Molecular dynamics of some liquid crystal glass-formers

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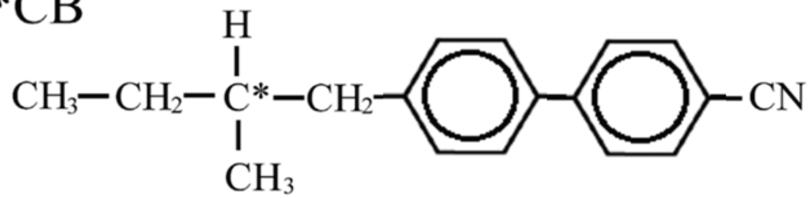
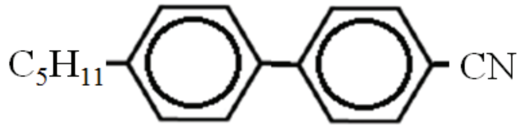
Cyanobiphenyls

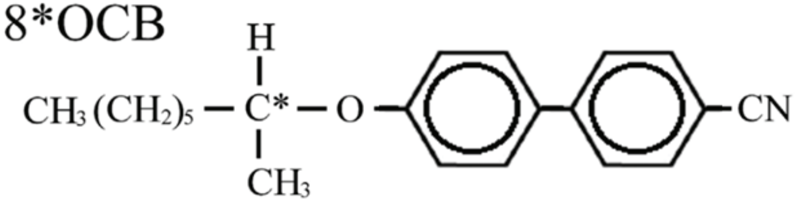
5*CB



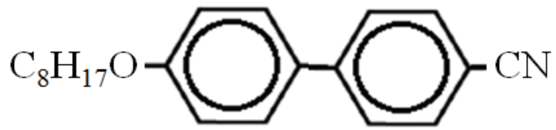
5CB



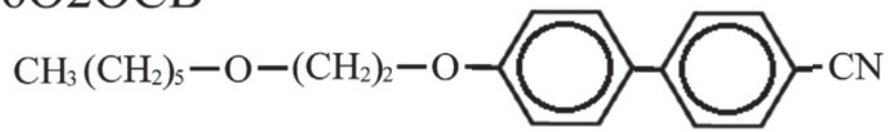
8*OCB

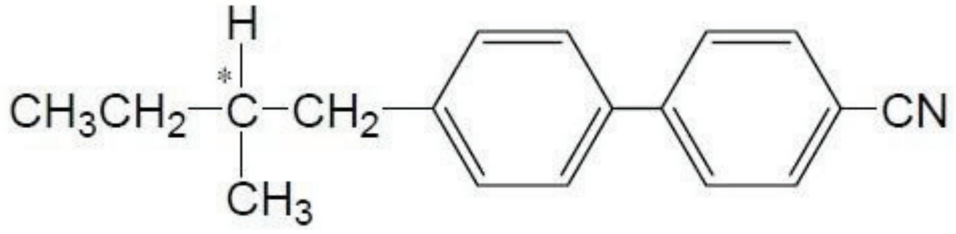


8OCB

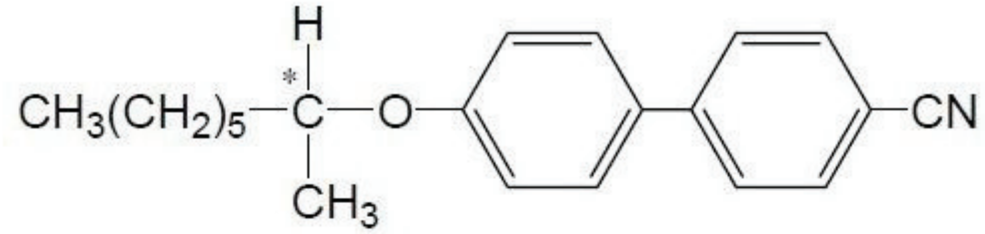


6O2OCB

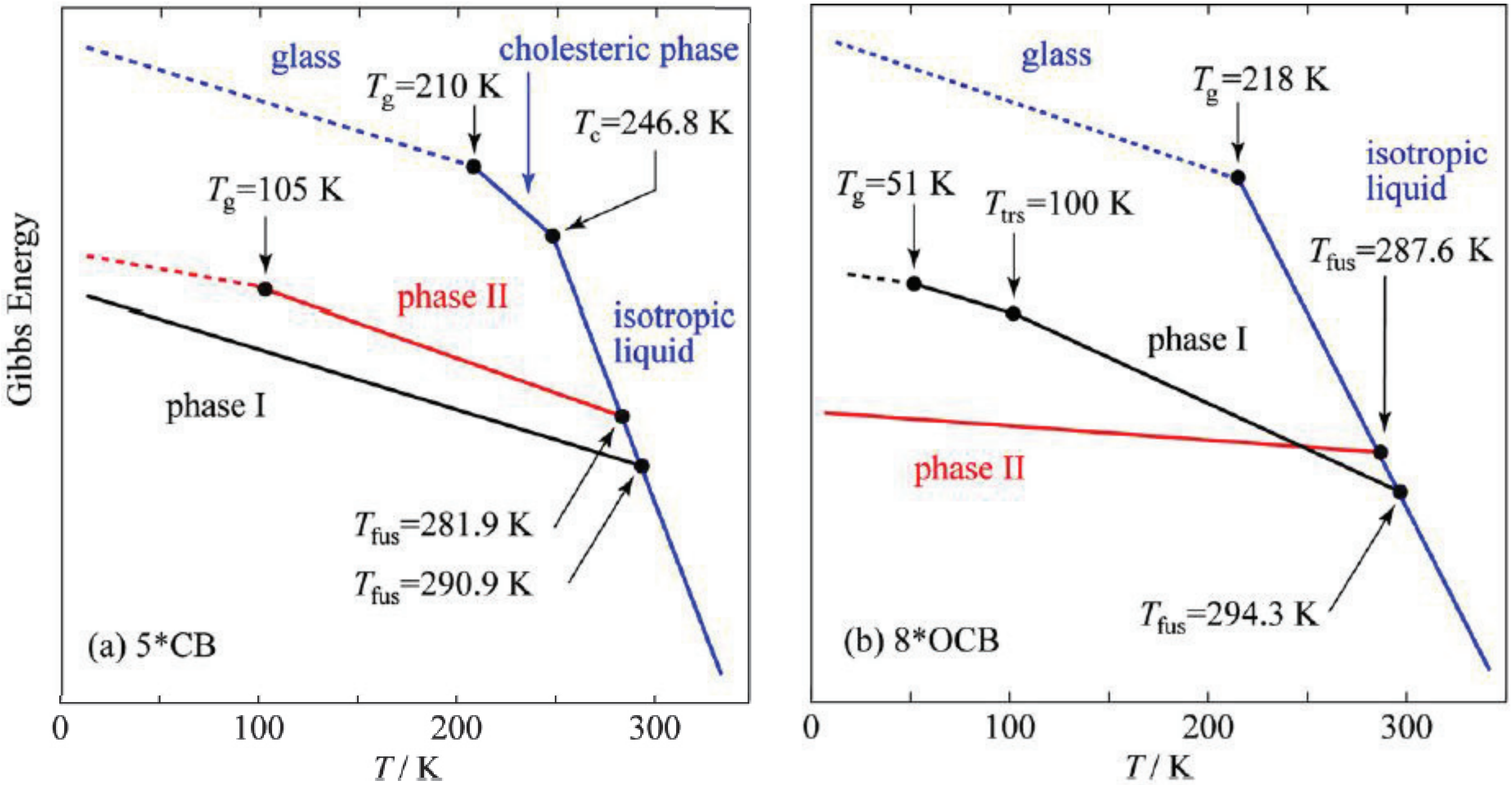




5*CB (S)-4-(2-methylbutyl)-4'-cyanobiphenyl
(isopentyl cyanobiphenyl)



8*OCB (S)-4-(1-methylheptyloxy)-4’-cyanobiphenyl
(izooctyloxy cyanobiphenyl)



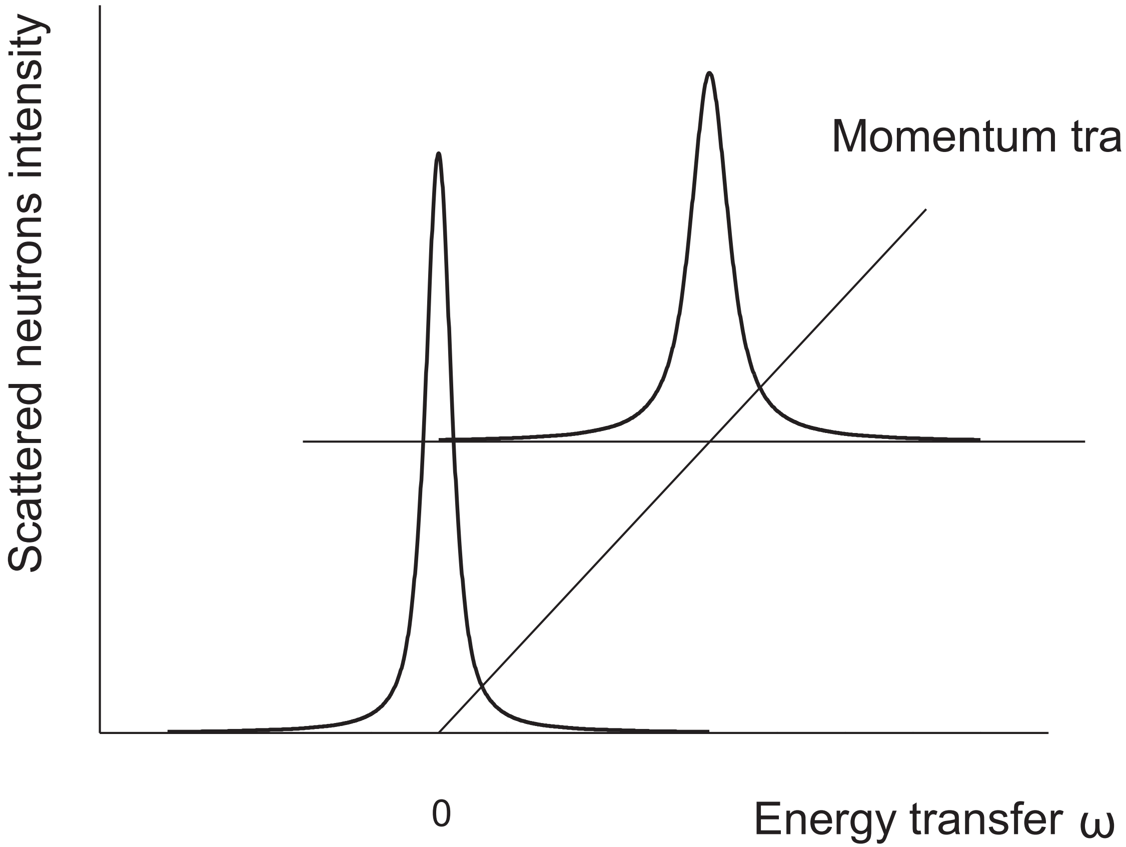
A. Inaba, H. Suzuki, J. Krawczyk, M. Massalska-Arodź, Chemical Physics Letters, **463** (2008) 90

