

NMR and Raman Spectroscopy to Study the Structure and Dynamics of Glasses

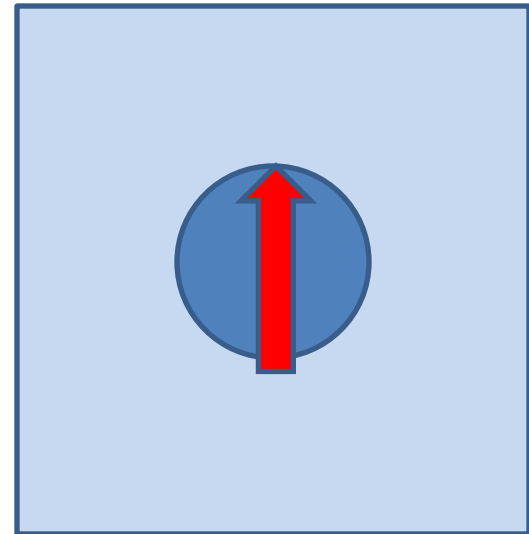
T. Egami

University of Tennessee
Oak Ridge National Laboratory

Nuclear Magnetic Resonance

- RF field screened by free electrons (Knight shift) and electric field gradient of the neighbors.
- Applied dc field modified by hyperfine field.
- Relaxation by free electrons (Korringa process) and spin-lattice interaction.

$$\Delta = \hbar\omega = \mu g H I$$



Nuclear Magnetic Resonance

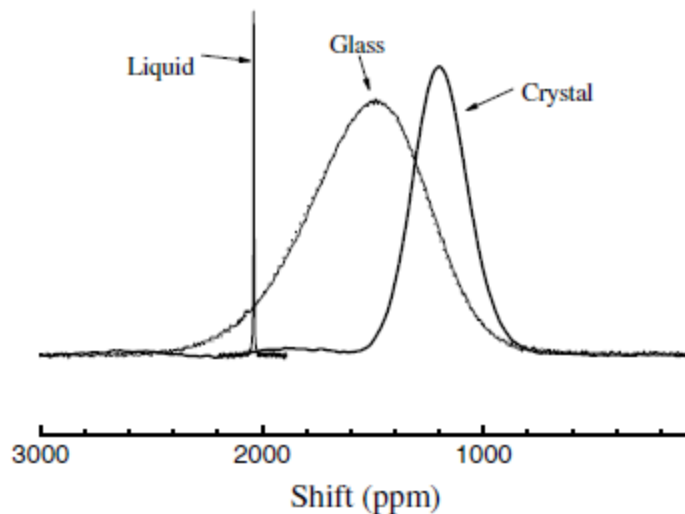
- Local structure
 - Knight shift
 - Electric field gradient
 - NQR
 - NMR Peak shape
 - Hyperfine field
- Dynamics
 - T_1 ; spin-lattice relaxation time
 - Diffusion; escaping the cage.
 - Dynamic heterogeneity.

Crossover of Microscopic Dynamics in Metallic Supercooled Liquid Observed by NMR

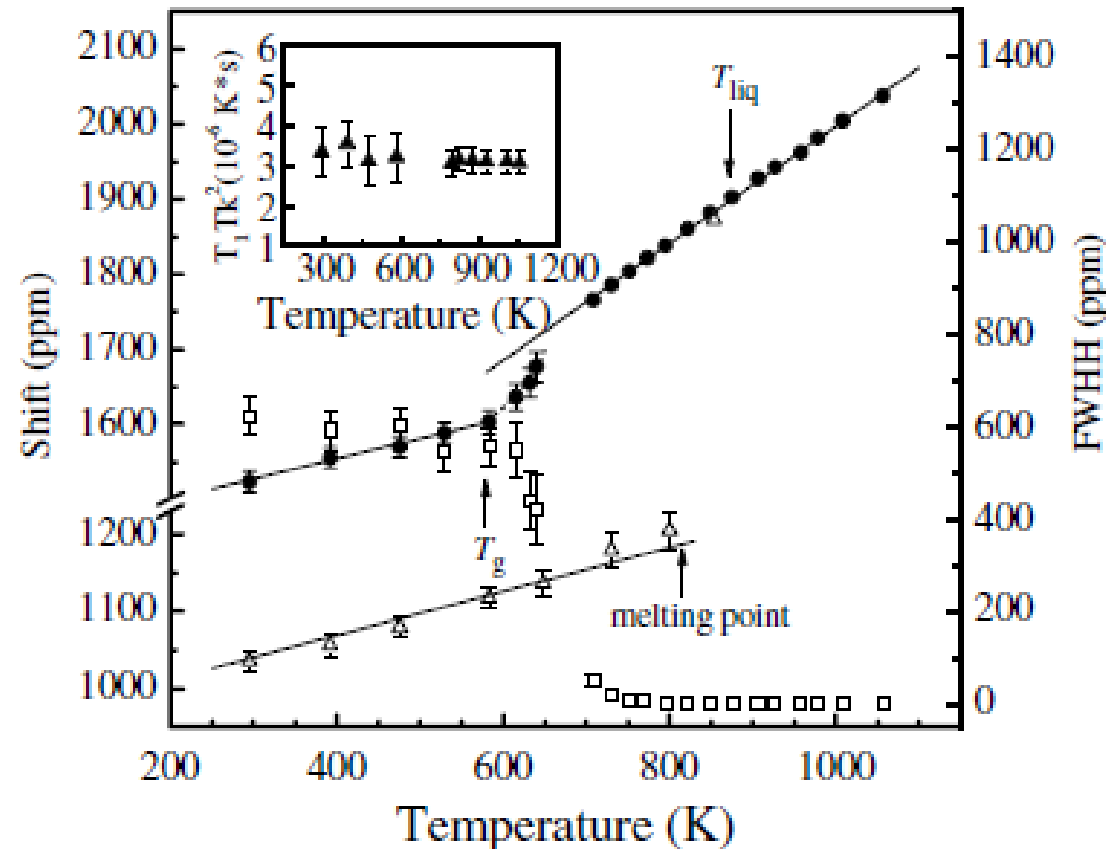
Lilong Li,¹ Jan Schroers,² and Yue Wu^{1,*}

¹*Department of Physics and Astronomy and Curriculum in Applied and Materials Sciences, University of North Carolina, Chapel Hill, North Carolina 27599-3255, USA*

²*W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125, USA*
(Received 7 July 2003; published 29 December 2003)



- Motion narrowing above T_g .



Local Symmetry around the Glass-Former Sites in Amorphous Metallic Alloys through Electric Quadrupole Effects

P. Panissod, D. Aliaga Guerra, A. Amamou, and J. Durand

Laboratoire de Structure Electronique des Solides, Université Louis Pasteur, F-67070 Strasbourg, France

and

W. L. Johnson

W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91109

and

W. L. Carter and S. J. Poon

*Edward L. Ginzton Laboratory, W. W. Hansen Laboratories of Physics,
Stanford University, Stanford, California 94305*

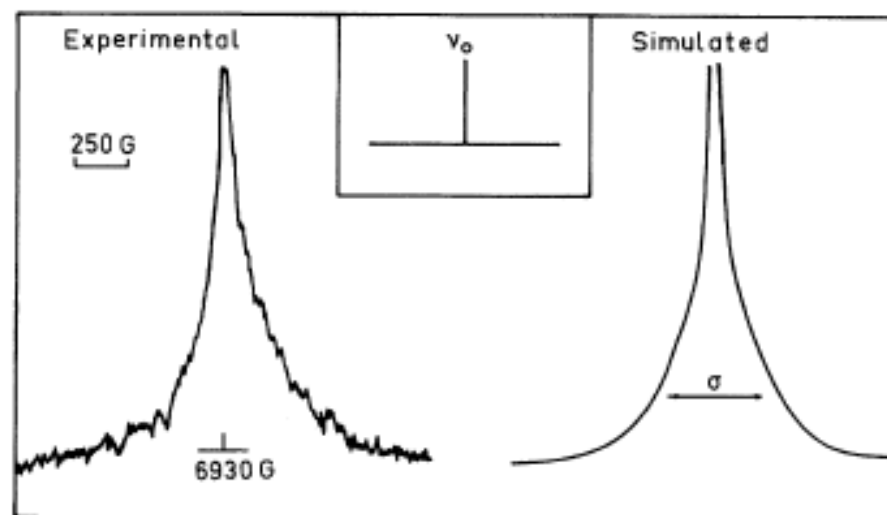


FIG. 1. Experimental ($T = 10^\circ\text{K}$) and simulated NMR spectra in $\alpha\text{-La}_{75}\text{Ga}_{25}$. Inset: unbrodened spectrum for cubic local symmetry ($\nu_Q = 0$; $\eta = 0$). $\nu_0 = \gamma_n H$ (Larmor frequency). For definition of ν_Q , η , and σ , see text.

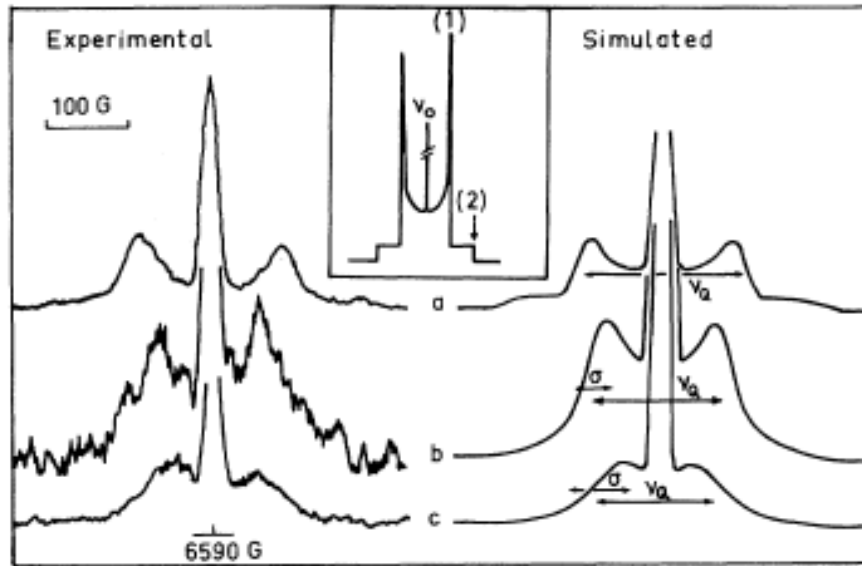


FIG. 2. Experimental ($T = 10^\circ\text{K}$) and simulated NMR spectra in (a) $c\text{-Mo}_2\text{B}$, (b) $\alpha\text{-Mo}_{70}\text{B}_{30}$, and (c) $\alpha\text{-Mo}_{48}\text{-Ru}_{32}\text{B}_{20}$. Inset: unbroadened "powder pattern" for cylindrical local symmetry ($\nu_Q \neq 0$; $\eta \neq 0$); (1) $\nu_0 + \frac{1}{2}\nu_Q$; (2) $\nu_0 + \nu_Q$.

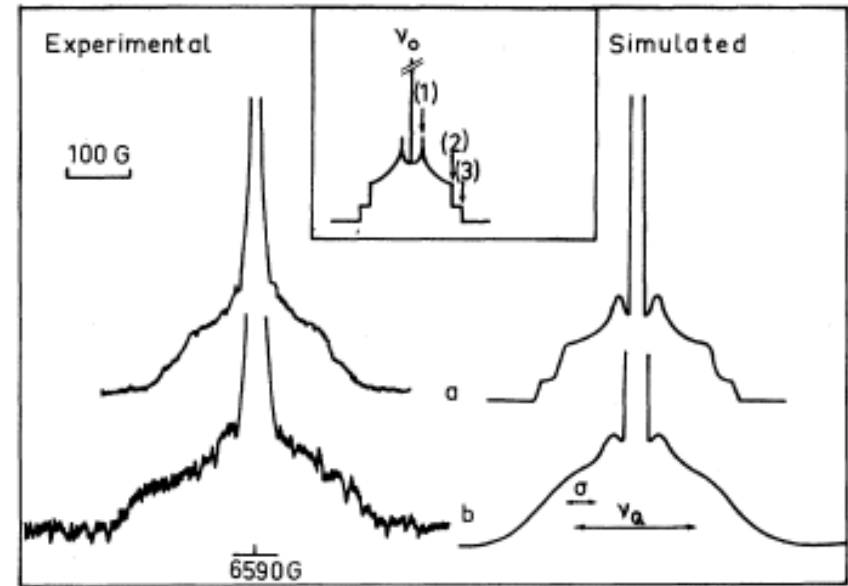


FIG. 3. Experimental ($T = 4.2^\circ\text{K}$) and simulated NMR spectra in (a) $c\text{-Ni}_3\text{B}$ and (b) $\alpha\text{-Ni}_{78}\text{P}_{14}\text{B}_8$. Inset: unbroadened "powder pattern" for nonuniaxial local symmetry ($\nu_Q \neq 0$; $\eta = 0.6$); (1) $\nu_0 + \frac{1}{2}\nu_Q(1 - \eta)$; (2) $\nu_0 + \frac{1}{2}\nu_Q(1 + \eta)$; (3) $\nu_0 + \nu_Q$.

