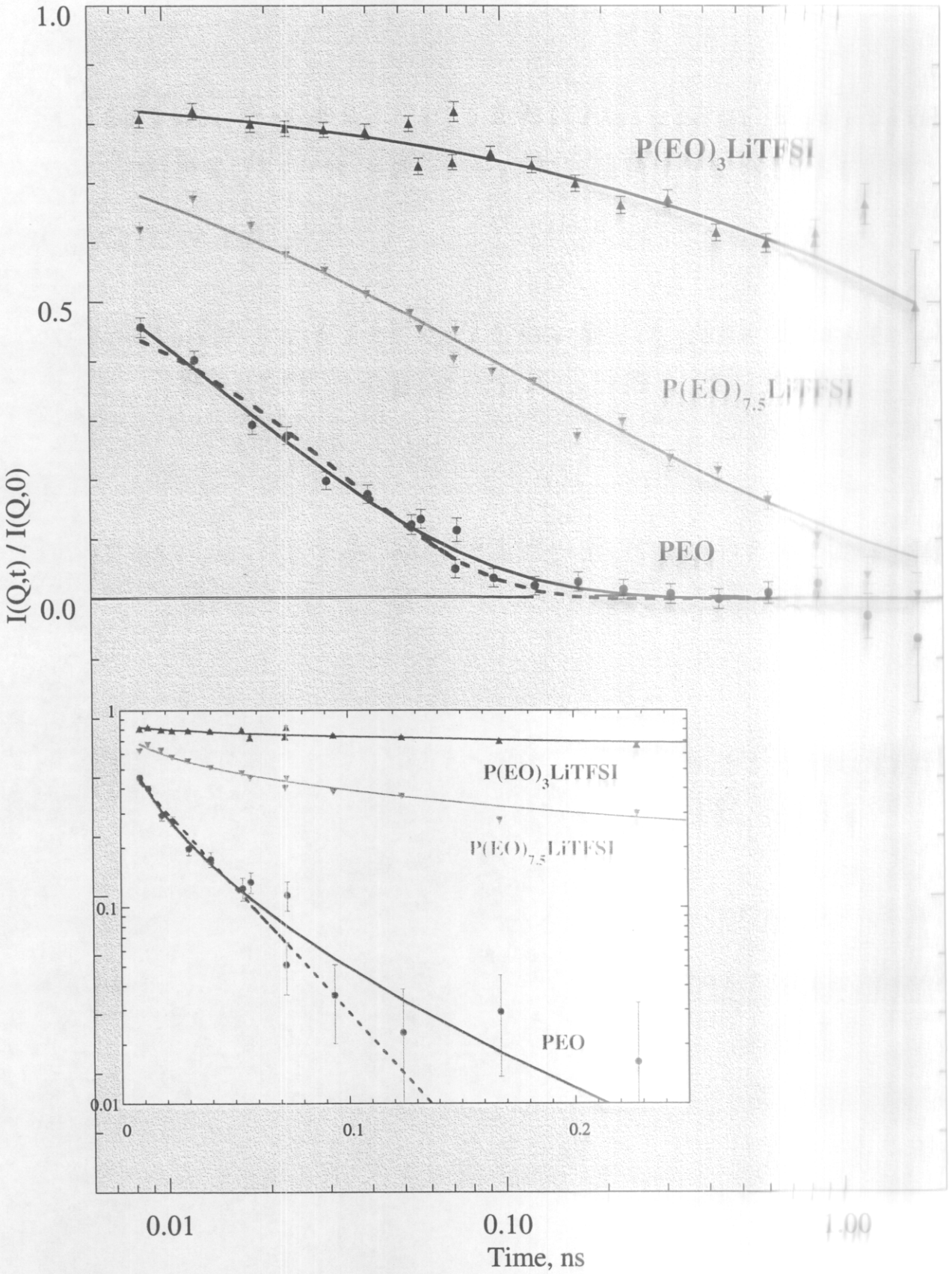


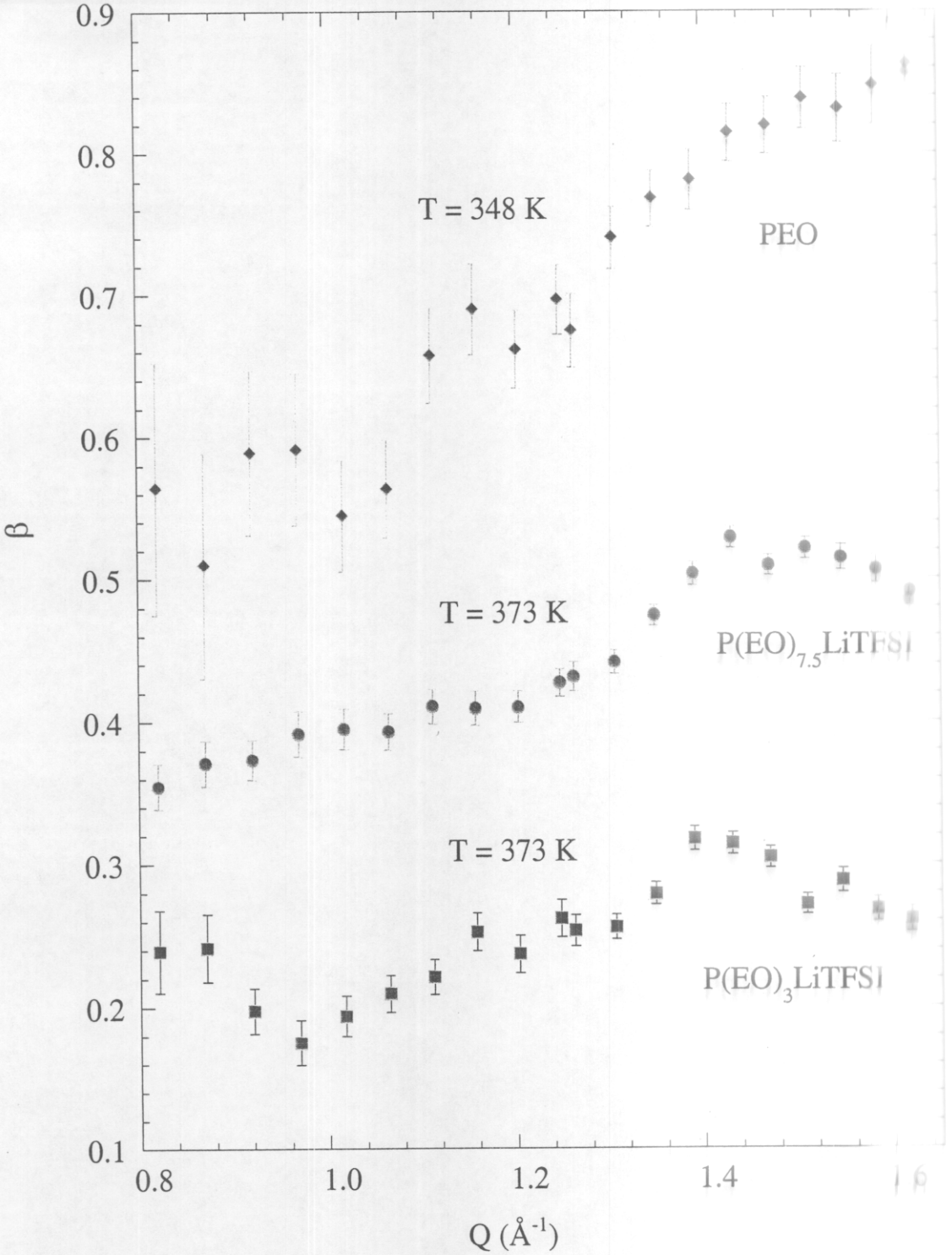
FIG. 28. The spin-echo spectrometer. Cold neutrons from a curved guide tube are monochromated to about 10% by a velocity selector and polarized by supermirrors. They are then turned horizontally by a $\pi/2$ spin flipper and precess through many turns in the precession field. After scattering they are reversed in direction by a π flipper