Quasi-elastic neutron scattering (QENS)

- powerful experimental method giving the information about both **time-scale** and **geometry** of **fast stochastic motions** of molecules and molecular groups.
- Both **translational** and **rotational** motions can be studied.
- Complementary method to Infrared Spectroscopy, Dielectric Relaxation, NMR, ...
- $I(Q,\omega) \sim \dfrac{d^2\sigma}{d\Omega\, d\omega} = \dfrac{1}{2\pi} \dfrac{k'}{k_0} \sigma\, S(Q,\omega)$

QENS **translations**

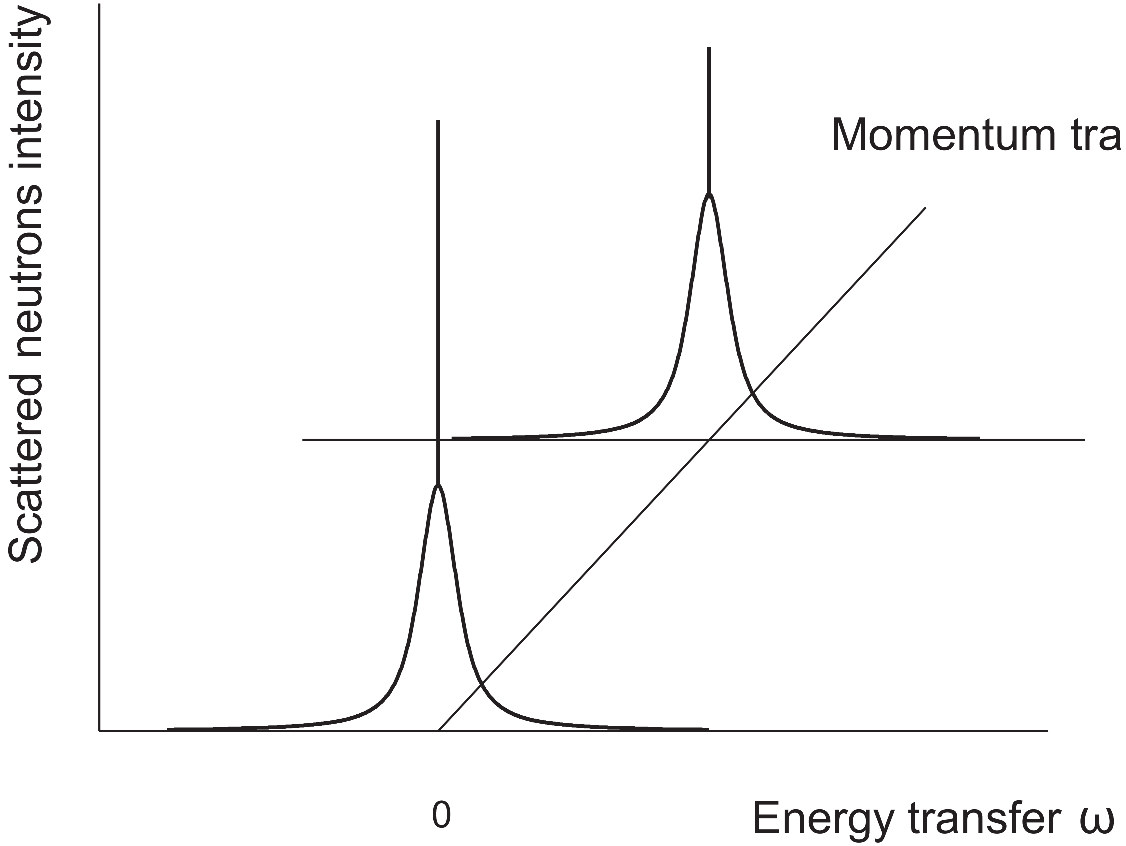
$$S(Q,\omega) = L(\Gamma,\omega) = \frac{1}{\pi}\frac{\Gamma}{\omega^2+\Gamma^2}$$



Γ = f(Q)

QENS **reorientations**

$$S(Q,\omega) = A_0(Q)\delta(\omega) + \sum_i A_i(Q)L(\Gamma_i,\omega)$$



$\Gamma \sim 1/\tau \neq$ f(Q)

$$EISF = \frac{I_{EL}}{I_{EL} + I_{QEL}} = \mathrm{f}(Q)$$

QENS Experiment

AGNES spectrometer at the JRR-3M reactor
at Tokai Research Establishment of JAERI

ΔE = 120 μeV
Q = 0.26 – 2.69 Å^{-1}

Five temperatures for isotropic phase of
5*CB (253 – 354 K) and 8*OCB (292 – 373 K)

Five temperatures for 6O2OCB
Three temperatures for 5CB and 8OCB

H. Suzuki, A. Inaba, J. Krawczyk, M. Massalska-Arodź, T. Kikuchi, O. Yamamuro,
Journal of Non-Crystalline Solids, **357** (2011) 734