- Local symmetry similar to the crystalline compounds.

Local boron environment in $\text{Ni}_{100-x}\text{B}_x$ metallic glasses: An NMR study

P. Panissod and I. Bakonyi*

Laboratoire de Magnetisme et de Structure Electronique des Solides (Laboratoire No. 306 associé au Centre National de la Recherche Scientifique), Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France.

R. Hasegawa

Corporate Research and Development Center, Allied Corporation, P.O. Box 1021R, Morristown, New Jersey 07960

(Received 4 April 1983)

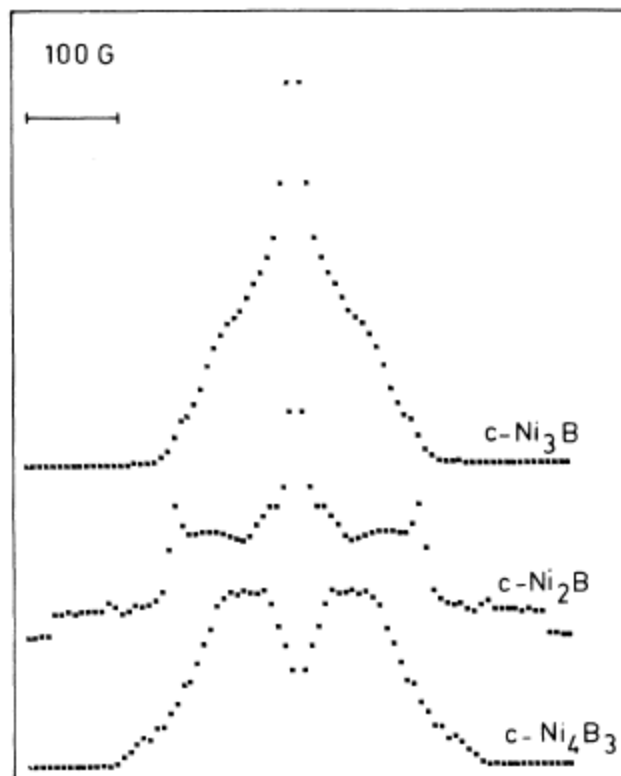


FIG. 3. Experimental NMR spectra in $c\text{-Ni}_3\text{B}$, $c\text{-Ni}_2\text{B}$, and $c\text{-Ni}_4\text{B}_3$ (orthorhombic) (Ref. 11).

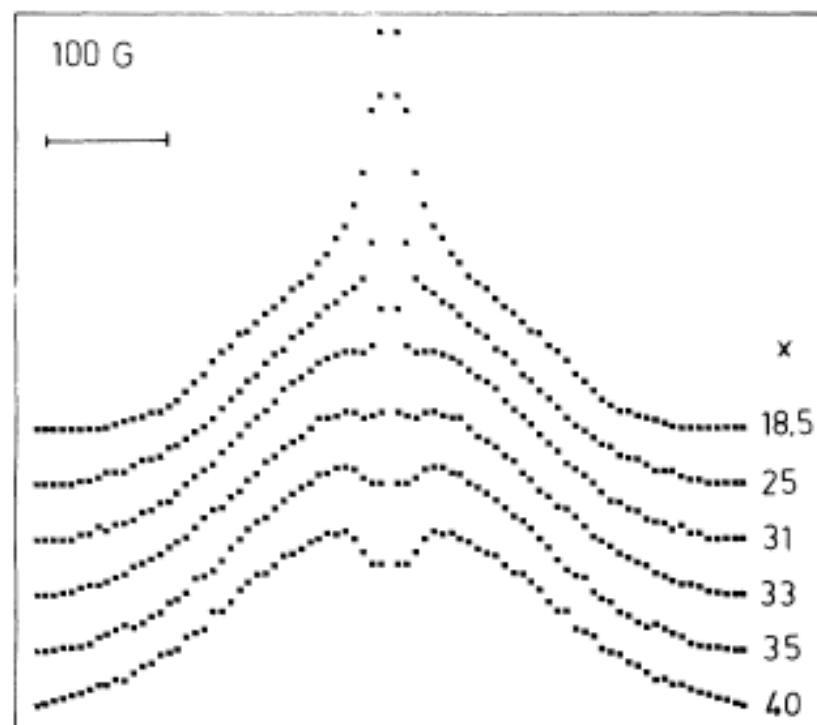
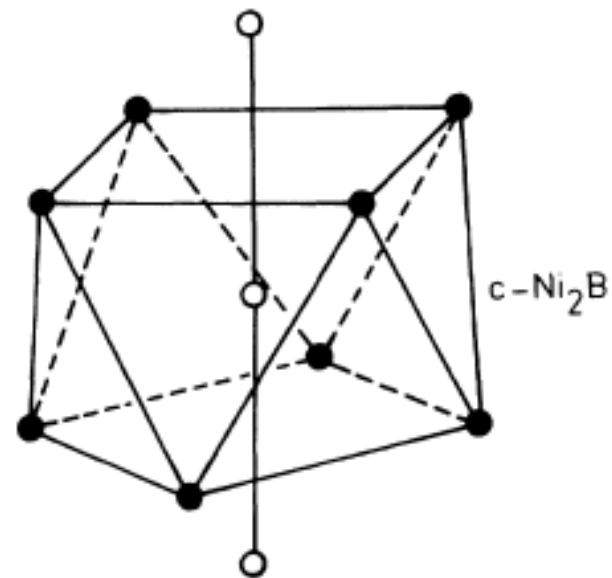
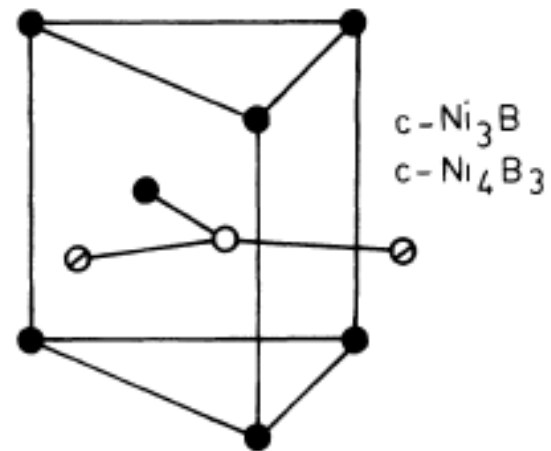


FIG. 2. Experimental NMR spectra in $a\text{-Ni}_{100-x}\text{B}_x$ samples. All spectra $T=4.2$ K except $x=18.5$ (100 K) (Ref. 11).



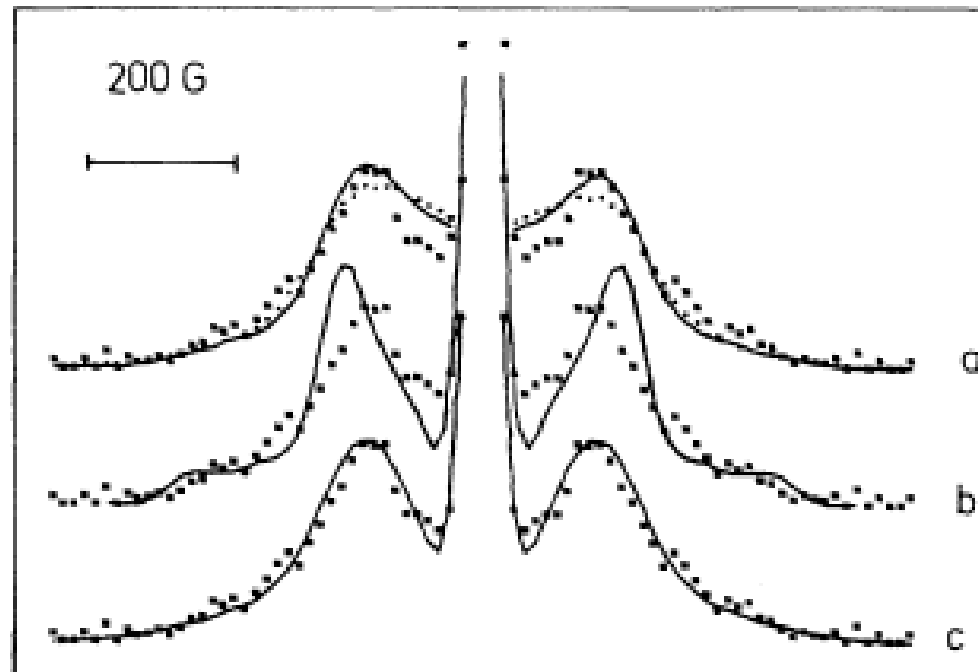
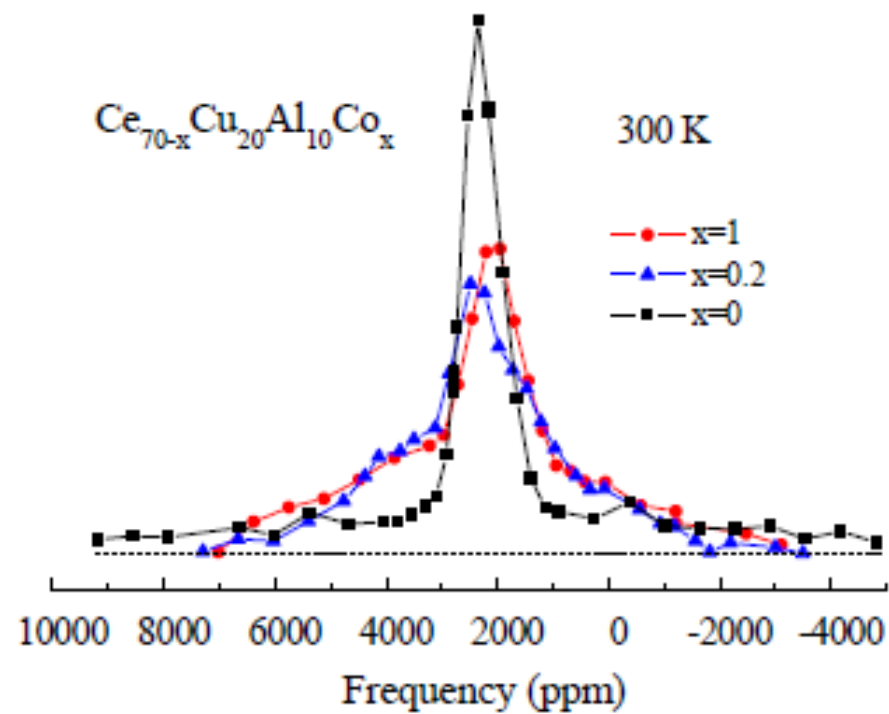
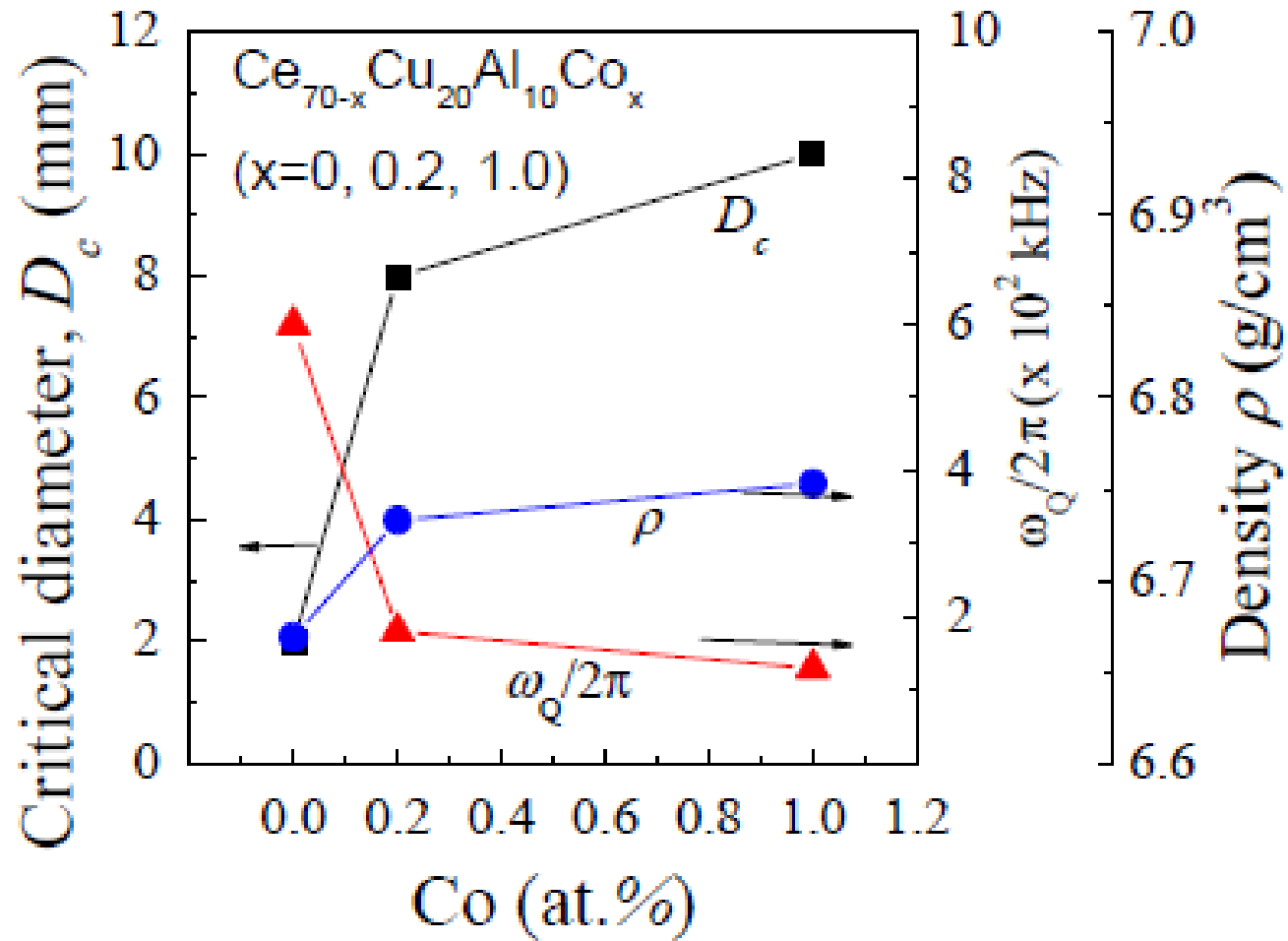


FIG. 12. B experimental spectrum in $a\text{-Mo}_{70}\text{B}_{30}$ (crosses). Curve a , simulated spectrum for $\bar{\nu}_Q = 420$ kHz, $\eta = 0$, $\sigma/\bar{\nu}_Q = 0.2$. (Dots: same except $\eta = 0$ and $\sigma > \bar{\nu}_Q = 0.25$ or $\eta = 0.2$ and $\sigma/\bar{\nu}_Q = 0.2$.) Curve b , B experimental spectrum in $c\text{-Mo}_2\text{B}$ compressed 10% along the horizontal axis. Curve c , same as b except 20% rms width distribution of the compression factor is added.