and precess in the reverse direction to form the "echo." Quasi-elastic energy changes spoil the echo, which can be restored by scanning one of the precession fields.

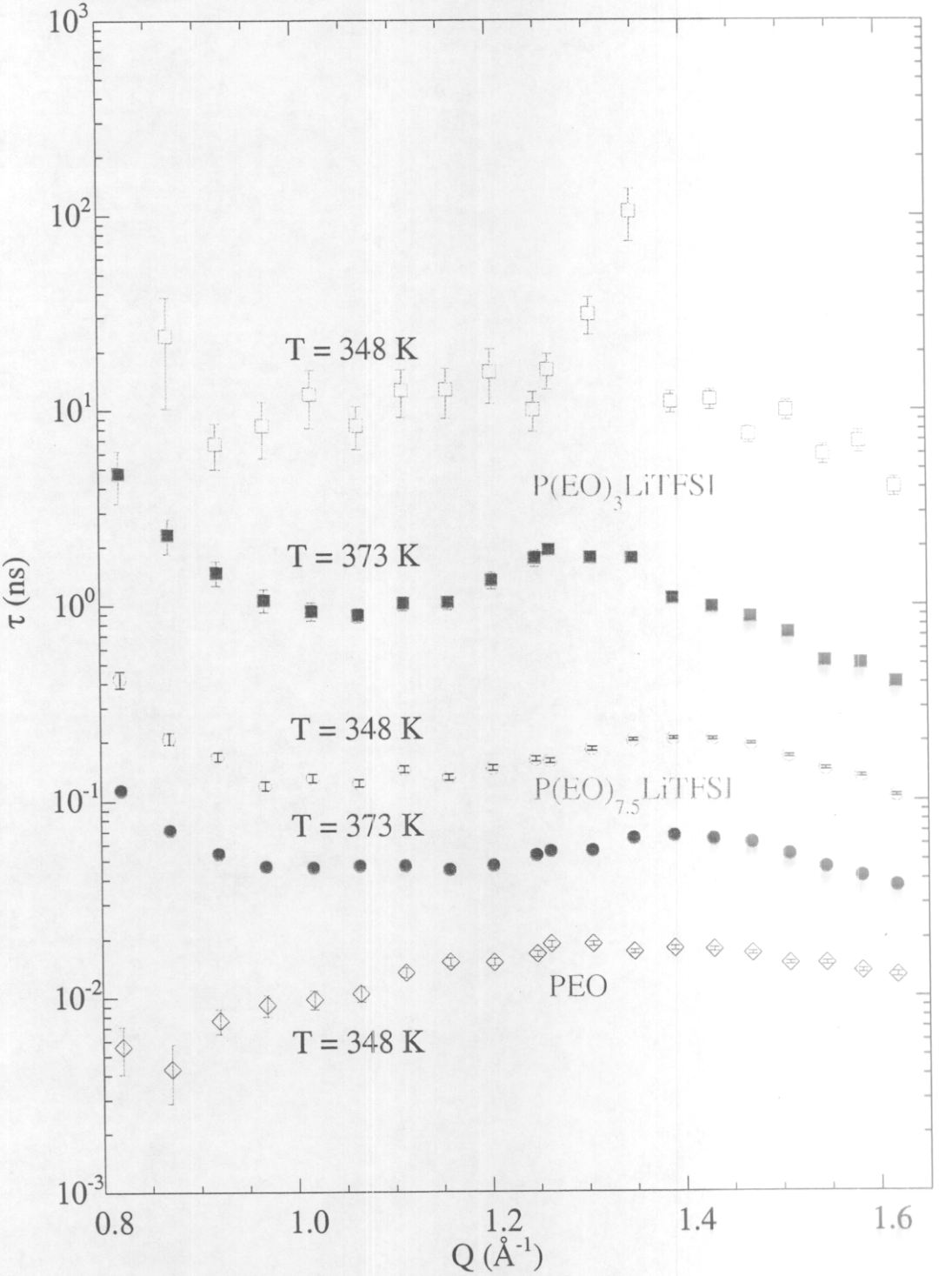
Thus the polarization yields directly the Fourier transform of $S(Q, \omega)$, that is, the intermediate scattering function $I(Q, t)$. The argument of the transform is varied by varying the precession field H.