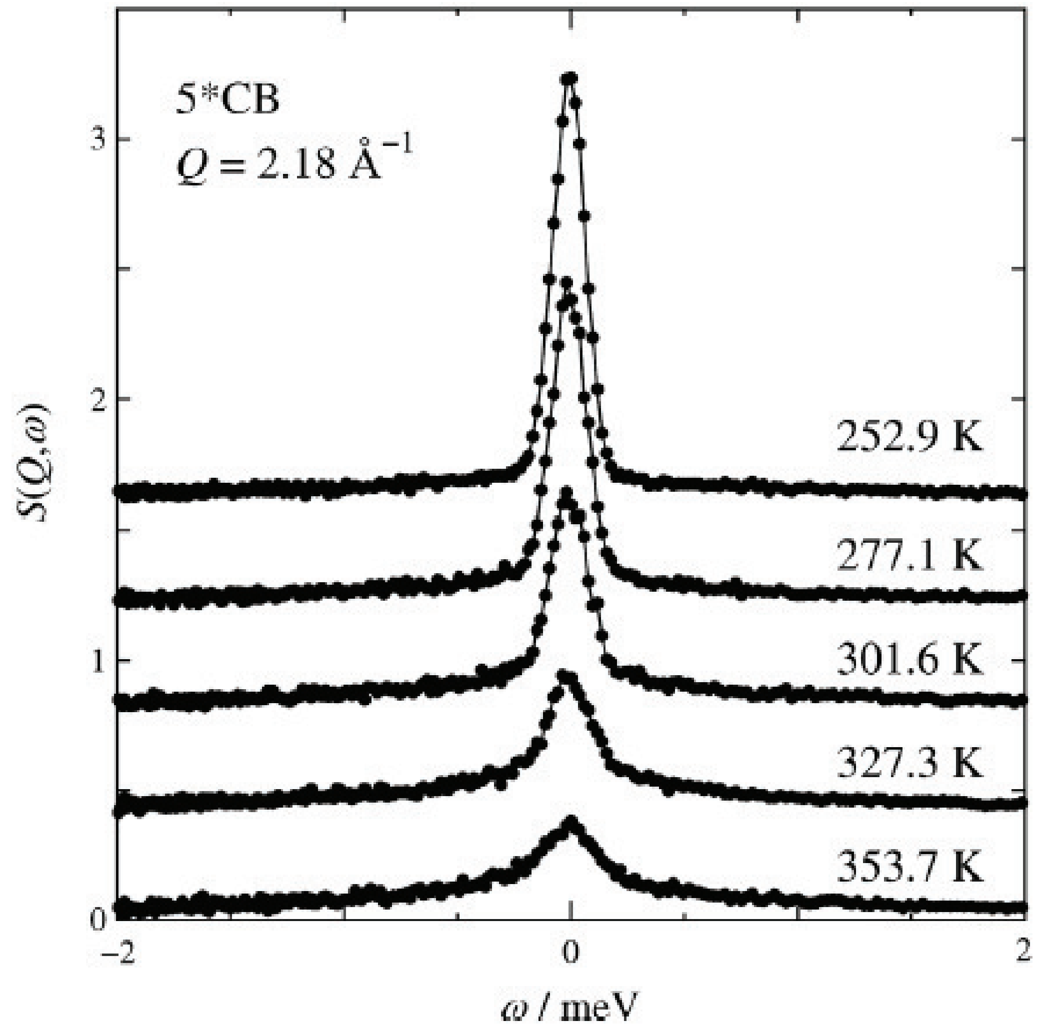
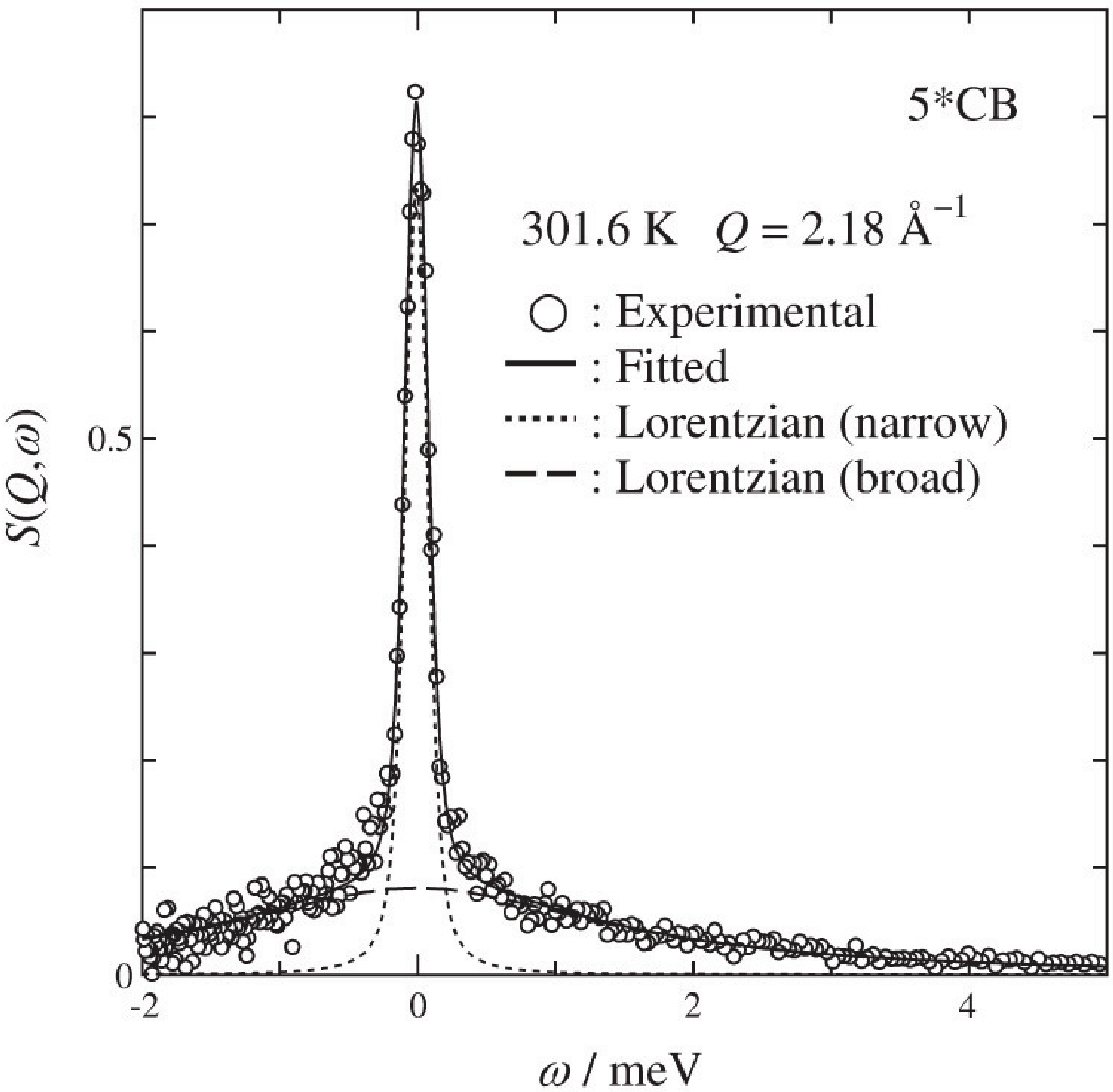


Fig. 2. Dynamic structure factor $S(Q, \omega)$ of 5*CB at $Q = 2.18$ Å^{-1} at 252.9 K, 277.1 K, 301.6 K, 327.3 K and 353.7 K. The ordinate is for the one at 353.7 K. The results for other four temperatures are successively shifted upward.

$$S_{\mathrm{rot}}(Q,\omega) = A(Q)\delta(\omega) + (1-A(Q))L(\Gamma_{\mathrm{rot}},\omega)$$

$$S_{\mathrm{rot}}(Q,\omega) = A(Q)\delta(\omega) + (1-A(Q))L(\Gamma_{\mathrm{rot}},\omega)$$

$$S_{\mathrm{trans}}(Q,\omega) = \frac{1}{\pi}\frac{D_{\mathrm{trans}}Q^2}{\omega^2 + (D_{\mathrm{trans}}Q^2)^2}$$



5*CB
301.6 K Q = 2.18 Å⁻¹
: Experimental
: Fitted
: Lorentzian (narrow)
: Lorentzian (broad)
S(Q,ω)
0.5
0
-2
0
2
4
ω / meV

$$S_{\mathrm{rot}}(Q,\omega) = A(Q)\delta(\omega) + (1-A(Q))L(\Gamma_{\mathrm{rot}},\omega)$$

$$S_{\mathrm{trans}}(Q,\omega) = \frac{1}{\pi}\frac{D_{\mathrm{trans}}Q^2}{\omega^2 + (D_{\mathrm{trans}}Q^2)^2}$$

$$S(Q,\omega) = S_{\mathrm{trans}}(Q,\omega)\otimes S_{\mathrm{rot}}(Q,\omega) =$$

$$= A(Q)L(\Gamma_{\mathrm{trans}},\omega) + (1-A(Q))L(\Gamma_{\mathrm{trans}} + \Gamma_{\mathrm{rot}},\omega)$$

$$S(Q,\omega) = A(Q)L(\Gamma_{trans},\omega) + (1-A(Q))L(\Gamma_{trans}+\Gamma_{rot},\omega)$$

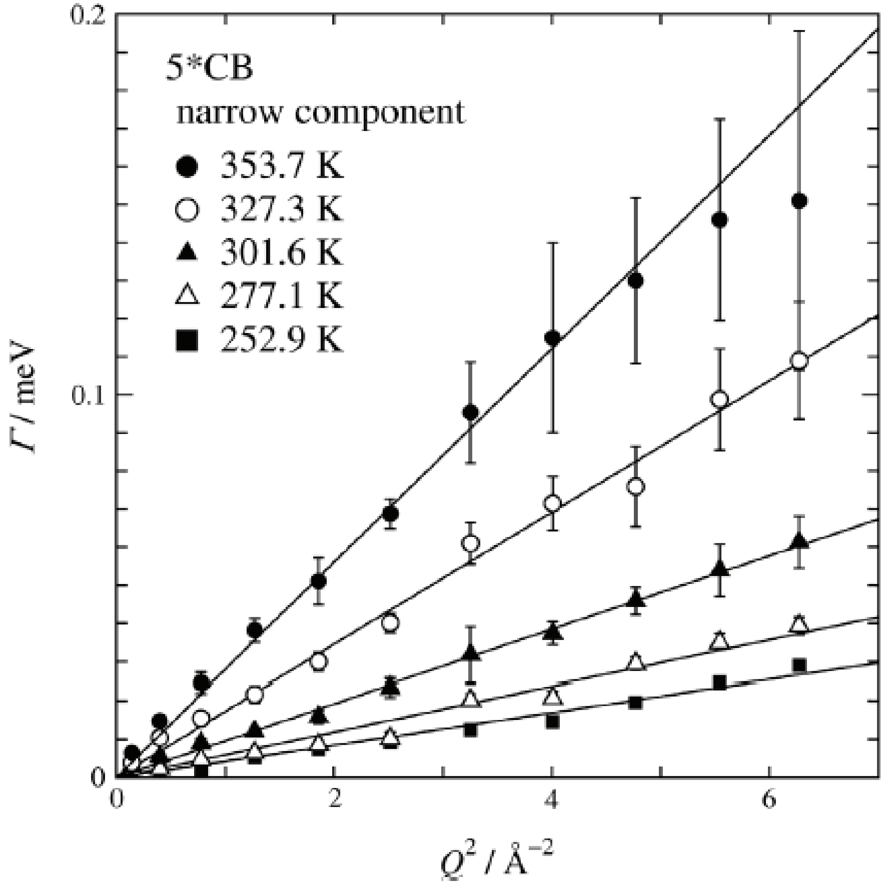


Fig. 4. HWHM of the narrow component of 5*CB plotted against Q^2 for five temperatures. The lines show the fitted functions.