Correlation of atomic cluster symmetry and glass-forming ability of metallic glass

Xue kui Xi¹, Li long Li¹, Bo Zhang², Wei hua Wang², and Yue Wu^{1*}



- Smaller ω_Q means more spherical symmetry around Al. It could imply smaller atomic level stresses.

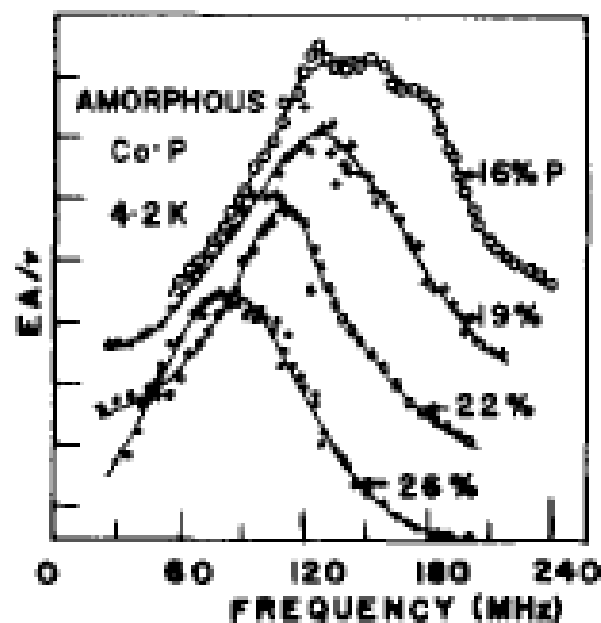


Fig.2 Hyperfine field distributions of ^{59}Co nuclei at various P compositions in amorphous Co-P alloys.

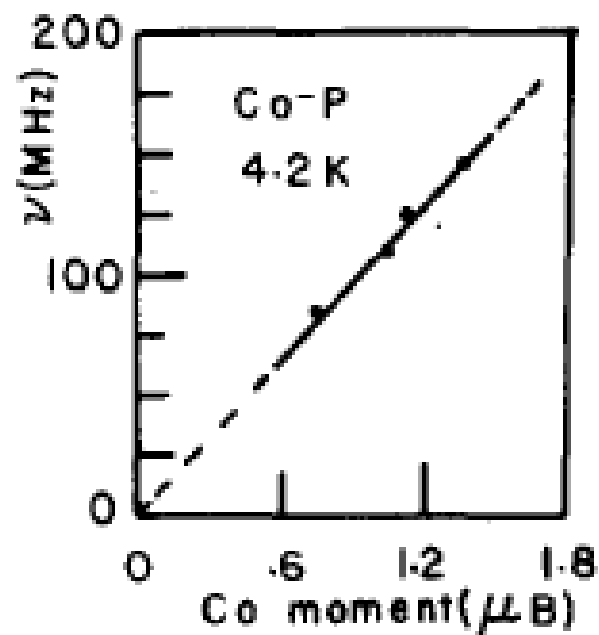


Fig.3 Variation of ^{59}Co NMR frequency with average Co moment in amorphous Co-P alloys.

Diffusion mechanisms in metallic supercooled liquids and glasses

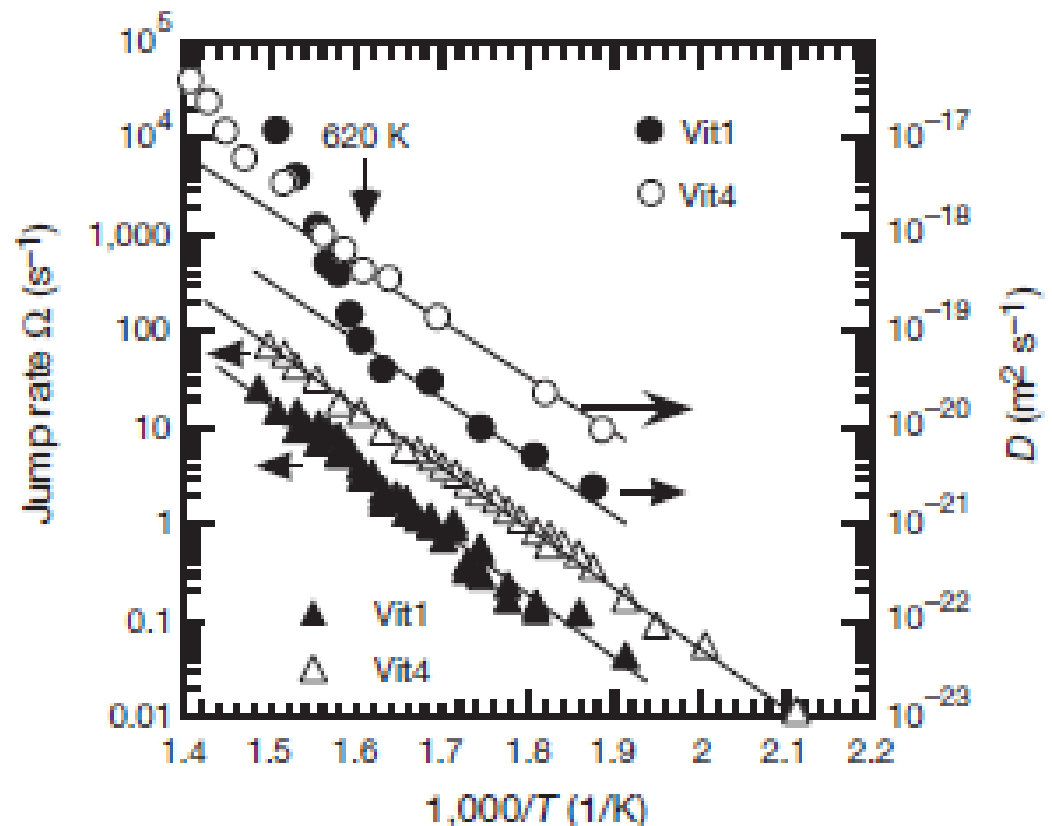
X.-P. Tang*, Ulrich Geyer†, Ralf Busch‡, William L. Johnson‡ & Yue Wu*

* Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255, USA

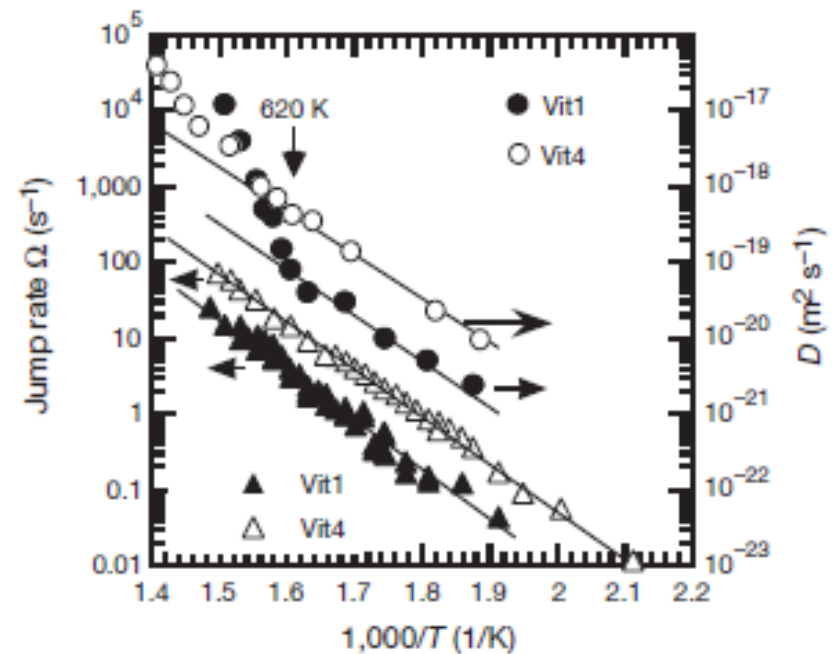
† Erstes Physikalisches Institut der Universität Göttingen, Bunsenstraße 9, D-37073 Göttingen, Germany

‡ W.M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125, USA

NATURE | VOL 402 | 11 NOVEMBER 1999 | www.nature.com



D of Be by He ion back scattering, jump rate by ^9Be NMR



- D shows a kink at T_g , but the jump rate does not.
- The kink at T_g is due to collective flow by other elements, not due to single jump of Be.

Nature of Nonexponential Loss of Correlation above the Glass Transition Investigated by Multidimensional NMR

K. Schmidt-Rohr and H. W. Spiess

Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500 Mainz, Germany

(Received 1 April 1991)

- Complex pulse sequence to extract detailed dynamic correlations, particularly the distribution in relaxation times.
- Non-exponential decay can be observed.