Relaxation in PEO-LiTFSI Polymer Electrolyte (Neutron spin-echo, IN11C, ILL)

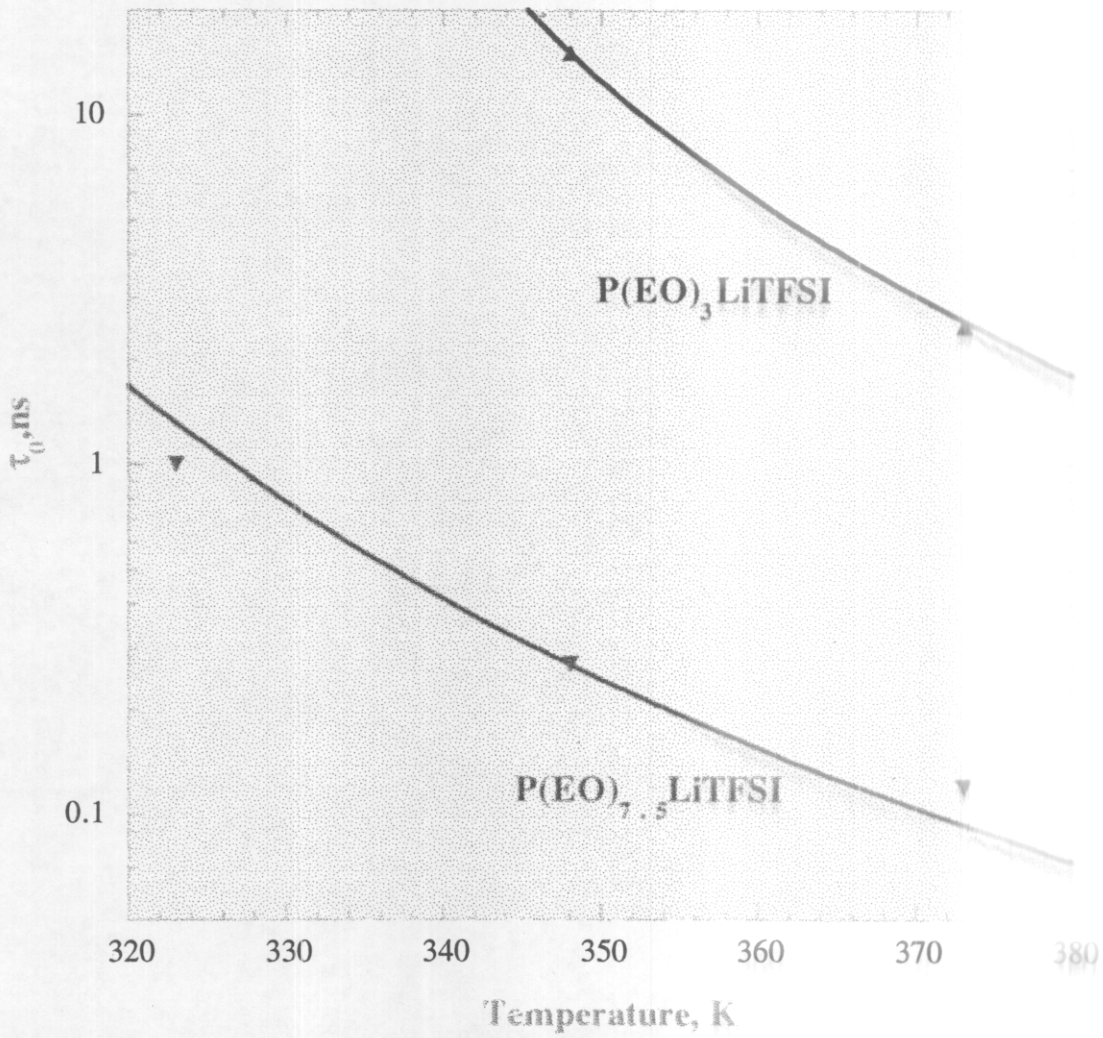


[G. Mao et al., Macromolecules (2001)]