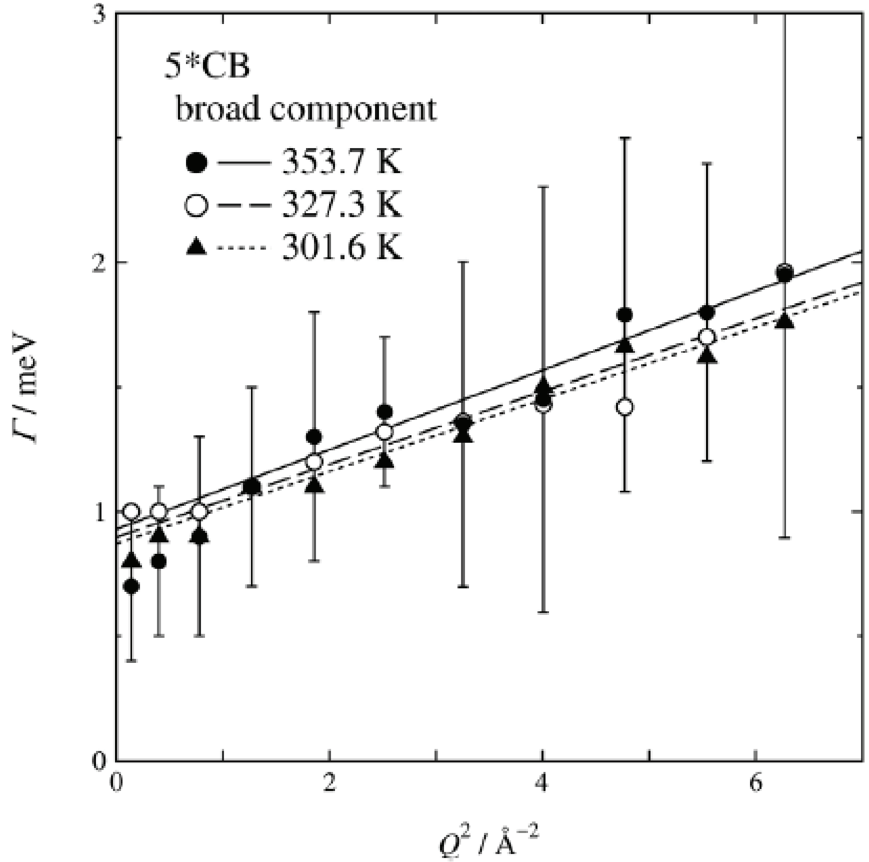


Fig. 5. HWHM of the broad component of 5*CB plotted against Q^2. The lines show the results of fitting. The error bars are of the data at 353.0 K.

$$\Gamma = D_{trans} Q^2$$

$$\Gamma = D_{trans} Q^2 + \Gamma_{rot}$$

5*CB

- Broad component assigned to the reorientational motion of the whole molecule around long molecular axis

  $D_{rot} \approx 0.24\ ps^{-1}$ ($\tau \approx 4$ ps), $E_{act} \approx 4$ kJ/mol

- Narrow component assigned to the diffusive motion of the terminal chain

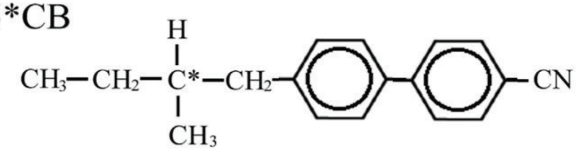
  $D_{trans} \approx 10^{-6}\ cm^2/s$, $E_{act} \approx 17$ kJ/mol

Similar results for 8*OCB

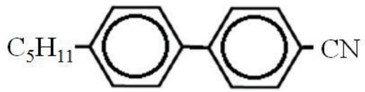
... and also for 5CB, 8OCB and 6O2OCB

- The width of the narrow component of chiral compunds is significantly smaller than that of non-chiral - the branching reduces the chain mobility. The reorientation does not change.

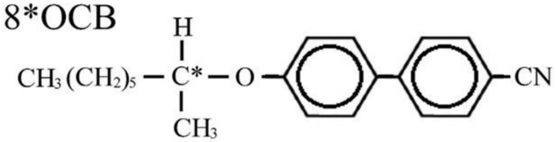
5*CB



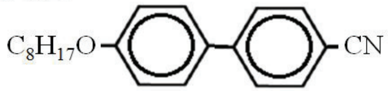
5CB



8*OCB

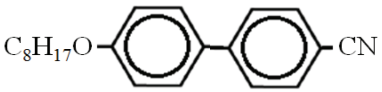


8OCB

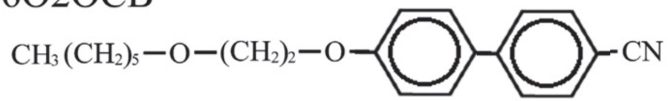


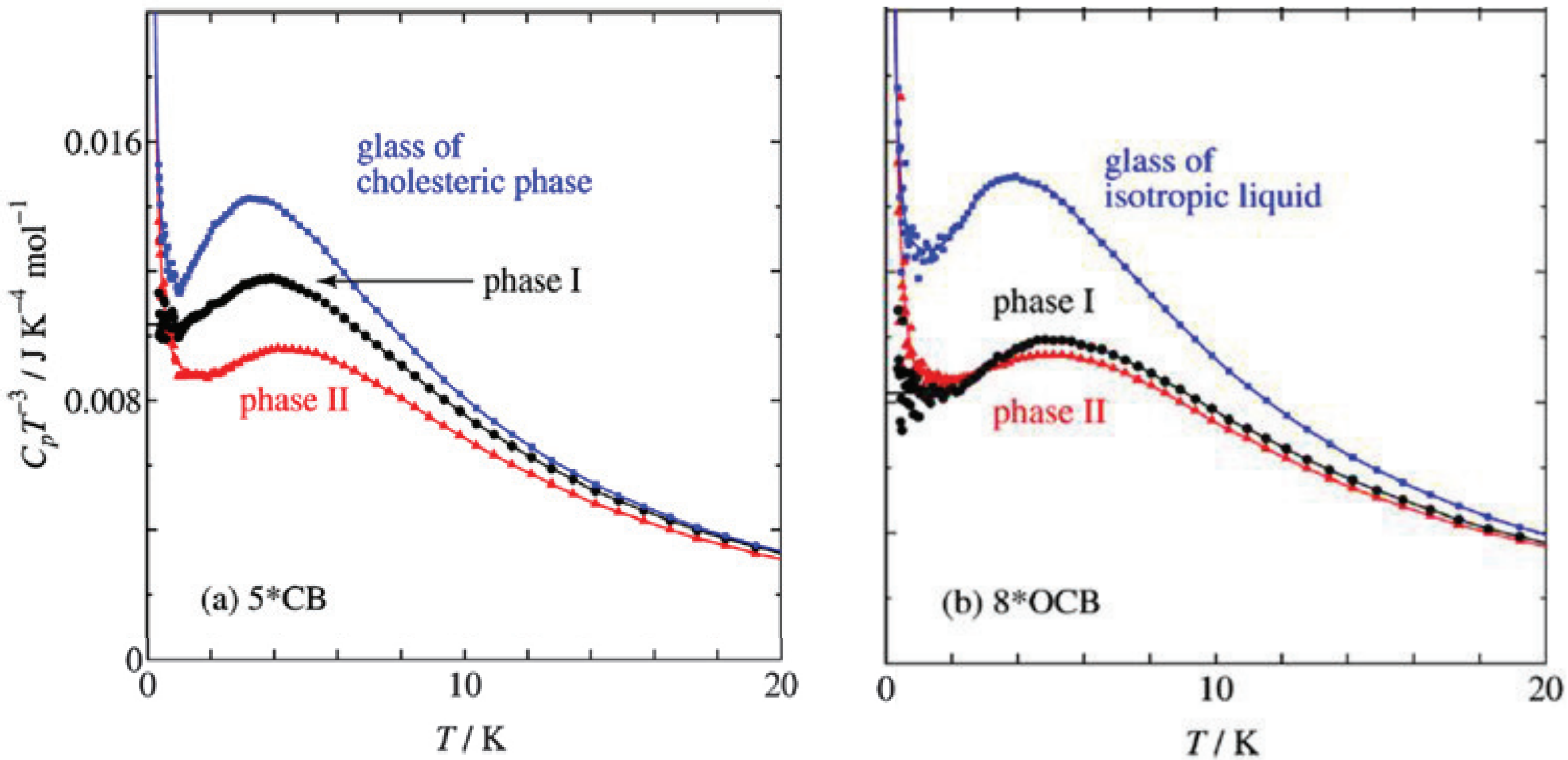
- The insertion of an oxygen atom into the chain (6O2OCB) does not change significantly the rate of chain motion or the reorientation.

8OCB



6O2OCB





$$C_p(T) = b_D T^3 + C_{exc}(T) + b_{TS} T$$

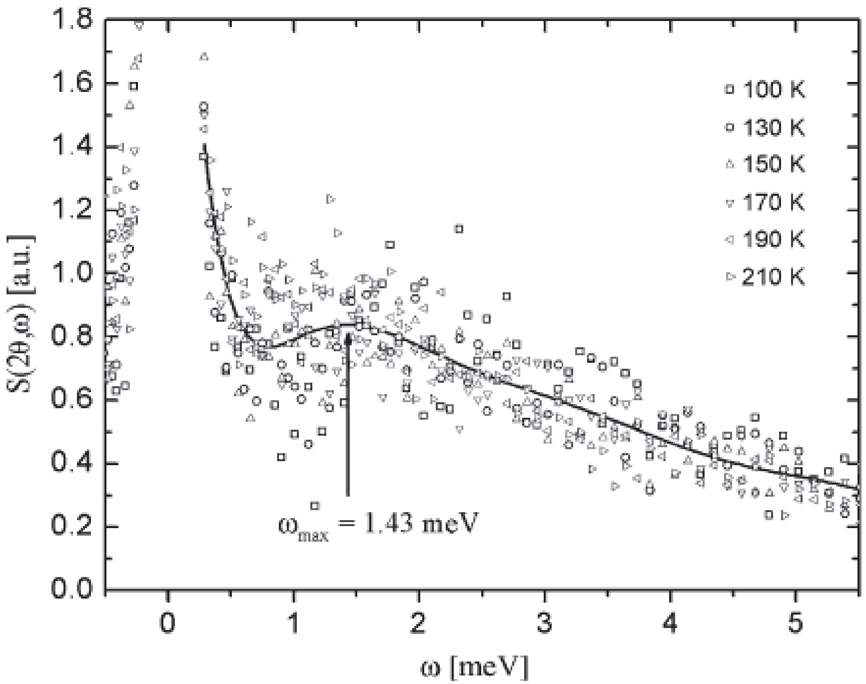
A. Inaba, H. Suzuki, J. Krawczyk, M. Massalska-Arodź, Chemical Physics Letters, **463** (2008) 90