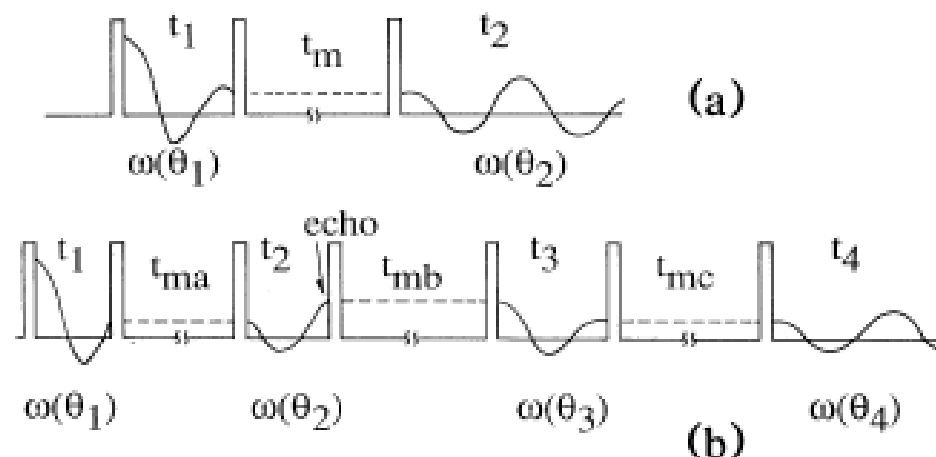
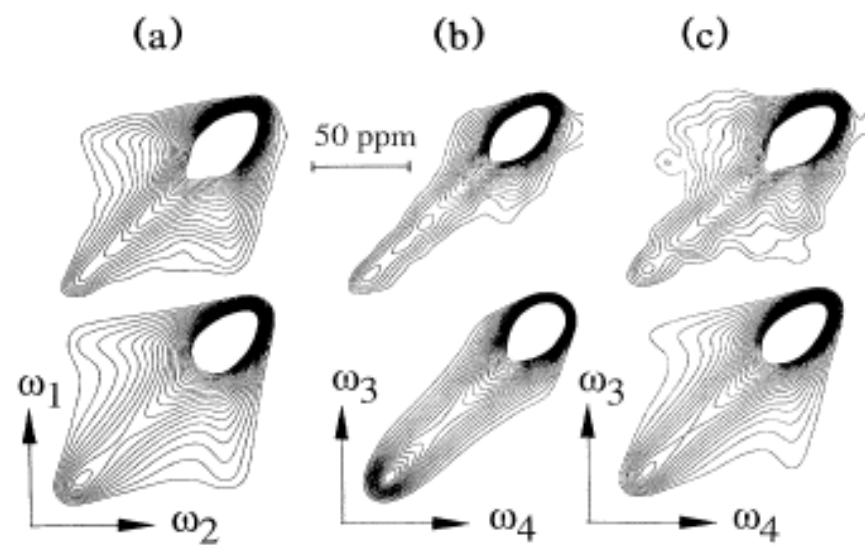
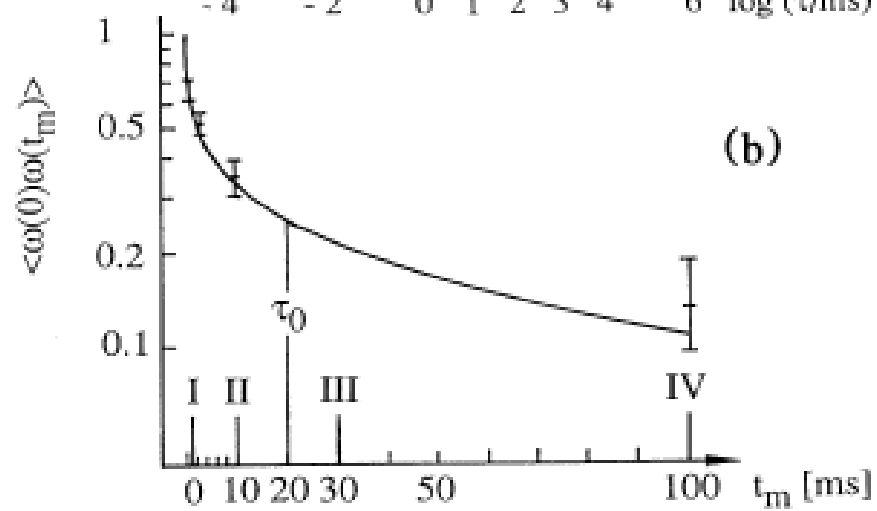
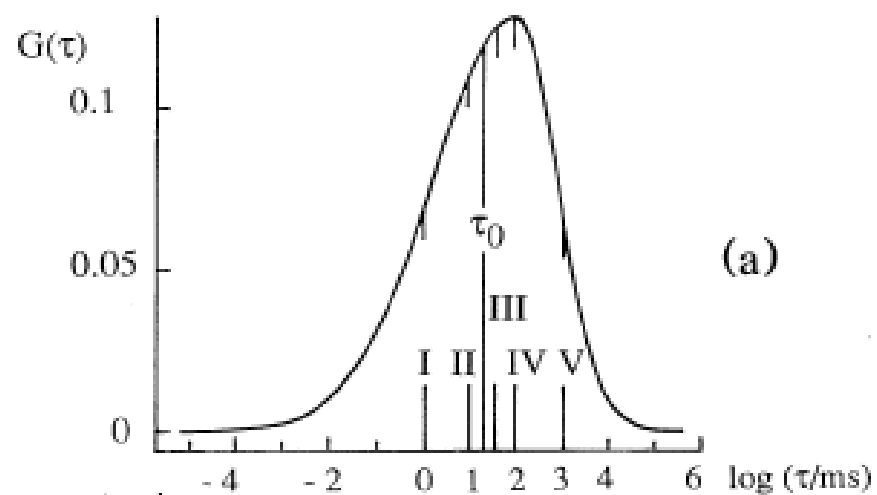


FIG. 1. Schematic pulse sequences for exchange NMR experiments: (a) 2D experiment, (b) 4D experiment. 90° pulses and a typical signal from an isotropic sample are indicated.



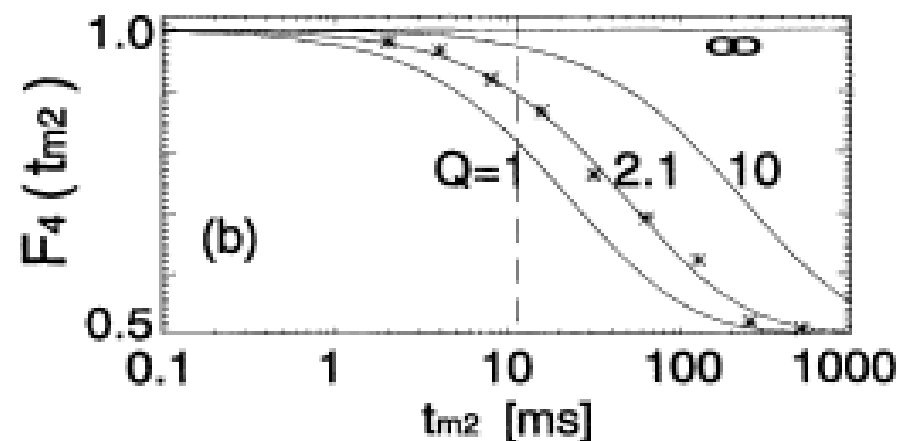
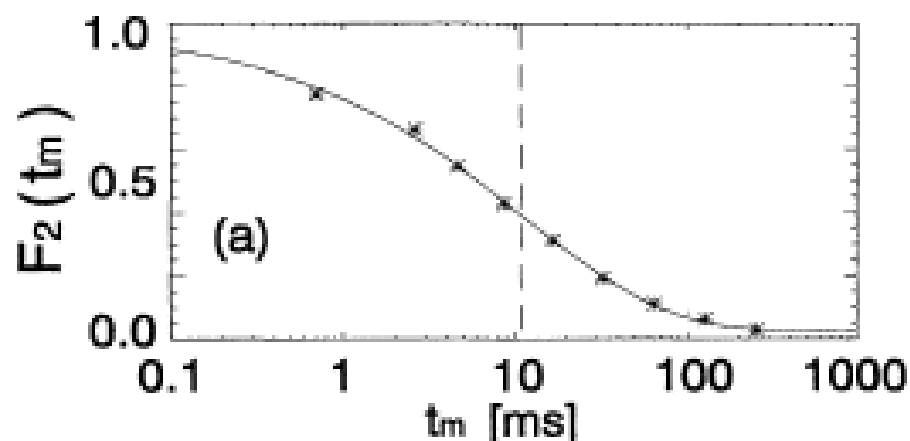
Rate Memory of Structural Relaxation in Glasses and Its Detection by Multidimensional NMR

A. Heuer,¹ M. Wilhelm,¹ H. Zimmermann,² and H. W. Spiess¹

¹Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

²Max-Planck-Institut für Medizinische Forschung, Jahnstrasse 29, D-69120 Heidelberg, Germany

(Received 5 June 1995)



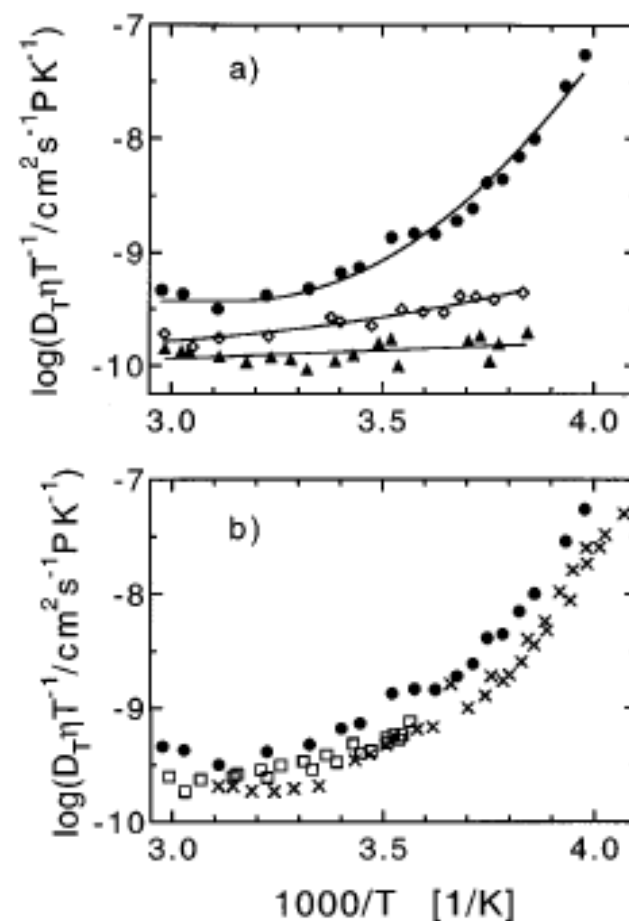
- $\beta = 0.52$.
- Distribution of relaxation times.

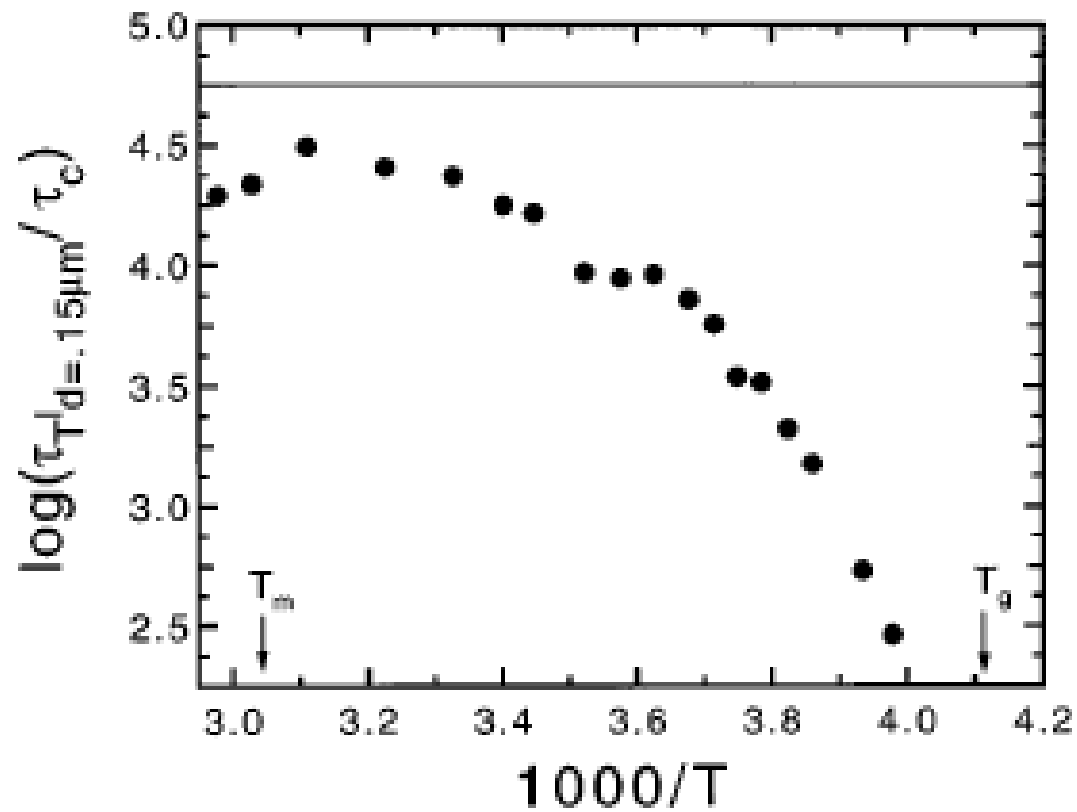
Enhanced translation of probe molecules in supercooled *o*-terphenyl: Signature of spatially heterogeneous dynamics?

Marcus T. Cicerone and M. D. Ediger

Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

- Deviation from S-E relationship.





- Ratio of translational relaxation time to rotational correlation time.