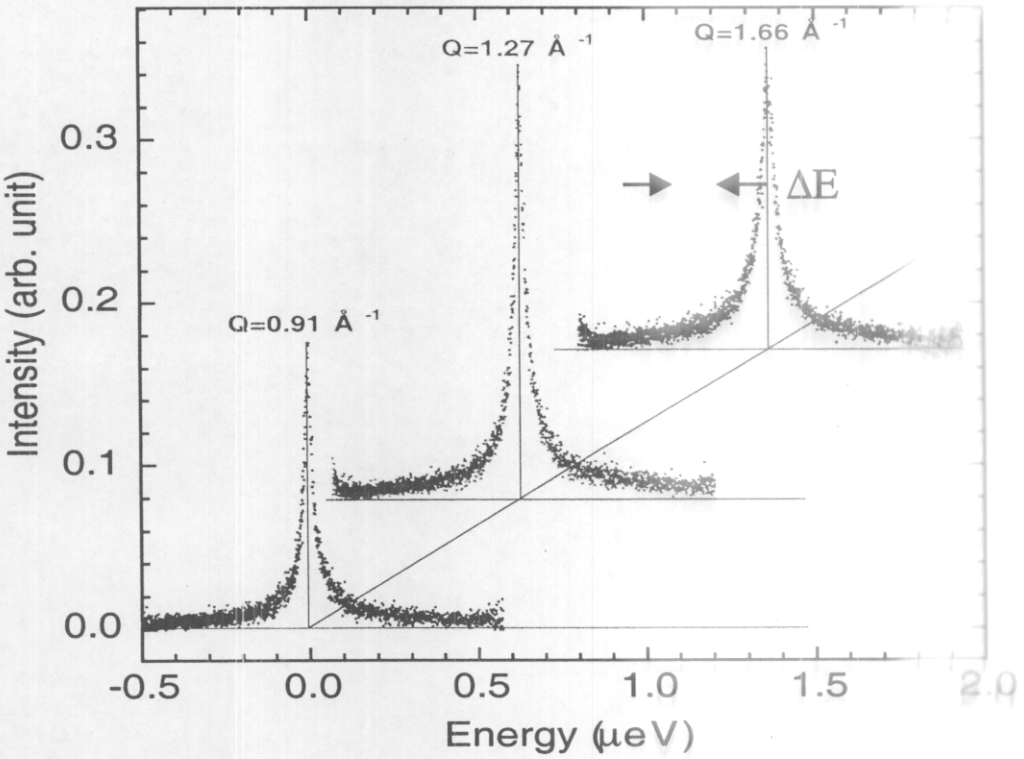

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
β
T = 348 K
PEO
T = 373 K
P(EO)7.5LiTFSI
T = 373 K
P(EO)3LiTFSI
0.8
1.0
1.2
1.4
Q (Å-1)


10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
τ (ns)
T = 348 K
P(EO)$_3$LiTFSI
T = 373 K
T = 348 K
P(EO)$_{7.5}$LiTFSI
T = 373 K
PEO
T = 348 K
0.8
1.0
1.2
1.4
1.6
Q (Å^{-1})

α Relaxation: Temperature Dependence of Polymer Electrolytes



Quasi-Elastic Neutron Scattering
PEO and PEO-salt



Pure PEO:

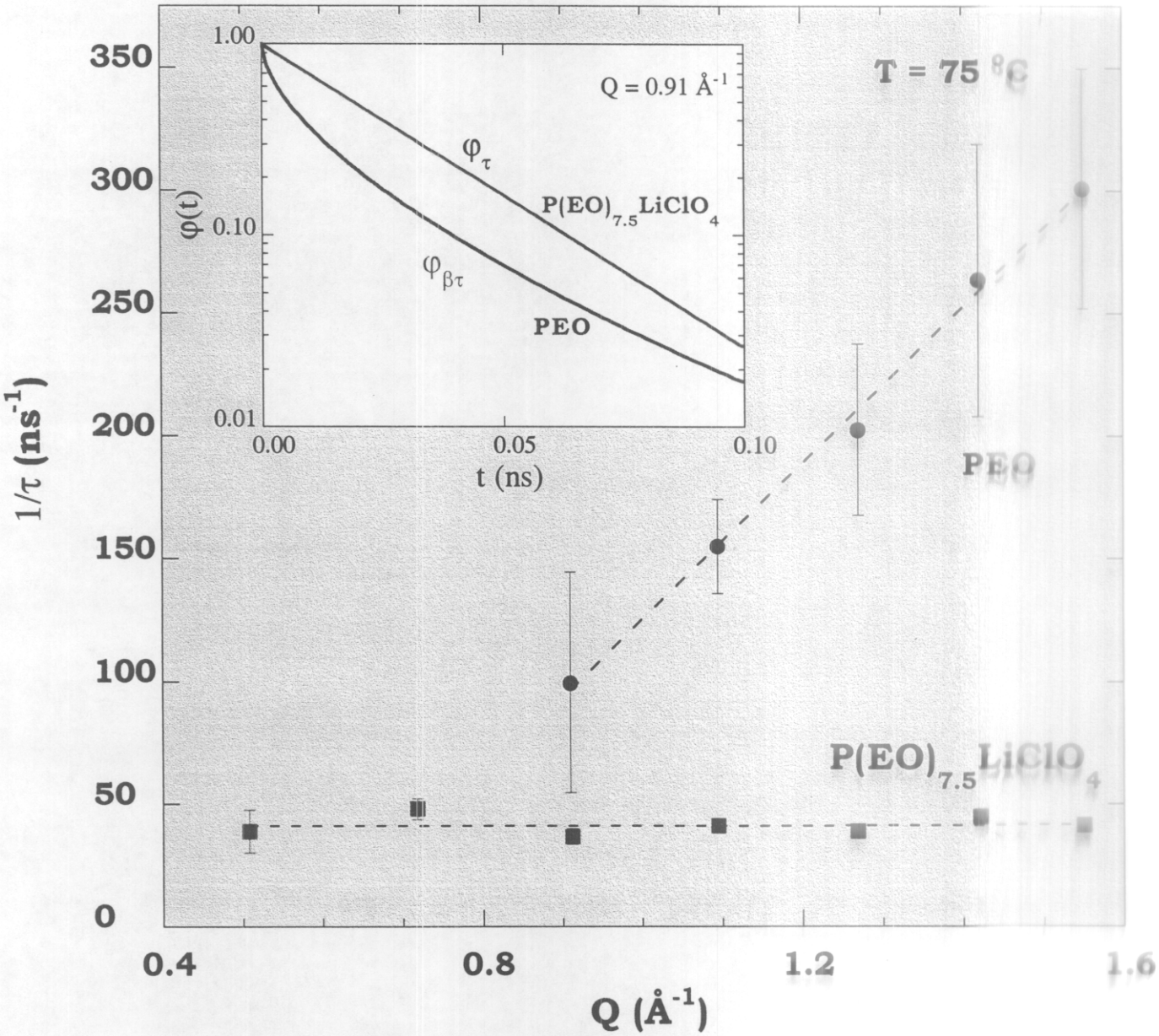
$$I(\omega) = A\varphi_{\beta\tau}(\omega) + C; \quad \varphi_{\beta\tau}(\omega) = \frac{1}{2\pi}\int \exp[-\left(\frac{t}{\tau}\right)^{\beta} + i\omega t]dt$$

PEO-Salt:

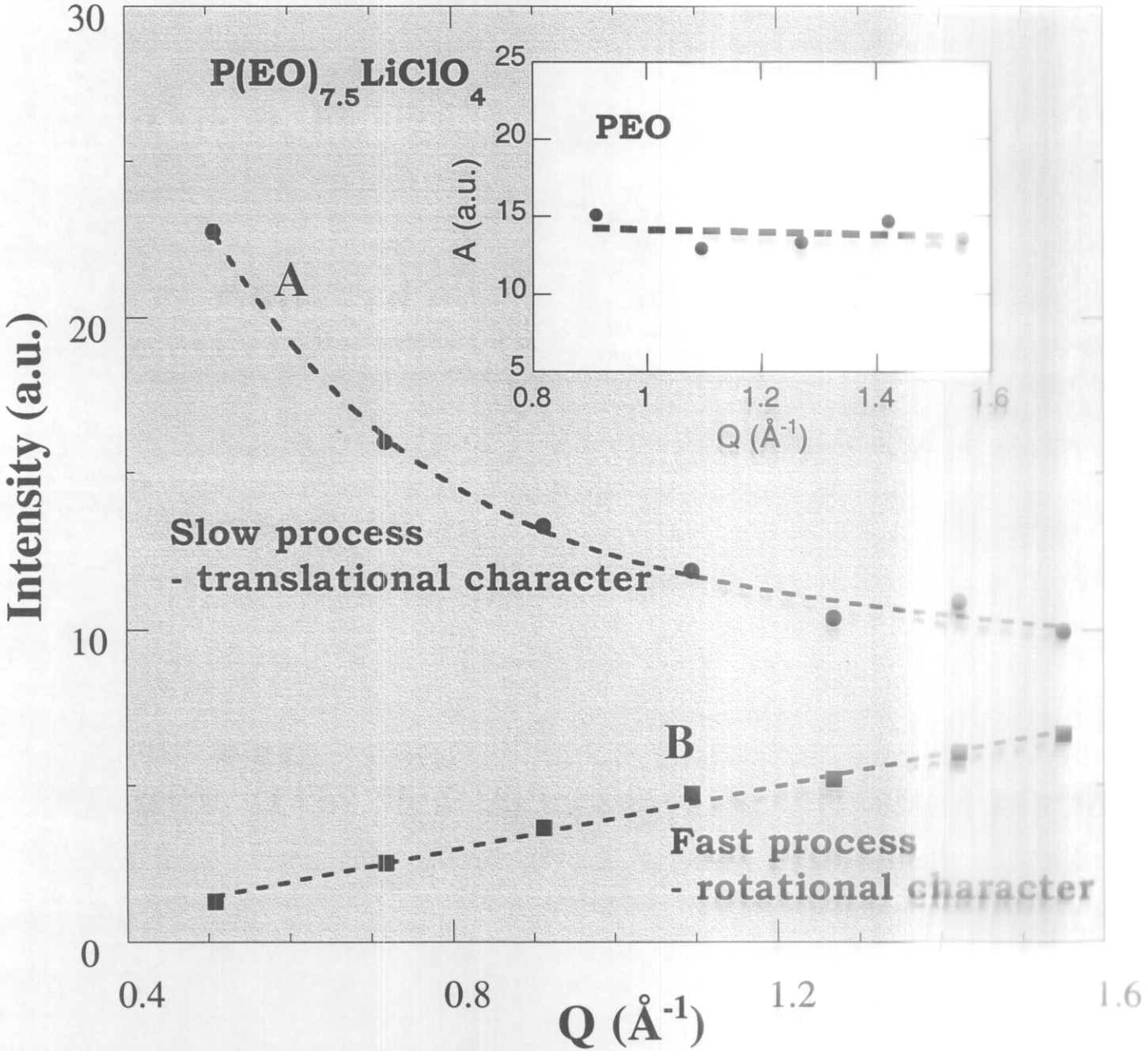
$$I(\omega) = A\delta(\omega) + B\varphi_{\tau}(\omega) + C; \quad \varphi_{\tau}(\omega) = \frac{1}{2\pi}\int \exp[-\left(\frac{t}{\tau}\right) + i\omega t]dt$$