Boson peak

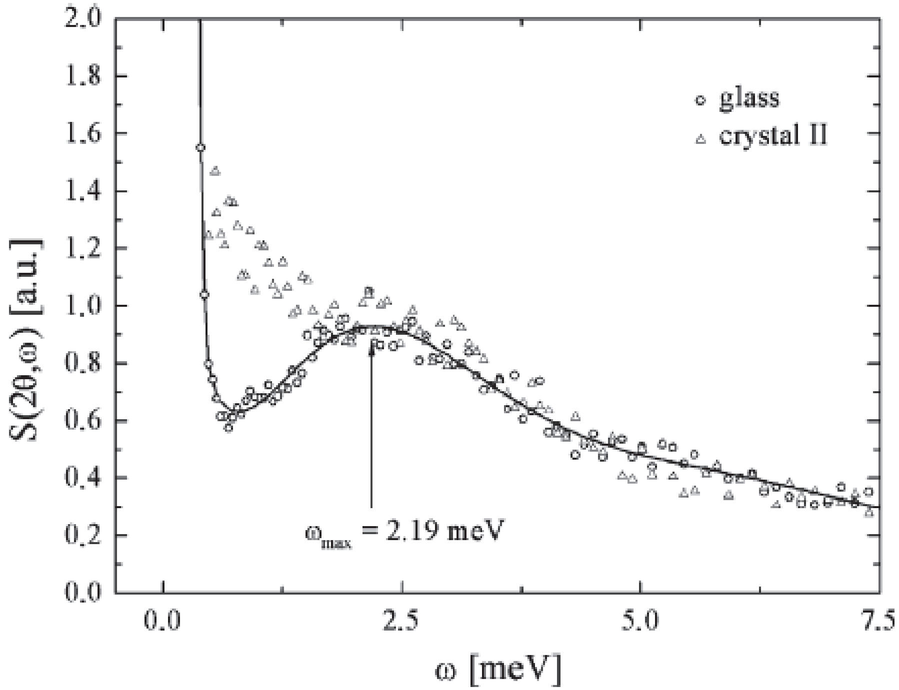
- Excess vibrational density of states over the Debye $G(\omega) \sim \omega^2$ law
- Universally observed at low frequencies for glasses by neutron, X-ray and light scattering
- Also observed in the specific heat as a low-temperature bump over $C(T) \sim T^3$
- There is no widely accepted explanation of Boson peak:
    - it may correspond to phonon degrees of freedom (unharmonic in a complex energy landscape) or
    - to some additional, localized modes (e.g. vibrations of clusters or parts of molecules).

INS experiment

TOF spectrometer at IFE in Kjeller, Norway



5*CB (glass of cholesteric)



8*OCB (T = 100 K)

J. Mayer, J. Krawczyk, M. Massalska-Arodź, I. Natkaniec, J.A. Janik. O. Steinsvoll, Physica B, **371** (2006) 249

INS experiment

SPHERES (SPectrometer for High Energy RESolution)
- third-generation backscattering instrument with focusing optics and a phase-space-transform chopper

Located at the 20 MW German neutron source FRM II (Garching, Munich) and operated by the Jülich Centre for Neutron Science

Offers an energy resolution (fwhm) better than 0.65 μeV,
a dynamic range of ±31 μeV, and a signal-to-noise ratio of up to 1750:1

- 8*OCB

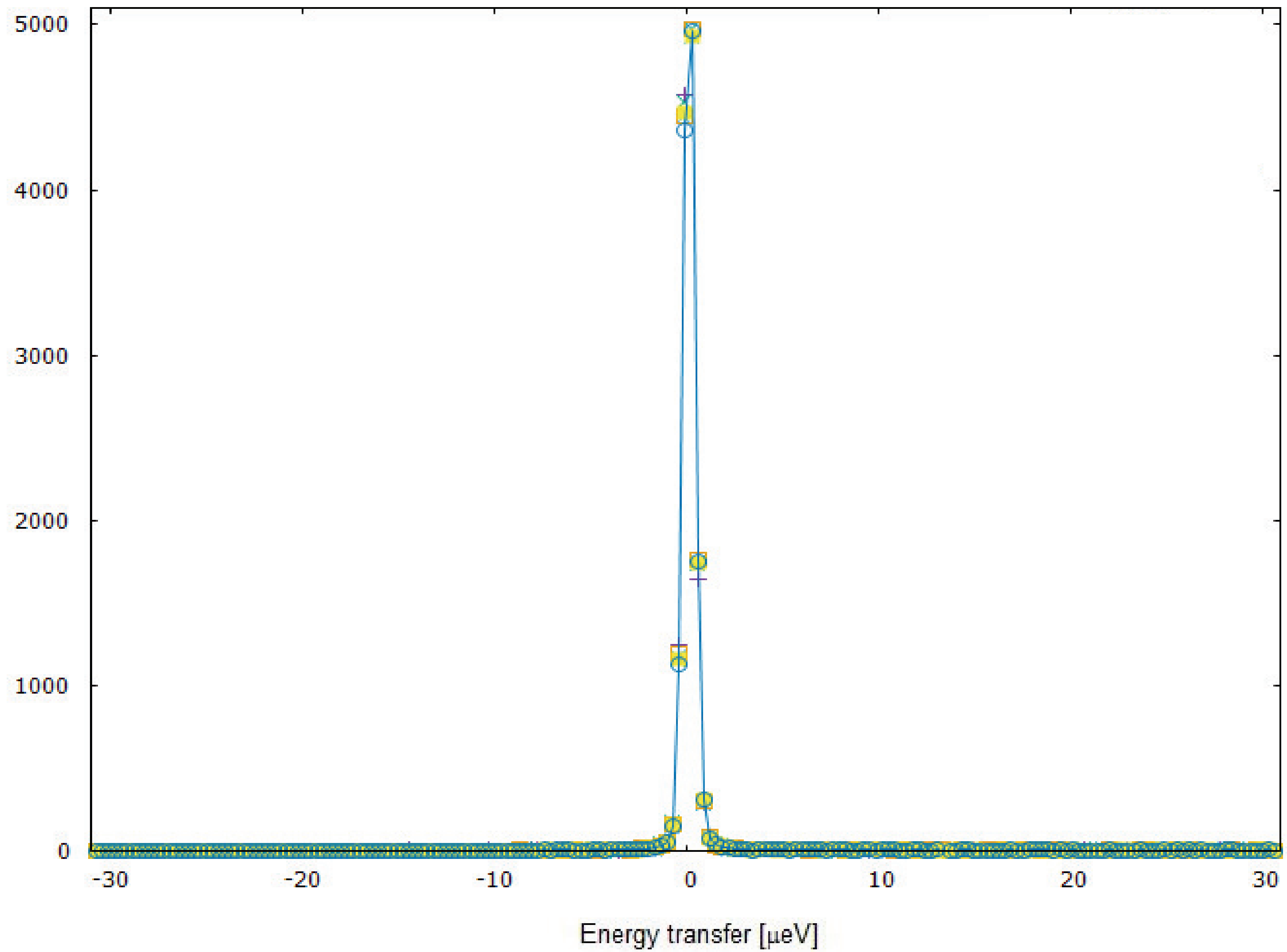
Phase II	5 – 30 K	(6 spectra)
Glass of phase I	5 – 30 K	(6 spectra)
Glass of isotropic liquid	5 – 35 K	(7 spectra)

- 5*CB

Phase I	5 – 33 K	(7 spectra)
Glass of phase II	4 – 35 K	(8 spectra)
Glass of cholesteric phase	4 – 25 K	(6 spectra)

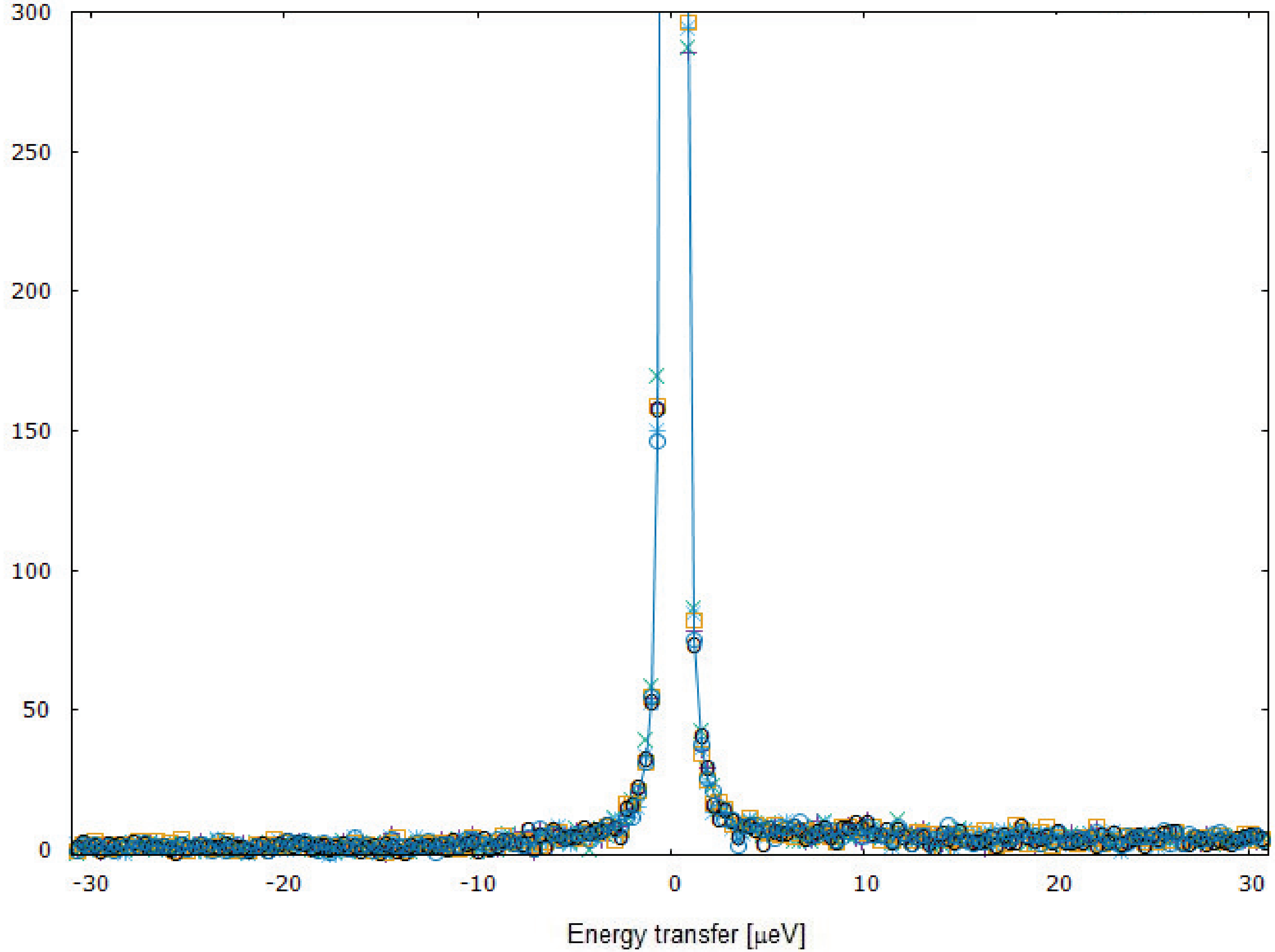
J. Krawczyk, M. Massalska-Arodź, T. Rozwadowski, G. Shneider, to be published