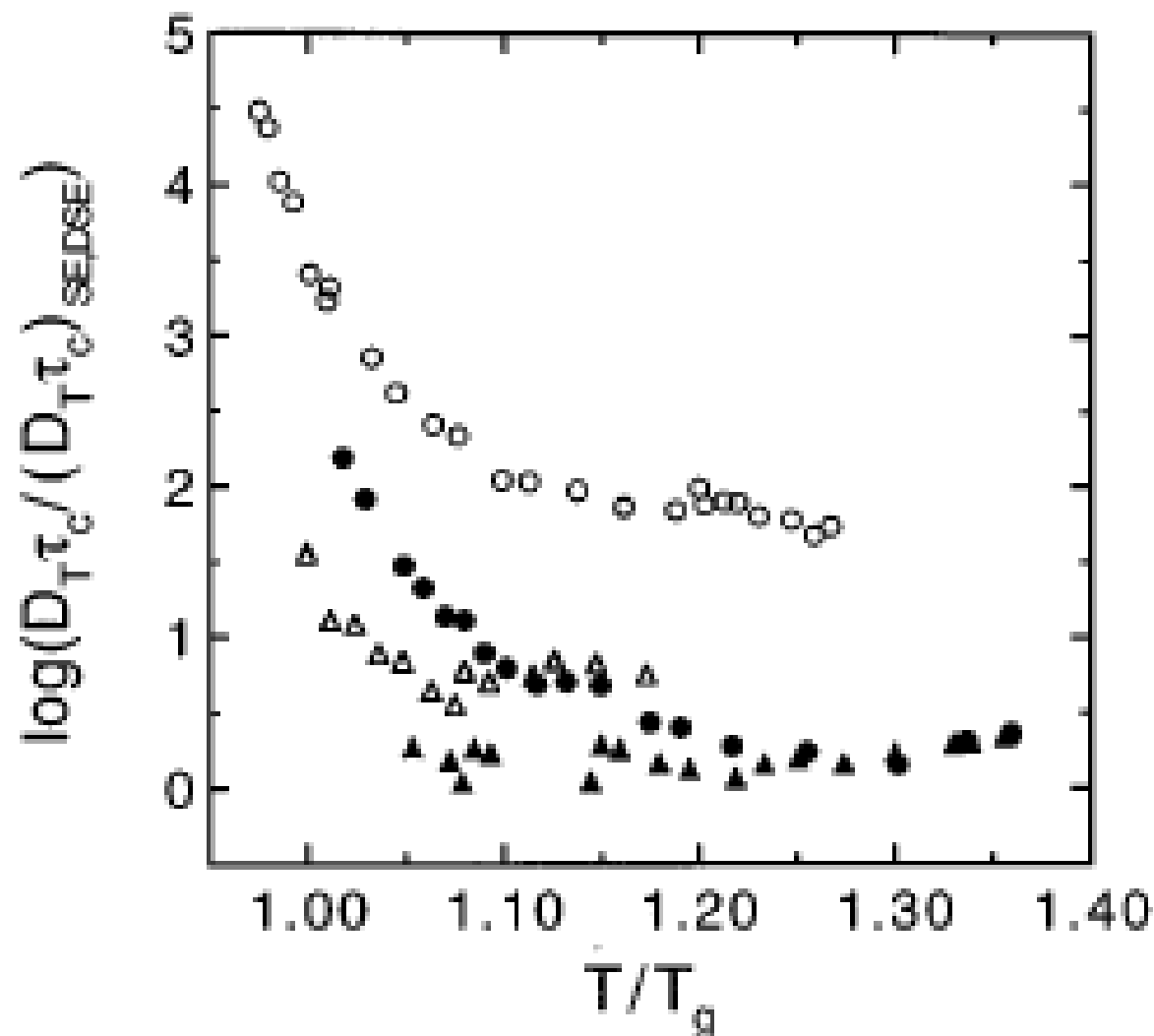


FIG. 8. Enhancement of $D_T \tau_c$ in OTP and polystyrene: (\blacktriangle) rubrene/OTP; (\bullet) tetracene/OTP; (\triangle) rubrene/polystyrene; (\circ) tetracene/polystyrene. D_T values are enhanced by up to 4 orders of magnitude as T_g is approached.

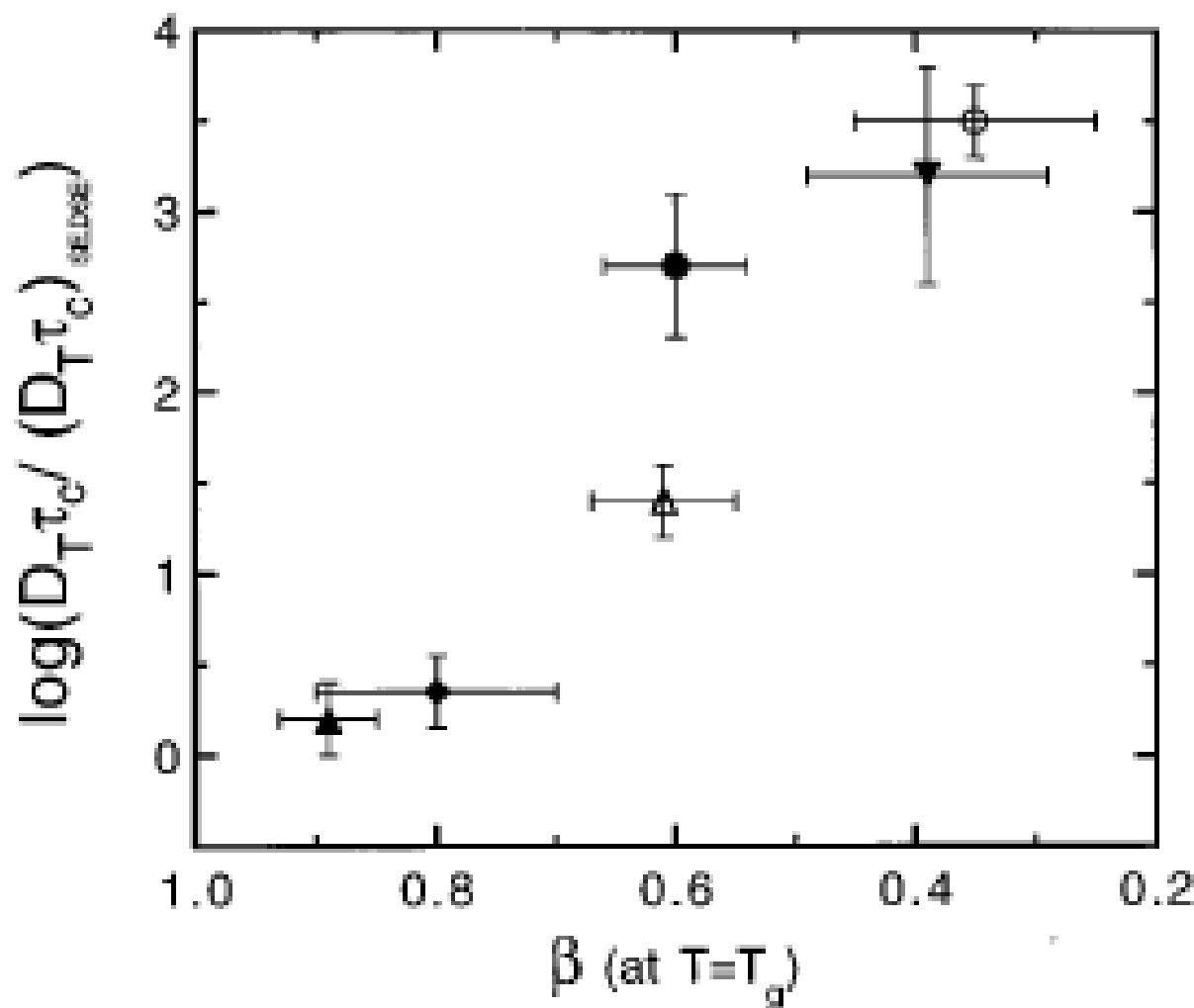
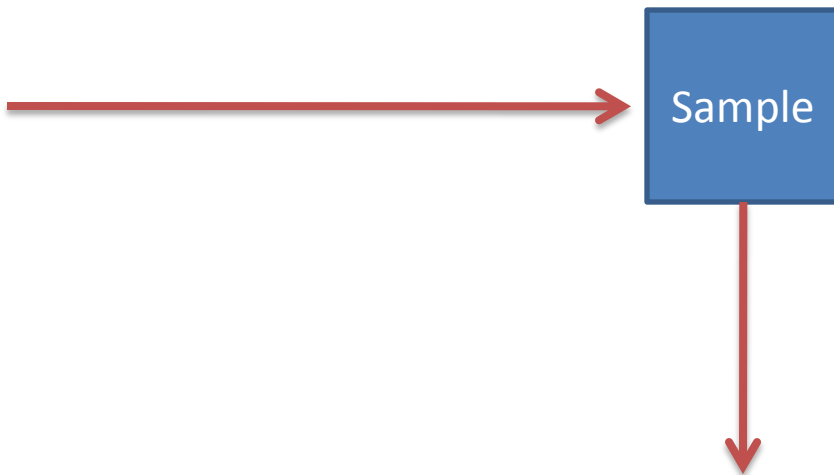


FIG. 9. Correlation of enhanced translation with KWW β parameter observed in probe rotation experiments: (\blacktriangle) rubrene/OTP; (\blacklozenge) BPEA/OTP; (\bullet) tetracene/OTP; (\blacktriangledown) anthracene/OTP; (\triangle) rubrene/polystyrene; (\circ) tetracene/polystyrene. Experimental values are evaluated at or extrapolated to T_g .

Raman Spectroscopy

- Discovered (Feb. 28, 1928) by Sir Venkata Raman of Calcutta Univ. (Nobel Prize 1930).

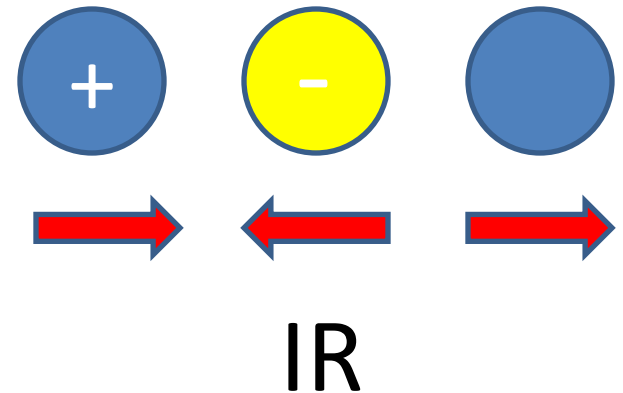


Professor, Indian Institute for Science, Bangalore (1933-48),
Director, Raman Inst. for Research, Bangalore (1948-70).

IR and Raman

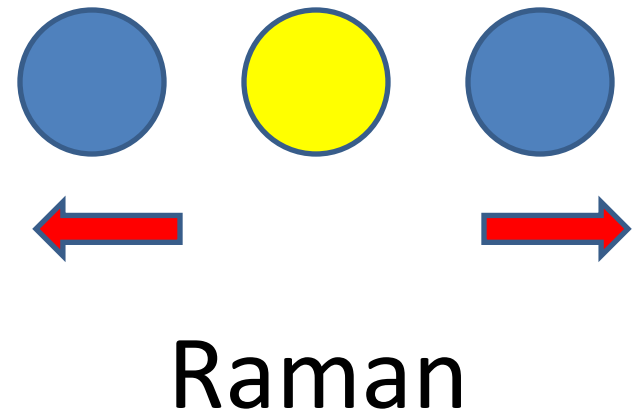
- IR mode absorbs IR photon.

$$\langle i | \mathbf{P}_{IR} | i \rangle \neq 0$$



- Raman mode scatters IR photon.

$$\langle i | \mathbf{P}_{Raman} | f \rangle \neq 0$$



Raman Selection Rule

- $Q = 0, nK$ for crystalline solids.
- All Q for amorphous solids because of incomplete umklapp. Thus obtains the phonon DOS.
- Thus Raman gives no information on the Q dependence; neutron or x-ray inelastic scattering does a better job.

THE NATURE OF BOSON PEAK IN RAMAN SCATTERING IN GLASSES

V.K. Malinovsky and A.P. Sokolov

Institute of Automation and Electrometry of Siberian Branch of the USSR Academy of Sciences,
630090, Novosibirsk, USSR

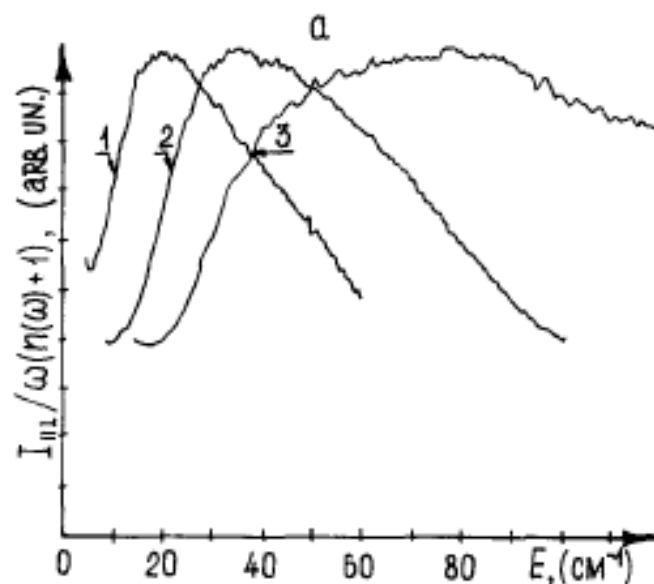


Fig. 1(a). Low-frequency Raman spectra of As_2S_8 - 1, $Bi_4Si_3O_{12}$ - 2, $La_2S_3^*Ga_2S_3$ - 3 glasses.

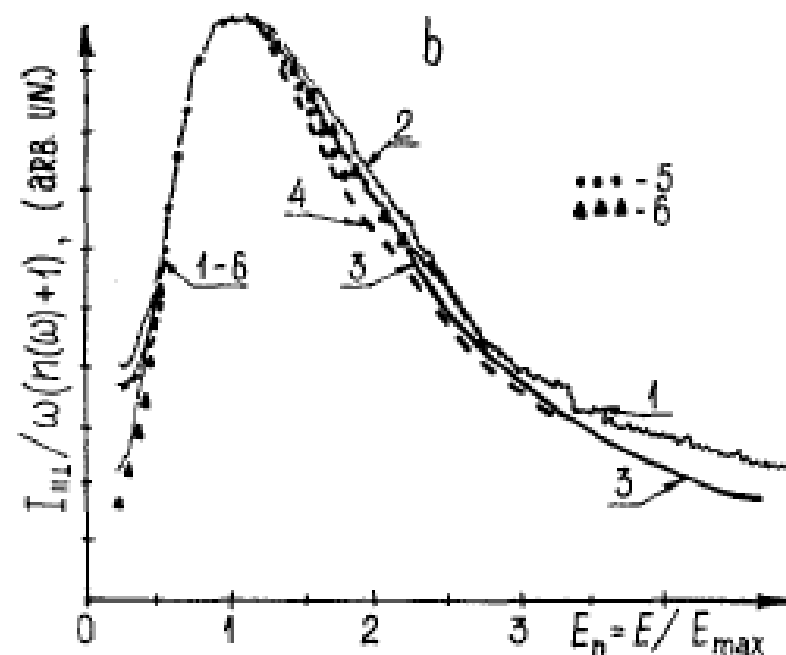


Fig. 1(b). Raman spectra of different glasses in a scale $E_n = E/E_{max}$: 1 - As_2S_3 ($E_{max} = 26 \text{ cm}^{-1}$), 2 - $Bi_4Si_3O_{12}$ (34 cm^{-1}), 3 - SiO_2 (52 cm^{-1}). In addition it is shown spectra: 4 - B_2O_3 (28 cm^{-1}) and 5 - $B_2O_3^*O$, 7 Li_2O (88 cm^{-1}) [8], GeS_2 (22 cm^{-1}) [9].