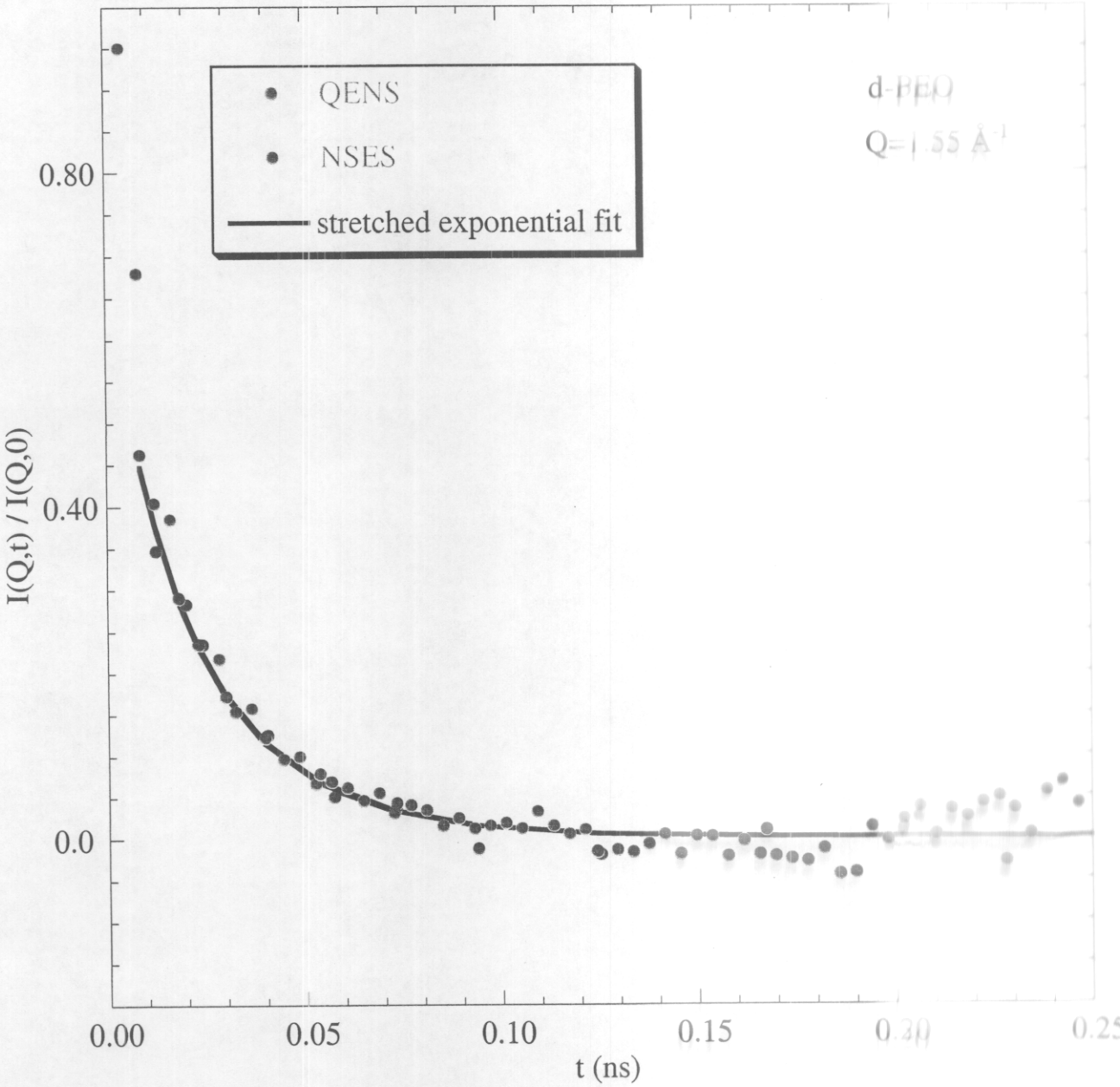
[G. Mao et al, Nature, 2000]