8*OCB, phase II



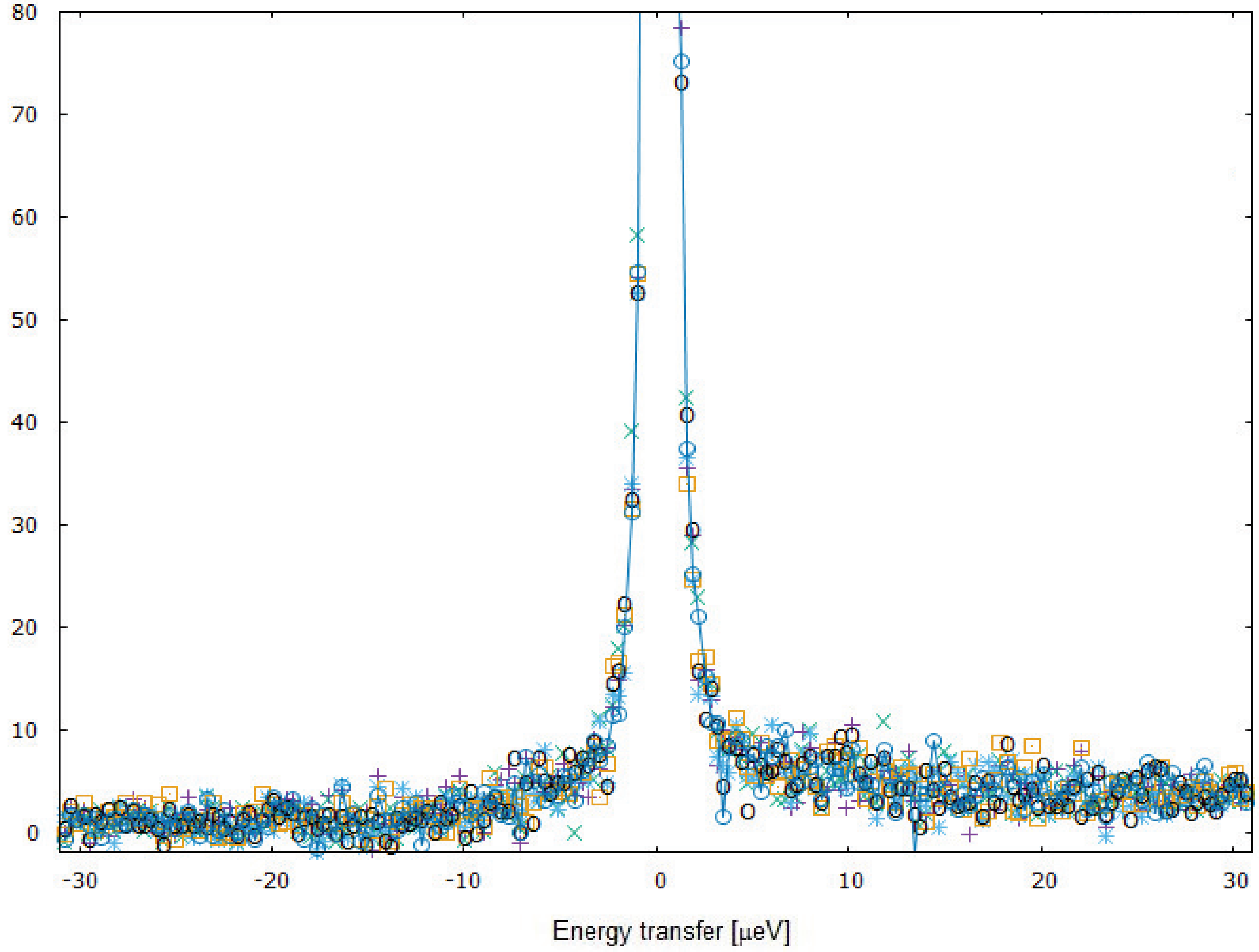
T = 4.6 K
10.1 K
15.0 K
19.9 K
25.0 K
30.0 K

8*OCB, phase II



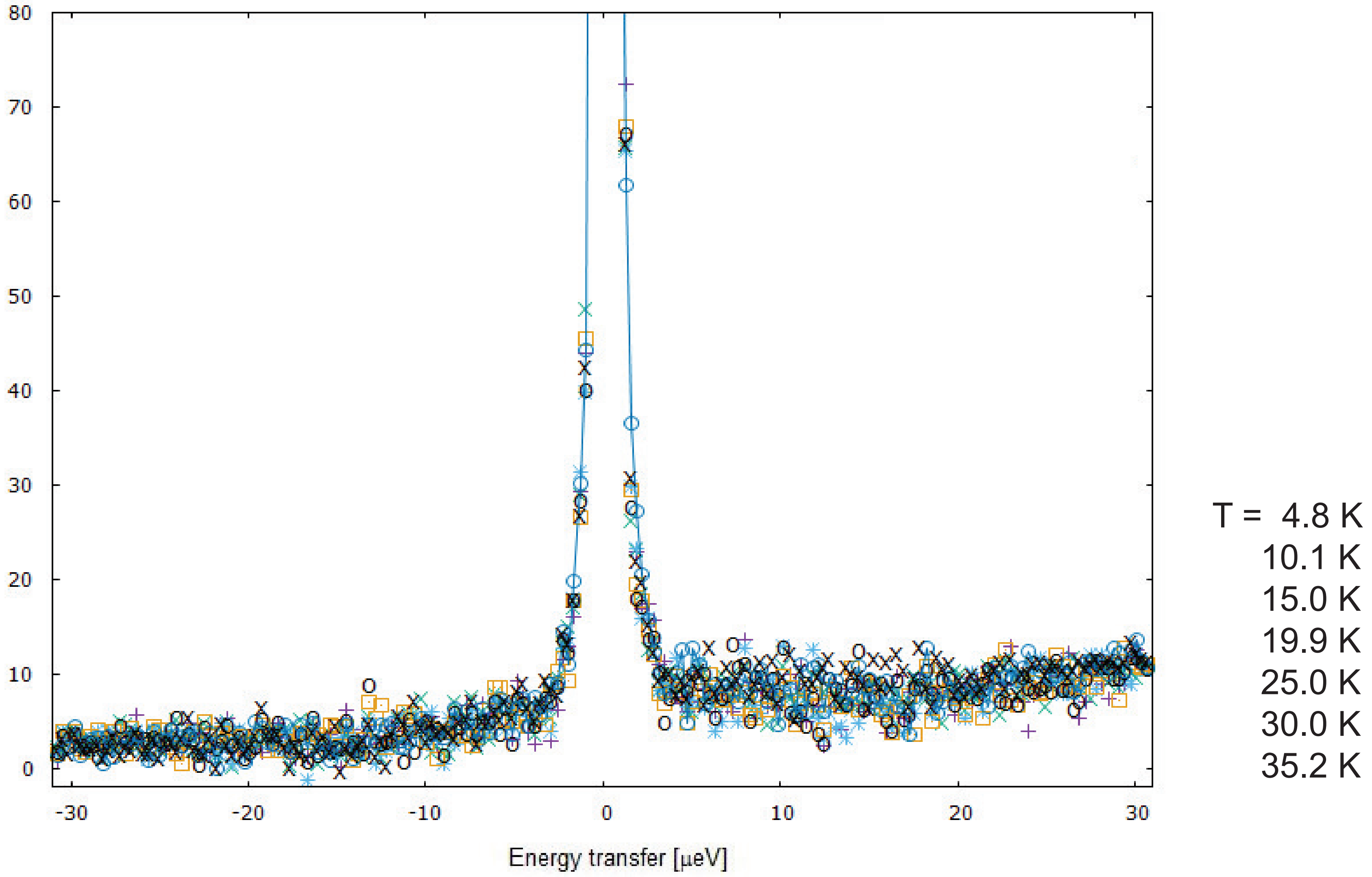
T = 4.6 K
10.1 K
15.0 K
19.9 K
25.0 K
30.0 K