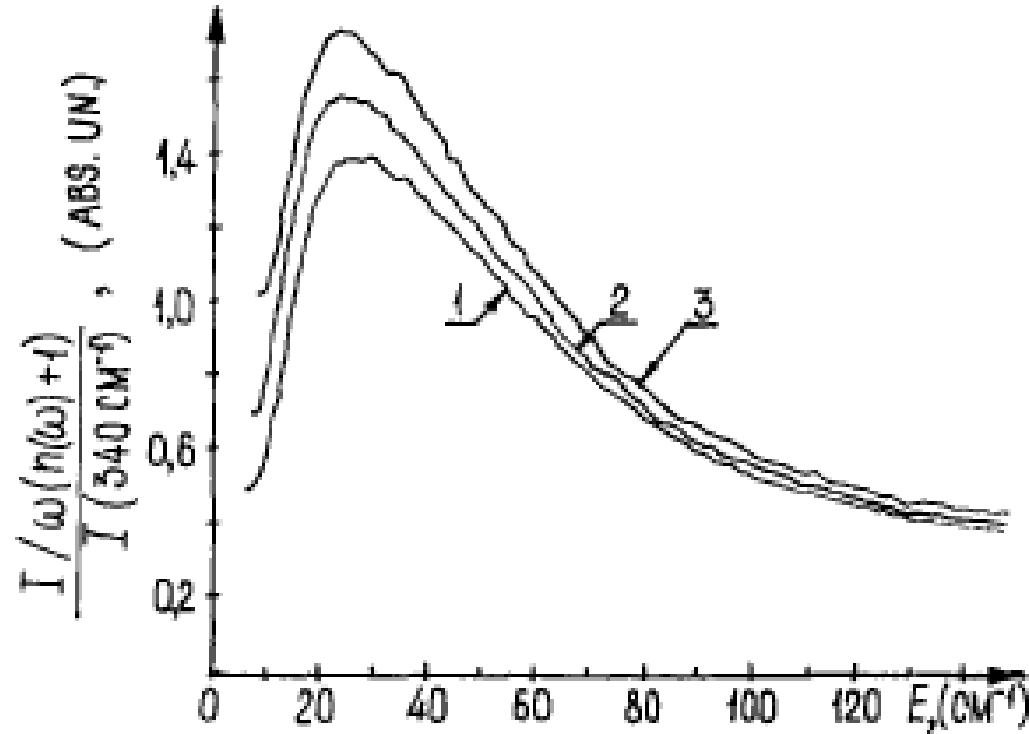
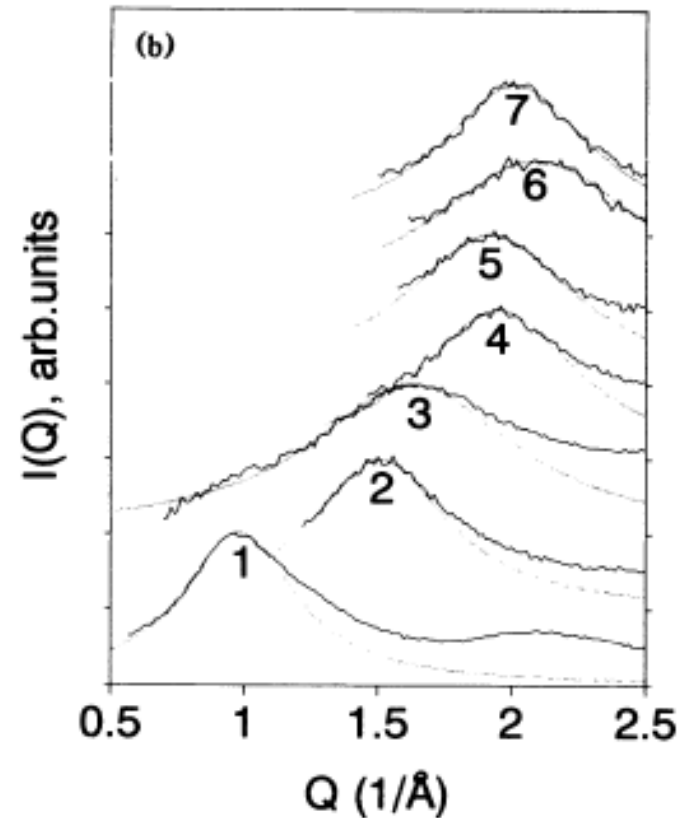
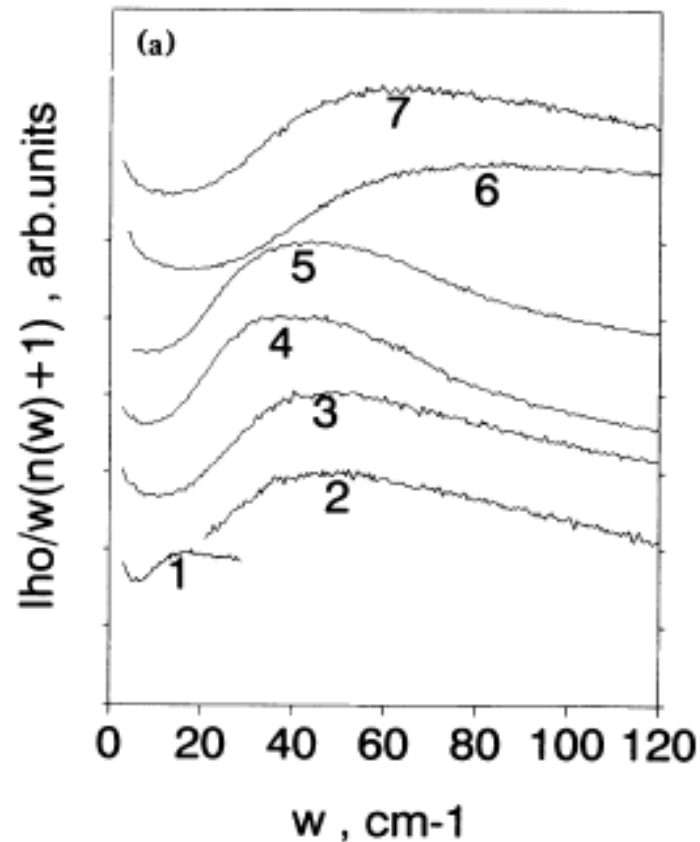


Fig. 4. Raman spectra of As_2S_3 glasses: 1 – well annealed sample, 2 – quenched in air from $T = 250^\circ\text{C}$, 3 – quenched in ice water from $T = 250^\circ\text{C}$.

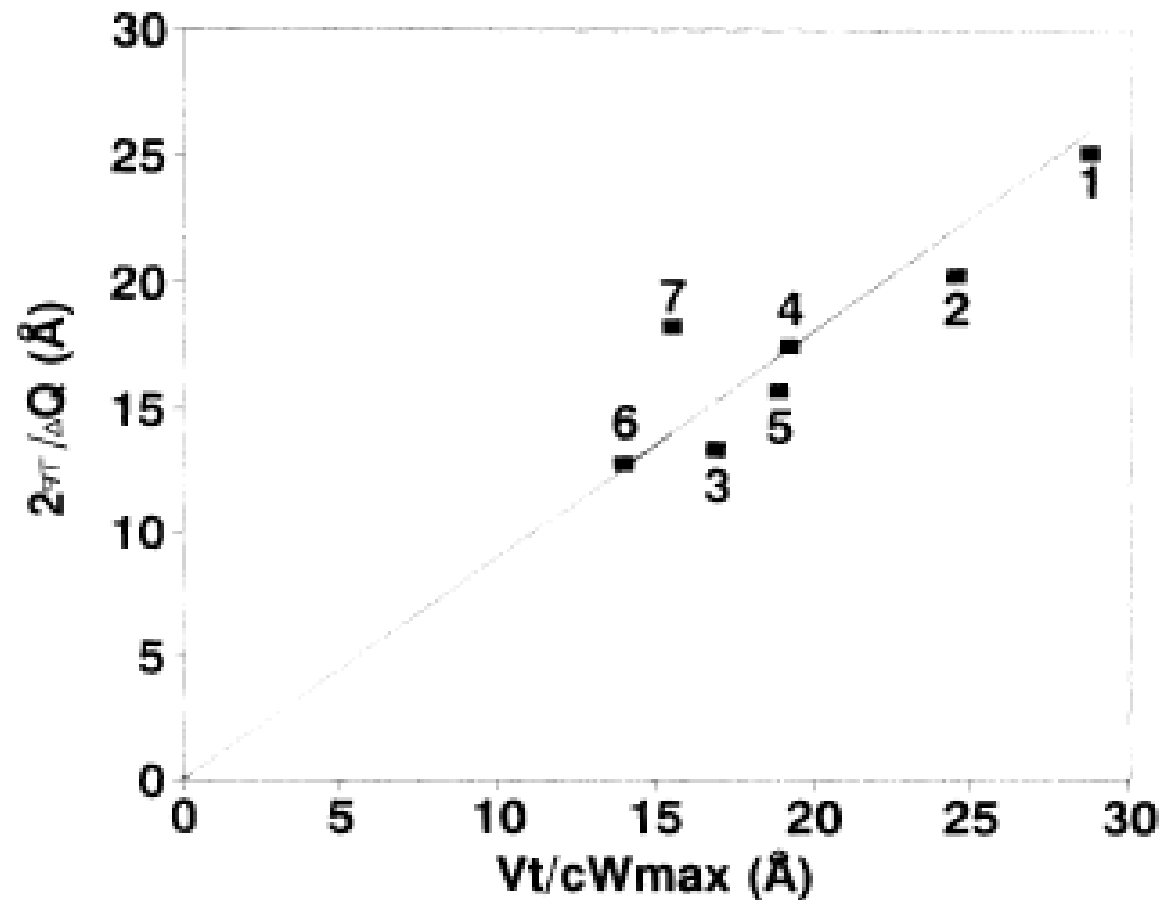
- Sensitivity to relaxation.

Medium-Range Order in Glasses: Comparison of Raman and Diffraction MeasurementsA. P. Sokolov,^(a) A. Kisliuk, M. Soltwisch, and D. Quitmann*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 1000 Berlin 33, Germany*

(Received 1 May 1992)



- Boson peak in many glasses.



- Connection to the diffraction peak.

A Unified Model for the Low-Energy Vibrational Behaviour of Amorphous Solids.

S. R. ELLIOTT(*)

*Laboratoire de Science des Matériaux Vitreux, Université de Montpellier II
Place Eugene Bataillon, 34095 Montpellier Cedex 5, France*

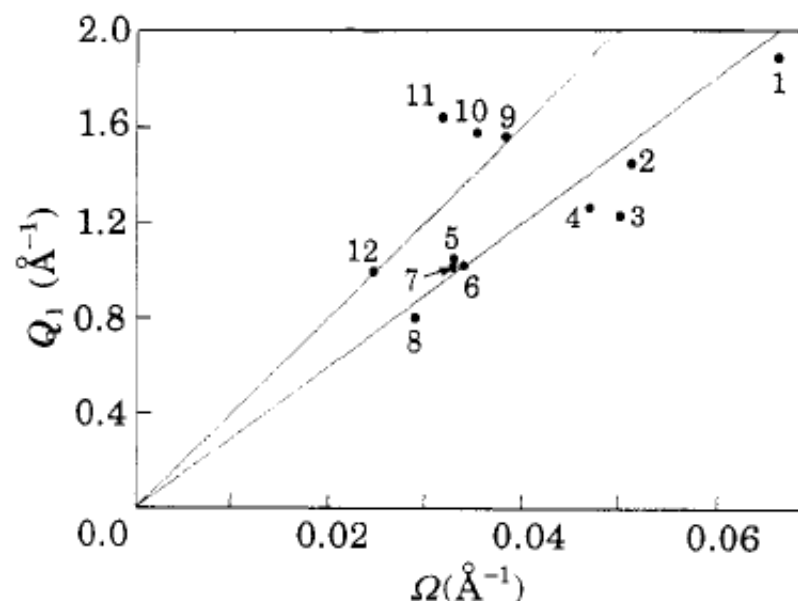


Fig. 1. - Plot of experimental values (points) for the FSDP position, Q_1 , vs. normalized boson peak frequency, $\Omega = v_0 c / v_s$ (v_0 in cm^{-1}) for a number of amorphous solids [25]; the straight lines are theoretical predictions of the model with gradients of 30 and 40. 1) Ge; 2) Se; 3) As_2Se_3 ; 4) As_2S_3 ; 5) GeS_2 ; 6) SiSe_2 ; 7) GeSe_2 ; 8) $\text{AgI-AgO-B}_2\text{O}_3$; 9) SiO_2 ; 10) BeF_2 ; 11) B_2O_3 ; 12) PMMA.