Inverse relaxation times:
PEO and $P(EO)_{7.5}LiClO_4$ electrolyte



Coefficients of the slow (A) and fast (B) relaxation processes




QENS
NSES
stretched exponential fit
d-PEO
Q=1.55 Å^{-1}
0.80
0.40
0.0
I(Q,t) / I(Q,0)
0.00
0.05
0.10
0.15
0.20
0.25
t (ns)

Molecular Dynamics of Polymer Electrolytes

Oleg Borodin and Grant D. Smith
University of Utah, Salt Lake City, UT

Quantum Chemistry based force field*

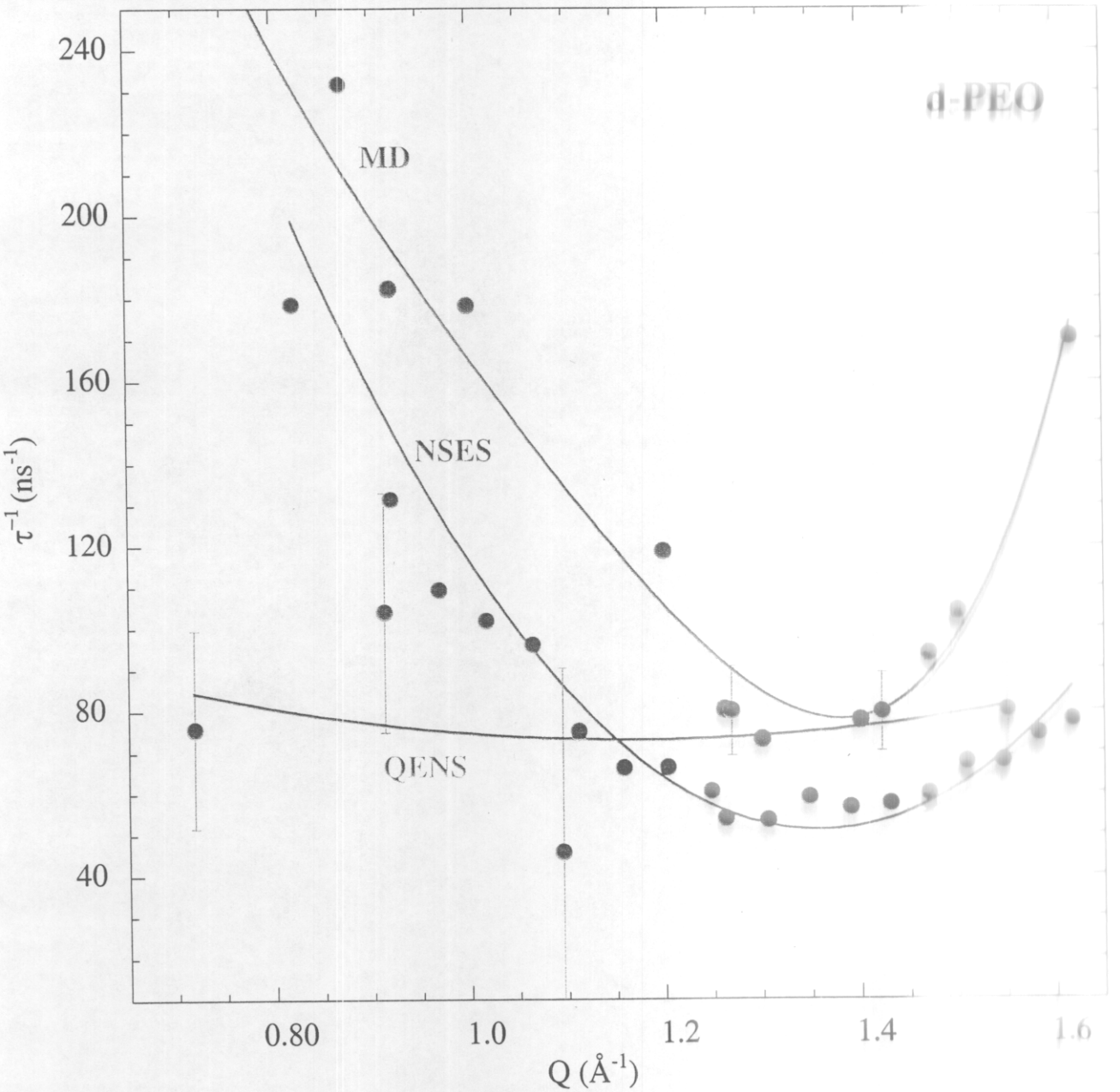
20 PEO chains of H-$[CH_2OCH_2]_{54}$-H

Initial configuration in gas phase with 100 Å box, shrunk to 43 Å and then temperature dropped to 348 K

Production runs performed for 4.5 ns in NVT ensemble

*G. D. Smith et al., J. Phys. Chem. 97, 12752 (1993)

Comparison of Neutron Scattering & Molecular Dynamics



[M.-L. Saboungi et al., Solid State Ionics (2001)]

Dynamics of Lithium Polymer Electrolytes

Pure PEO

Chain segments have liquid-like freedom, giving rise to diffusion with a translational character and a stretched-exponential (KWW) time behavior.