8*OCB, phase II

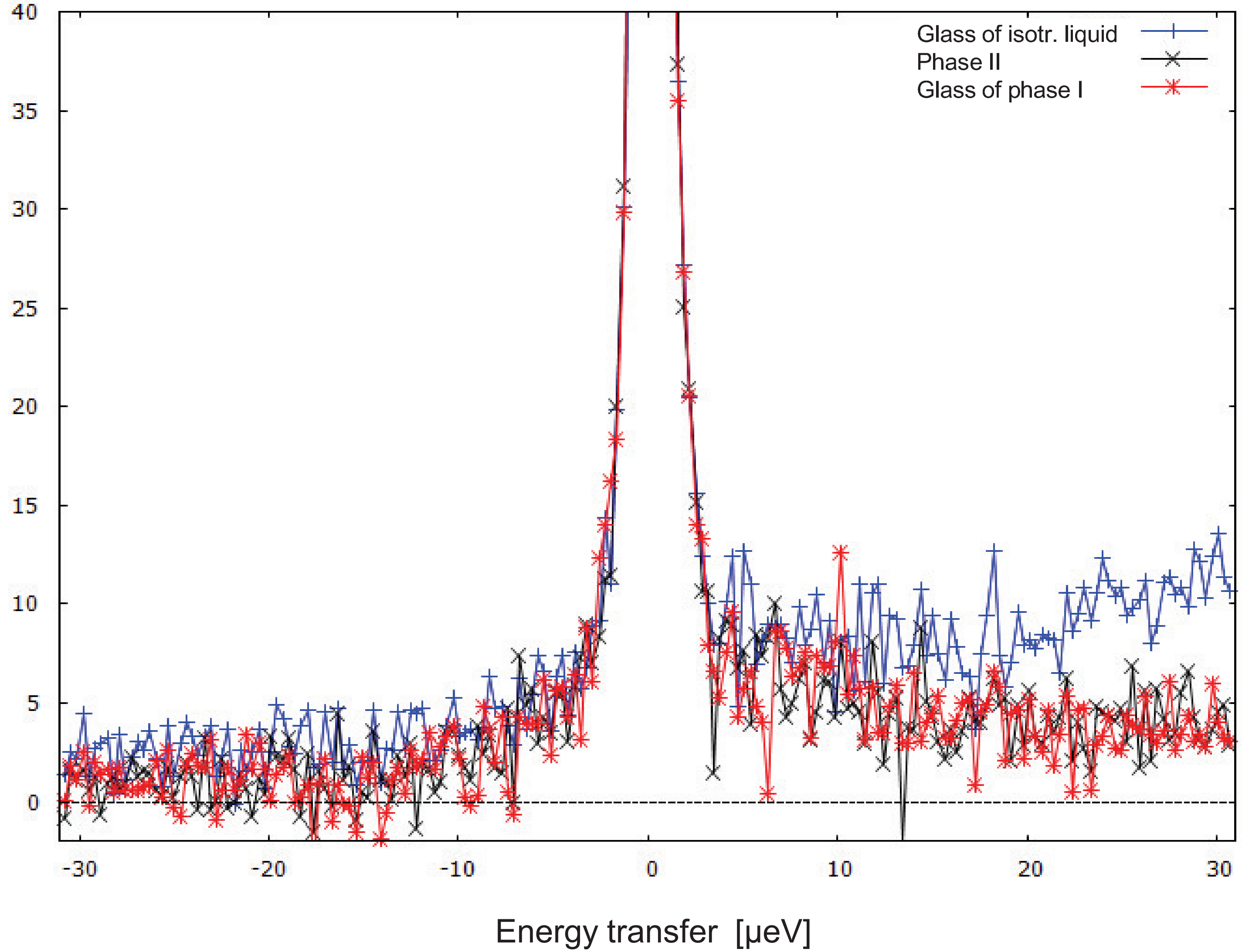


T = 4.6 K
10.1 K
15.0 K
19.9 K
25.0 K
30.0 K

8*OCB, glass of isotropic liquid



8*OCB, T = 30 K



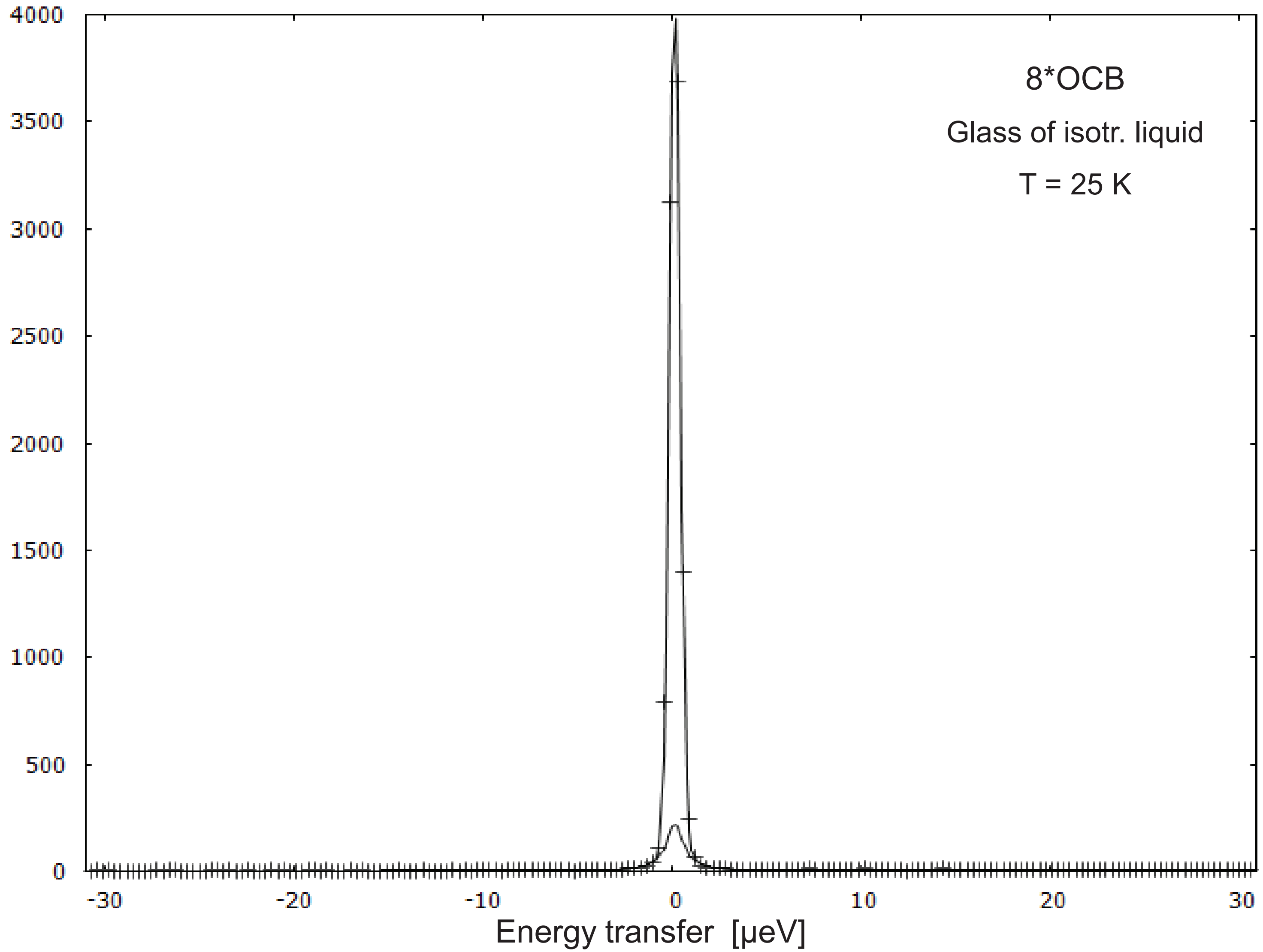
40
35
30
25
20
15
10
5
0
-30
-20
-10
0
10
20
30
Glass of isotr. liquid
Phase II
Glass of phase I
Energy transfer [µeV]

$$S(\kappa,\omega) = S_{QENS}(\kappa,\omega) + S_{BP}(\kappa,\omega) =$$

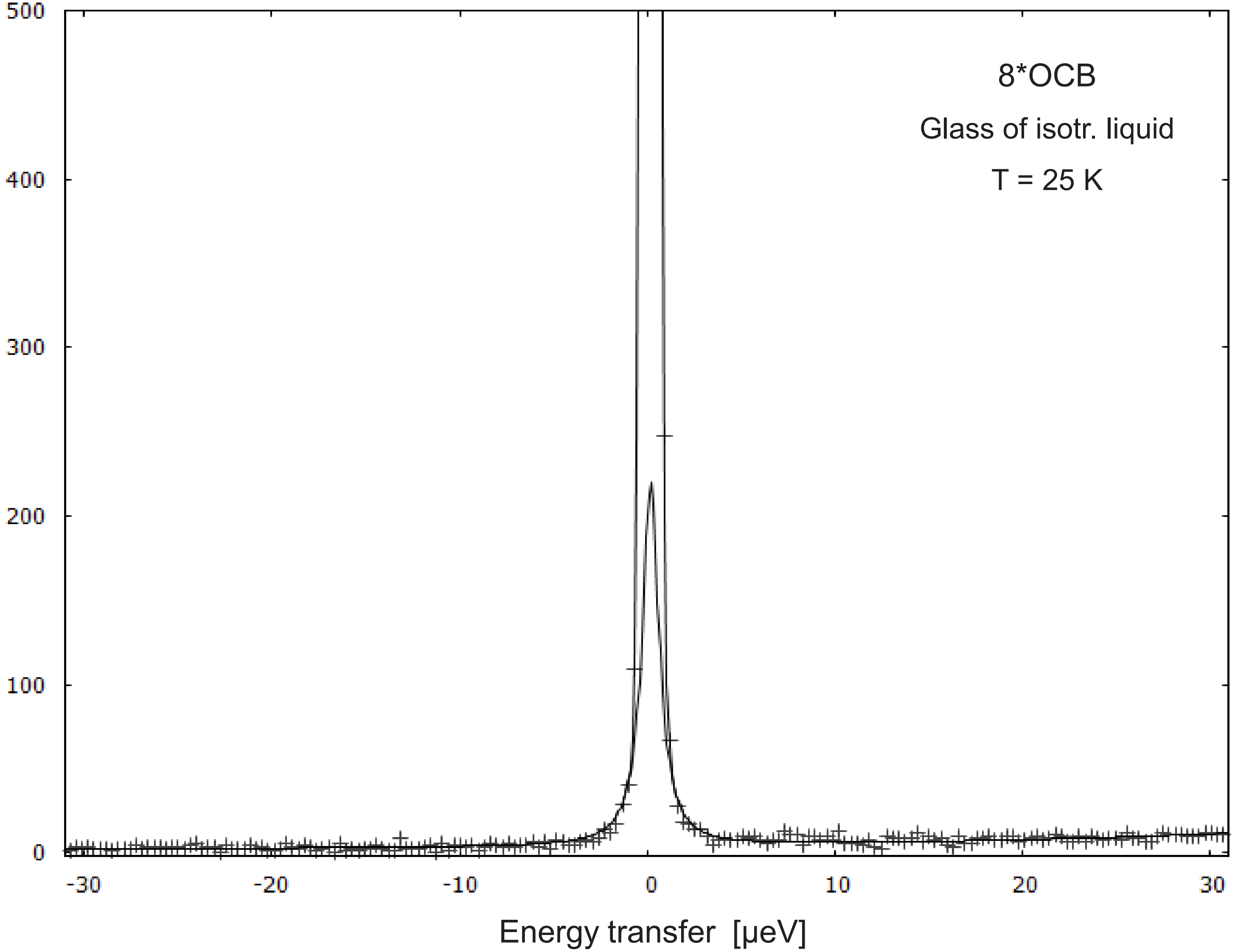
$$= A\exp\left(-\frac{\omega}{\Delta^2}^2\right) + B\frac{\Gamma_{QENS}}{\Gamma_{QENS}{}^2 + \omega^2} +$$