Boson peak in alkaline borate glasses: Raman spectroscopy, neutron scattering, and specific-heat measurements

G. D'Angelo,¹ G. Carini,¹ C. Crupi,² M. Koza,³ G. Tripodo,¹ and C. Vasi²

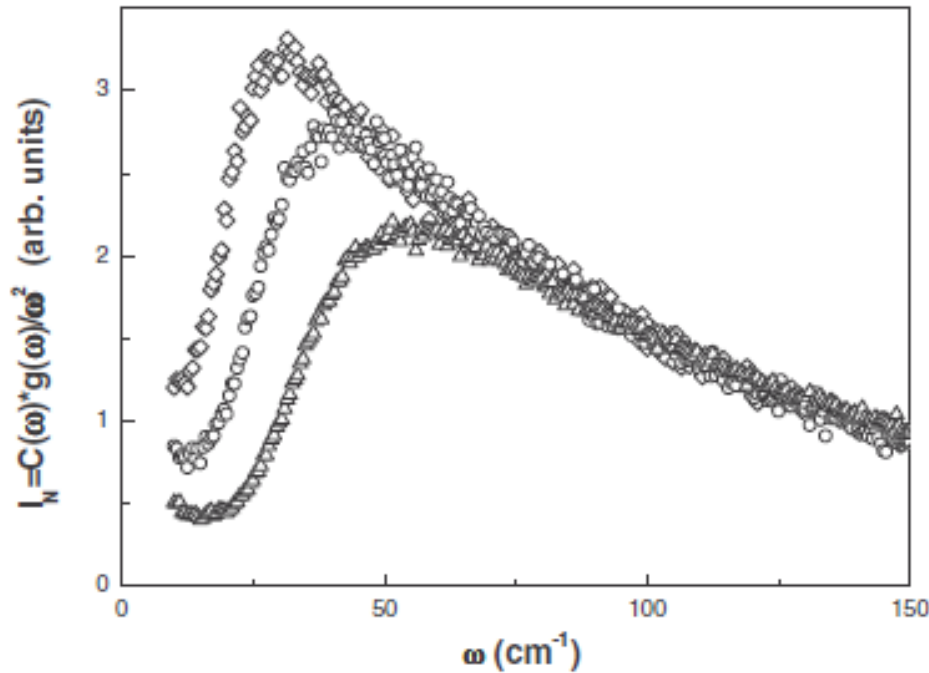


FIG. 2. Normalized Raman spectra of lithium (Δ), potassium (\circ), and cesium (\diamond) borate glasses in the BP region.

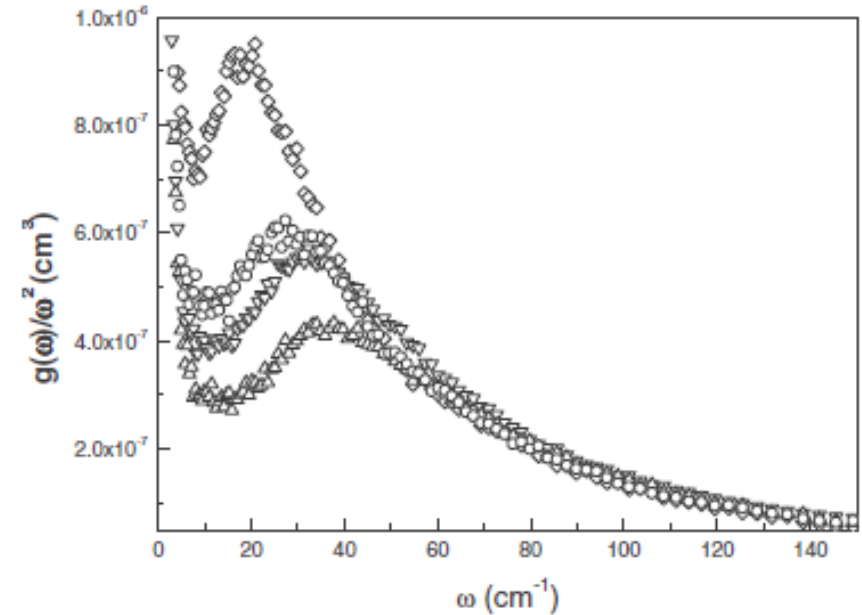


FIG. 3. Vibrational density of states $g(\omega)/\omega^2$ as a function of frequency for lithium (Δ), sodium (∇), potassium (\circ), and cesium (\diamond) borate glasses at the composition $x=0.14$.

- Raman and neutron data

Neutron scattering evidence on the nature of the boson peak

U Buchenau¹, A Wischnewski¹, M Ohl¹ and E Fabiani²

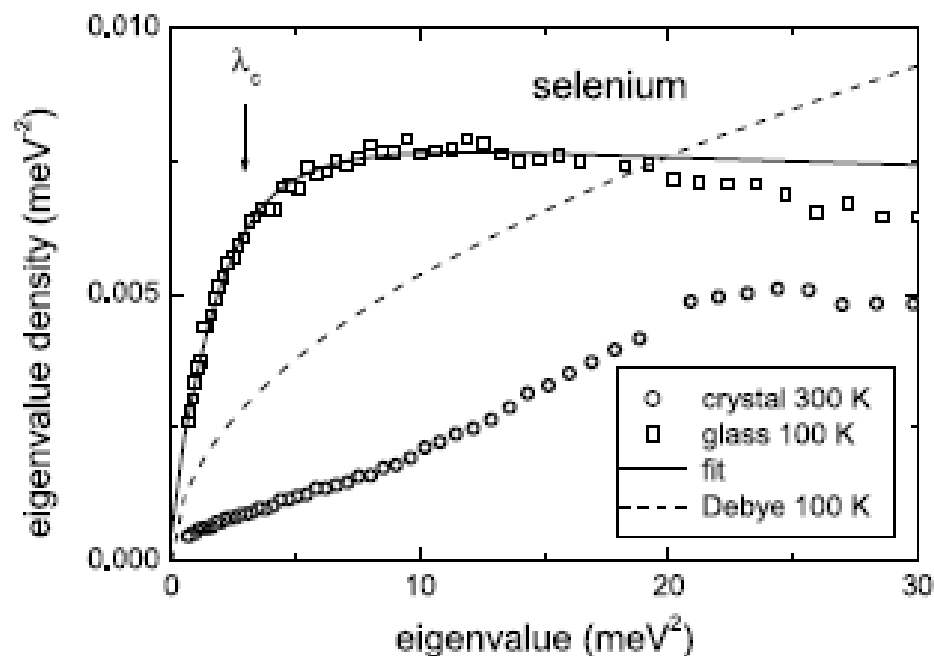


Figure 3. Eigenvalue density in crystalline and glassy selenium [25]. The continuous line is a fit in terms of equation (4); the dashed line shows the sound-wave fraction at 100 K according to the Debye model. The arrow denotes the fitted crossover eigenvalue λ_c from sound waves to excess modes.

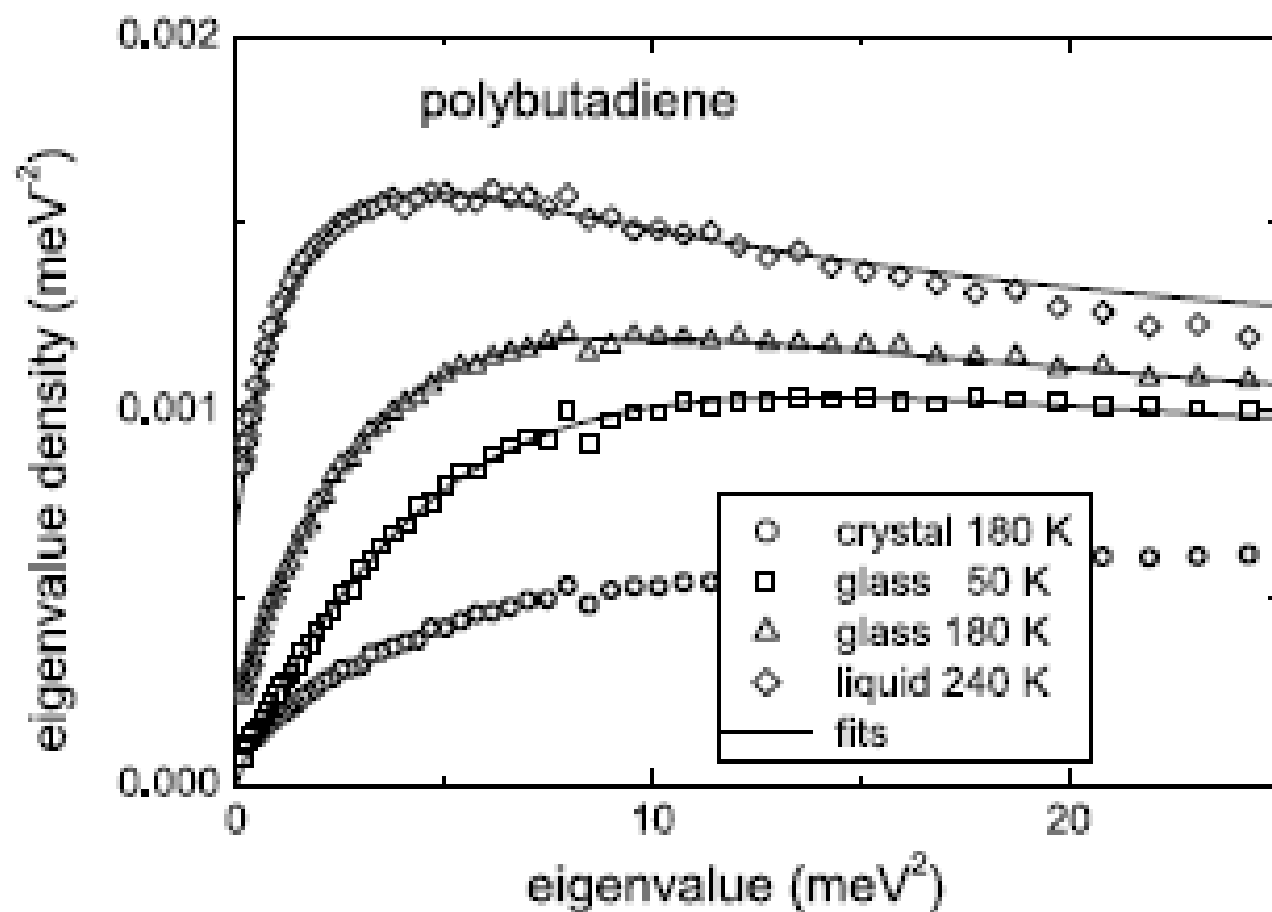
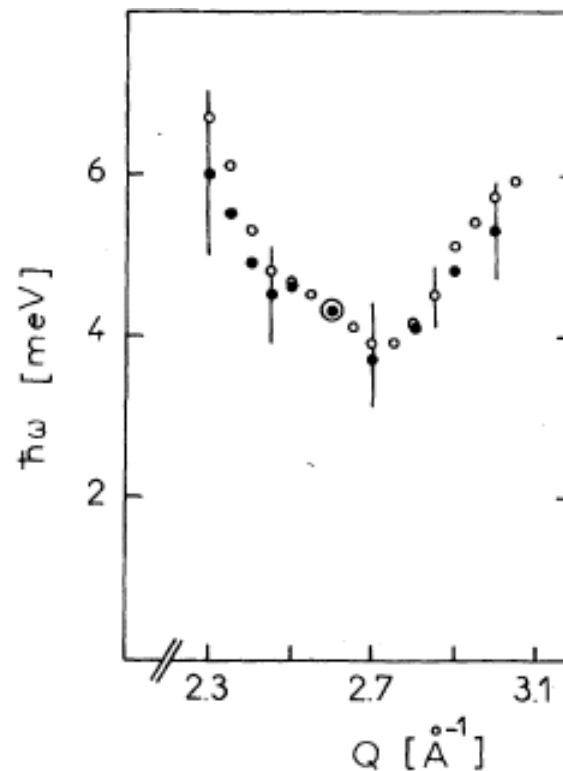


Figure 4. Eigenvalue density in crystalline, glassy and liquid polybutadiene [26]. Lines are fits in terms of equation (4).