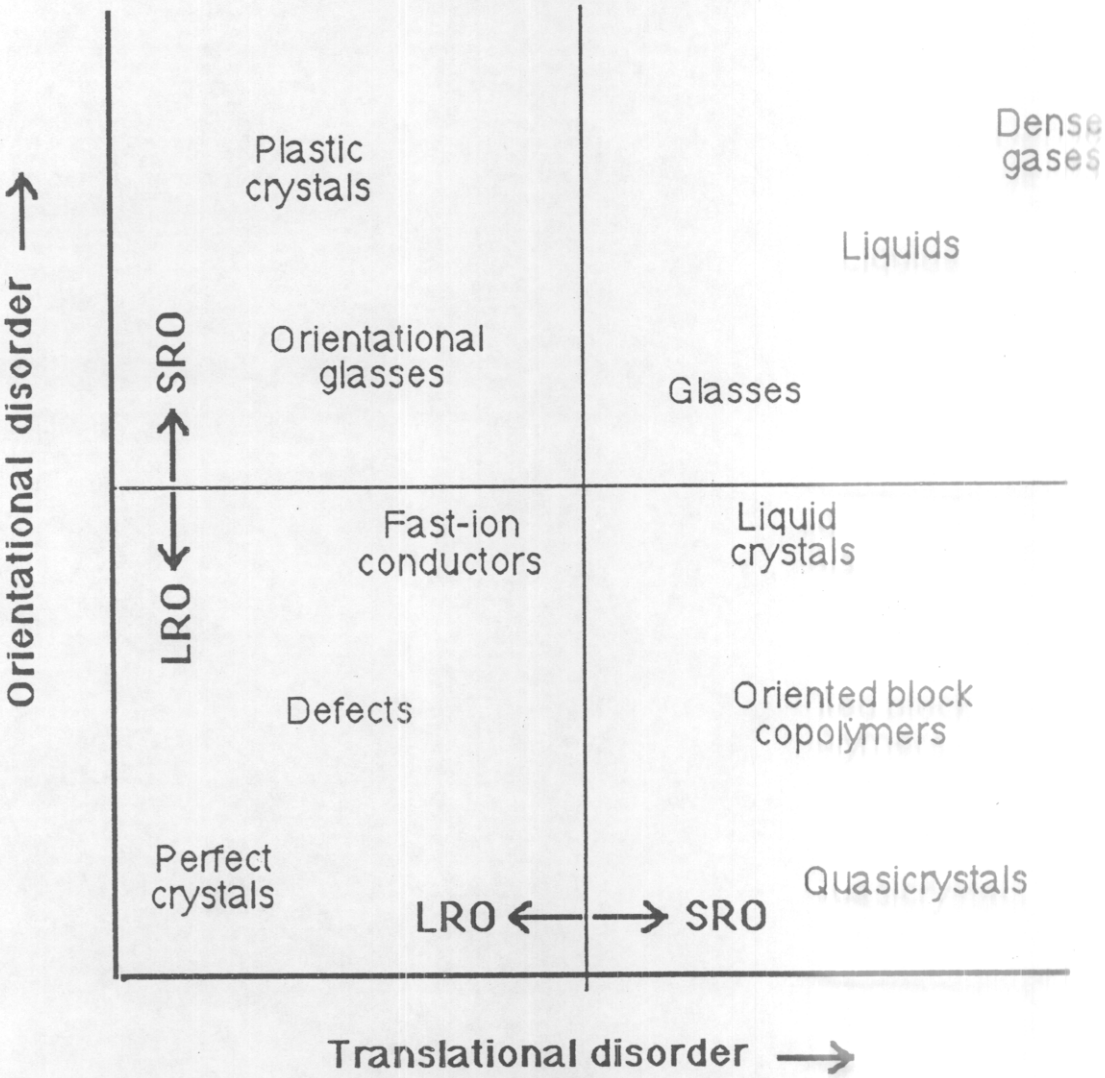
Lithium Polymer Electrolytes

The addition of salt to PEO results in the following changes:

- **The translational relaxation slows down dramatically due to increased rigidity arising from Li cross links**
- **A new fast process "skipping rope" is observed due to rotation of short polymer segments between Li cross links**

This dynamical scheme promotes the Li ionic conduction in amorphous regions of Li-PEO electrolytes.

TYPES OF ORDER AND DISORDER



Thanks to our collaborators

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Stephanie Pouget	Inst. Laue-Langevin, Grenoble, France
Guomin Mao	Now at Applied Materials, Inc., Sunnyvale, CA
Ricardo Fernandez-Perea	Now at CSIC, Madrid, Spain