Experimental Investigation of the Dispersion of Collective Density Fluctuations near Q_p in a Metallic Glass

J.-B. Suck^(a)

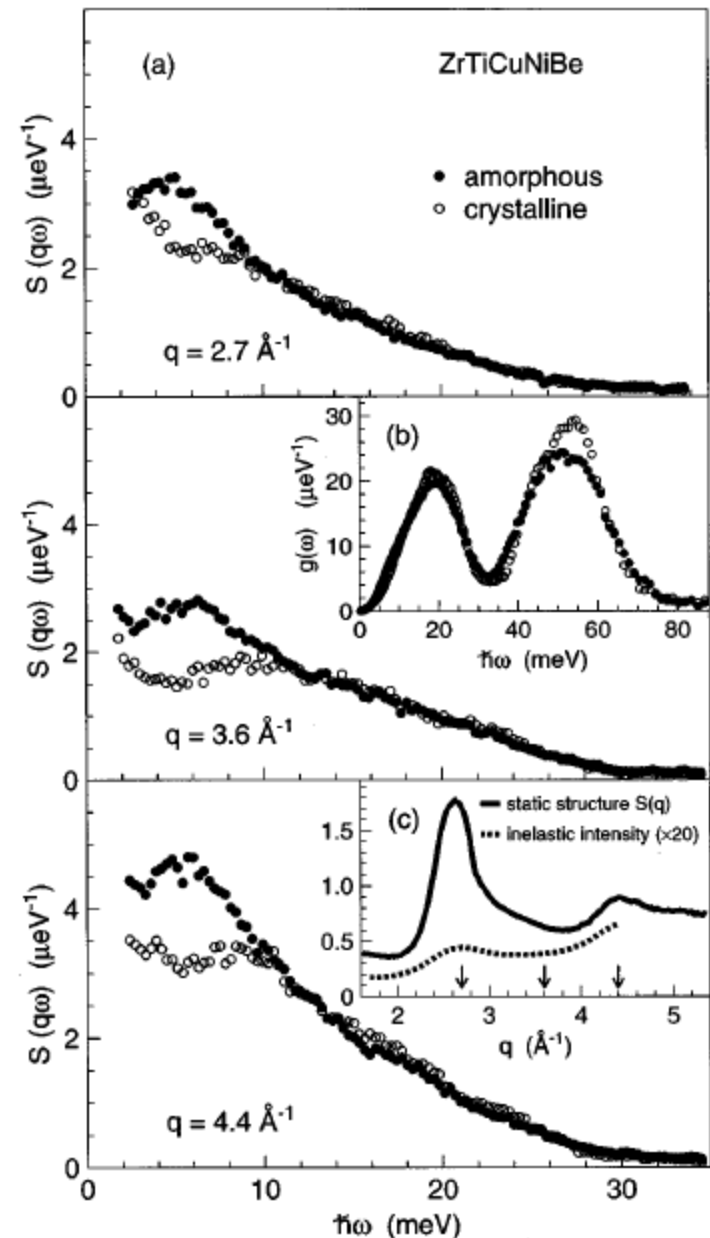
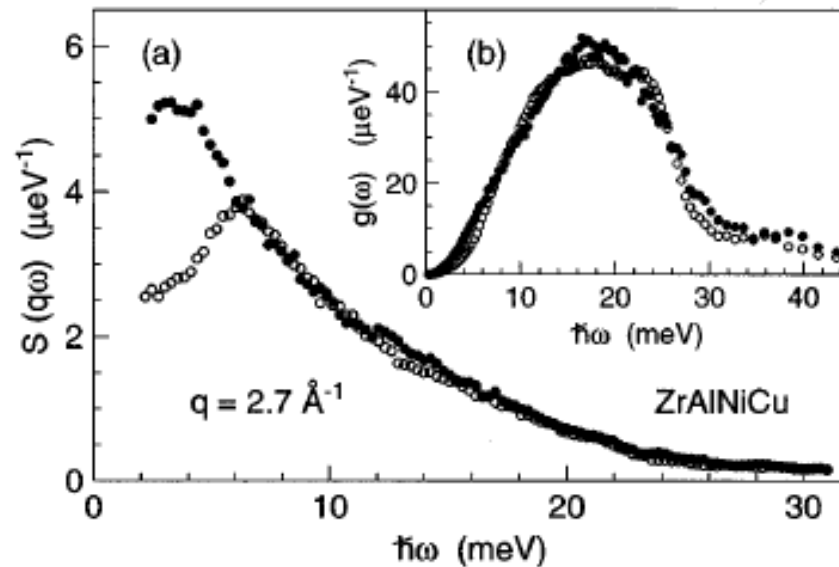


- Dispersion minimum at the peak of $S(Q)$.

Harmonic behavior of metallic glasses up to the metastable melt

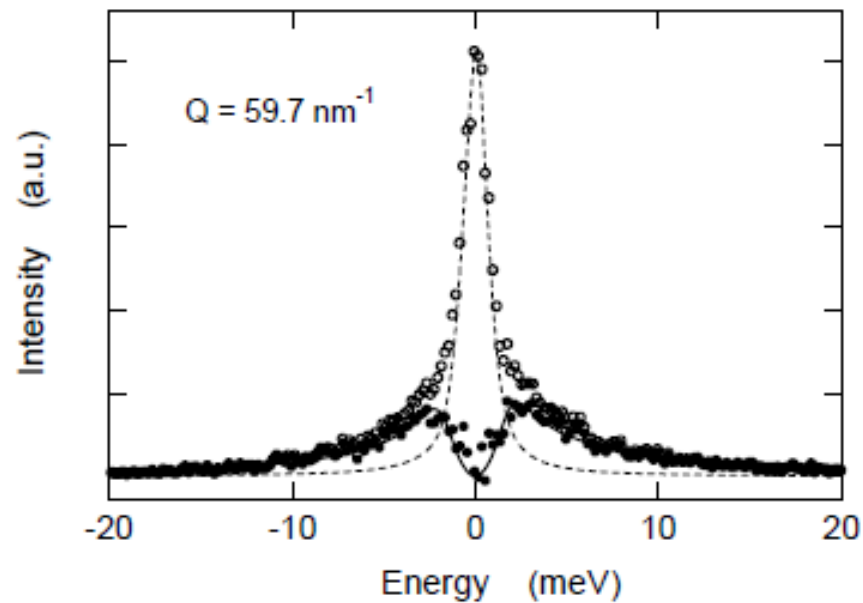
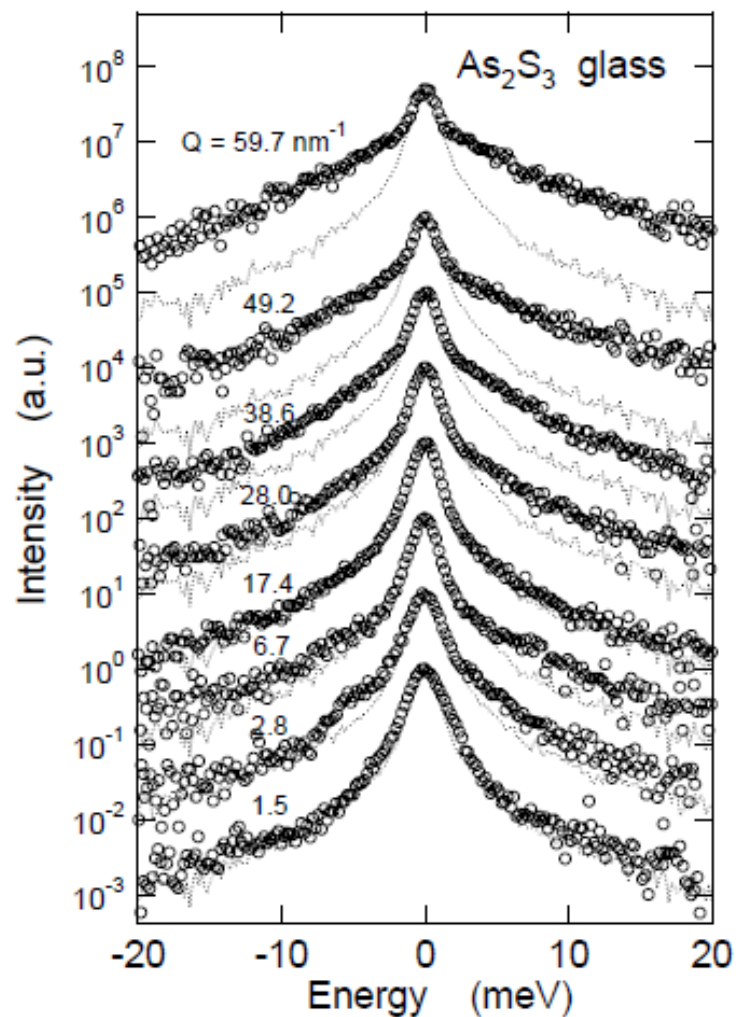
A. Meyer

- Vibrational DOS similar for glass and crystal, except for the low-energy peak.
- Inelastic intensity related to $S(Q)$.



Kiyoto Matsuishi^{a,*}, Shinya Hosokawa^b, Satoshi Tsutsui^c, and Alfred Q. R. Baron^{c,d}

JNCS 354 19 (2009)



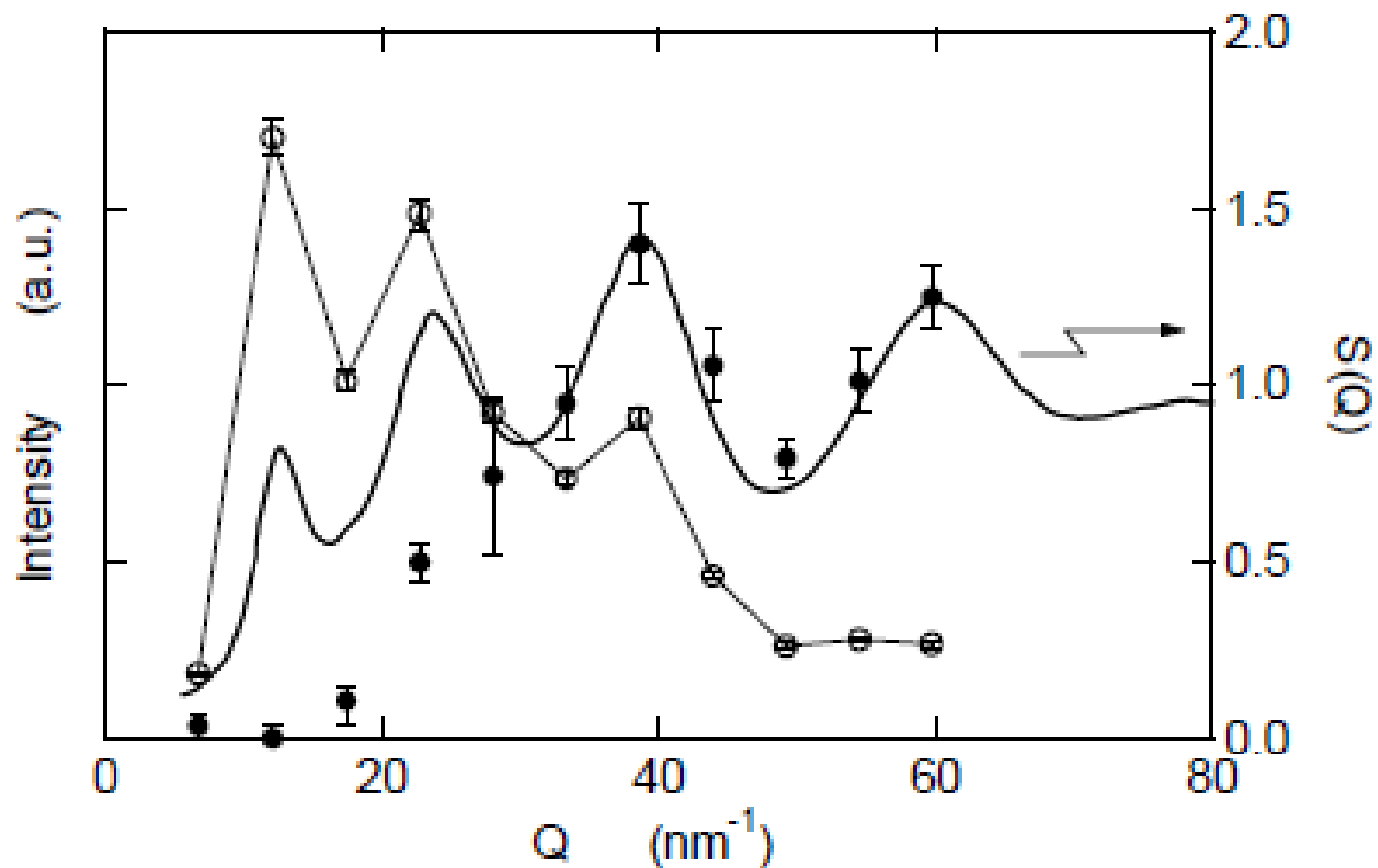


Fig. 4. Intensity of the Boson peak at 3 meV (solid circles) as a function of Q . The structural factor $S(Q)$ obtained by neutron diffraction [11] and the Q -dependence of the elastic scattering component (*i.e.*, the intensity at $\omega = 0$ meV) are also shown by the solid line and open circles, respectively, for comparison. The line for the open circles is drawn as guide for the eye.

Summary

- NMR offers information about the local symmetry and dynamics.
- Dynamic heterogeneity is detected by NMR.
- Raman scattering gives direct information on the boson peak.
- But the Q resolution by neutron and x-ray scattering is important.