$$+ C\frac{\Gamma_{BP}}{\Gamma_{BP}{}^2 + (\omega - \omega_{BP})^2}$$

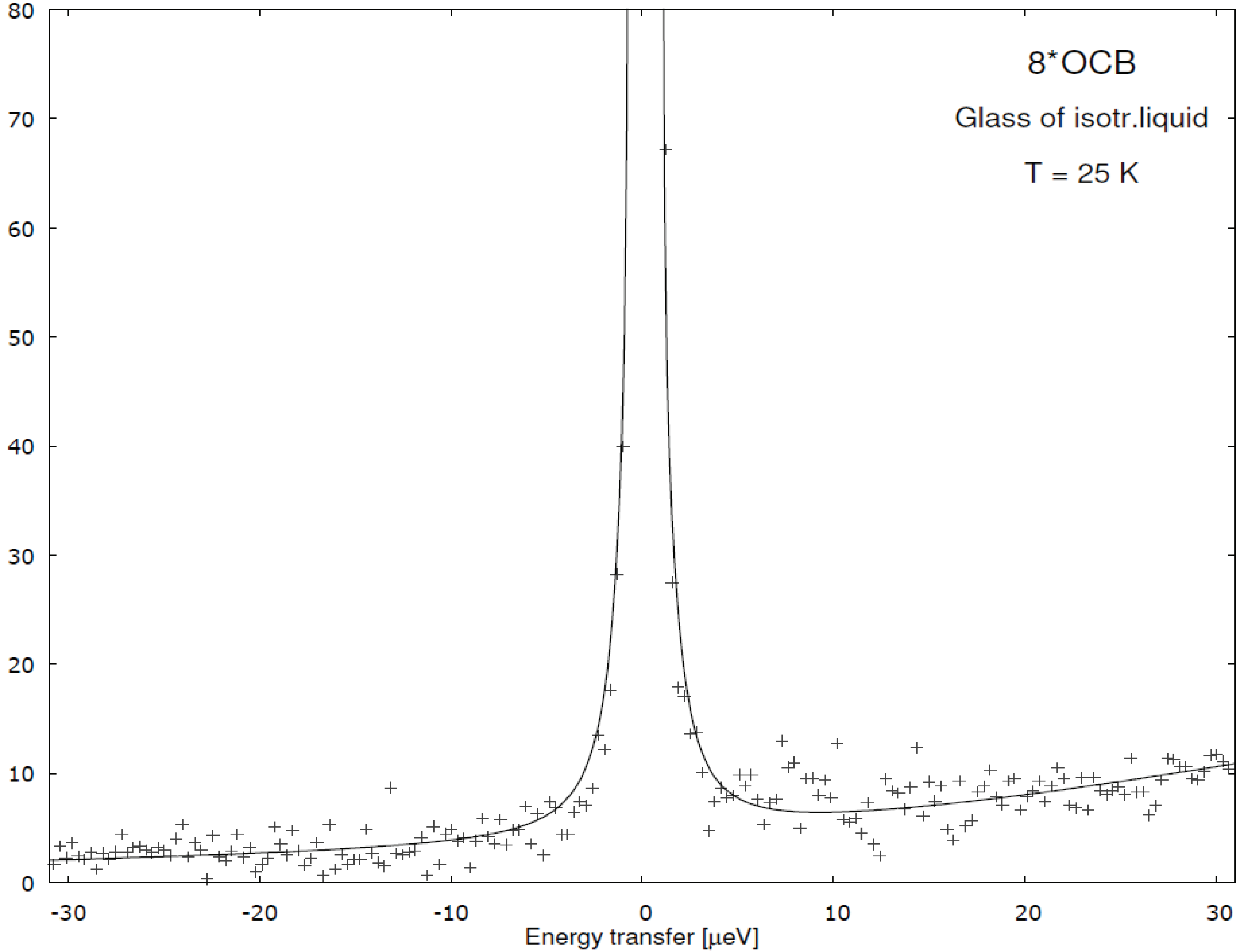
8*OCB, glass of isotropic liquid, T = 25 K



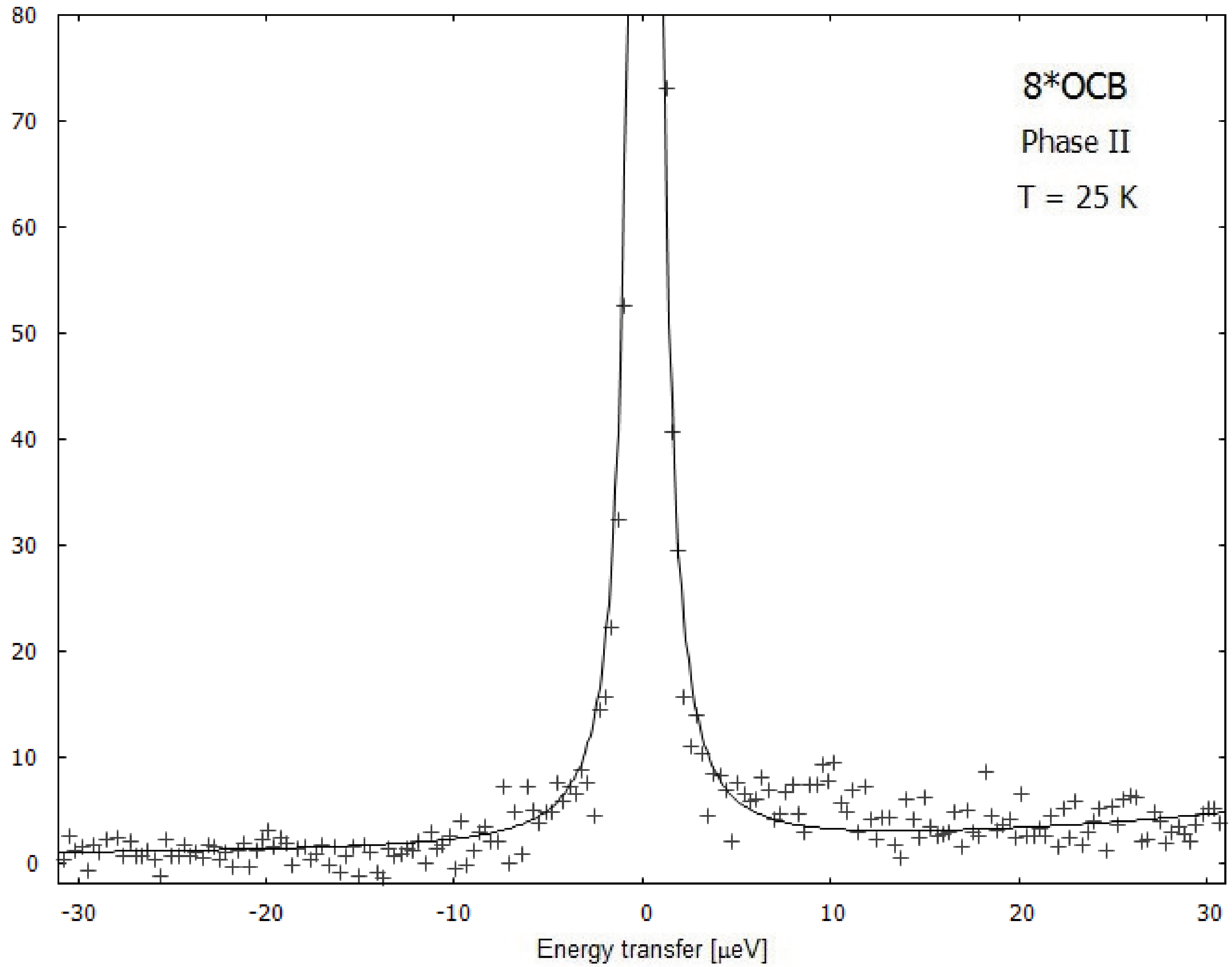
8*OCB,   glass of isotropic liquid, T = 25 K



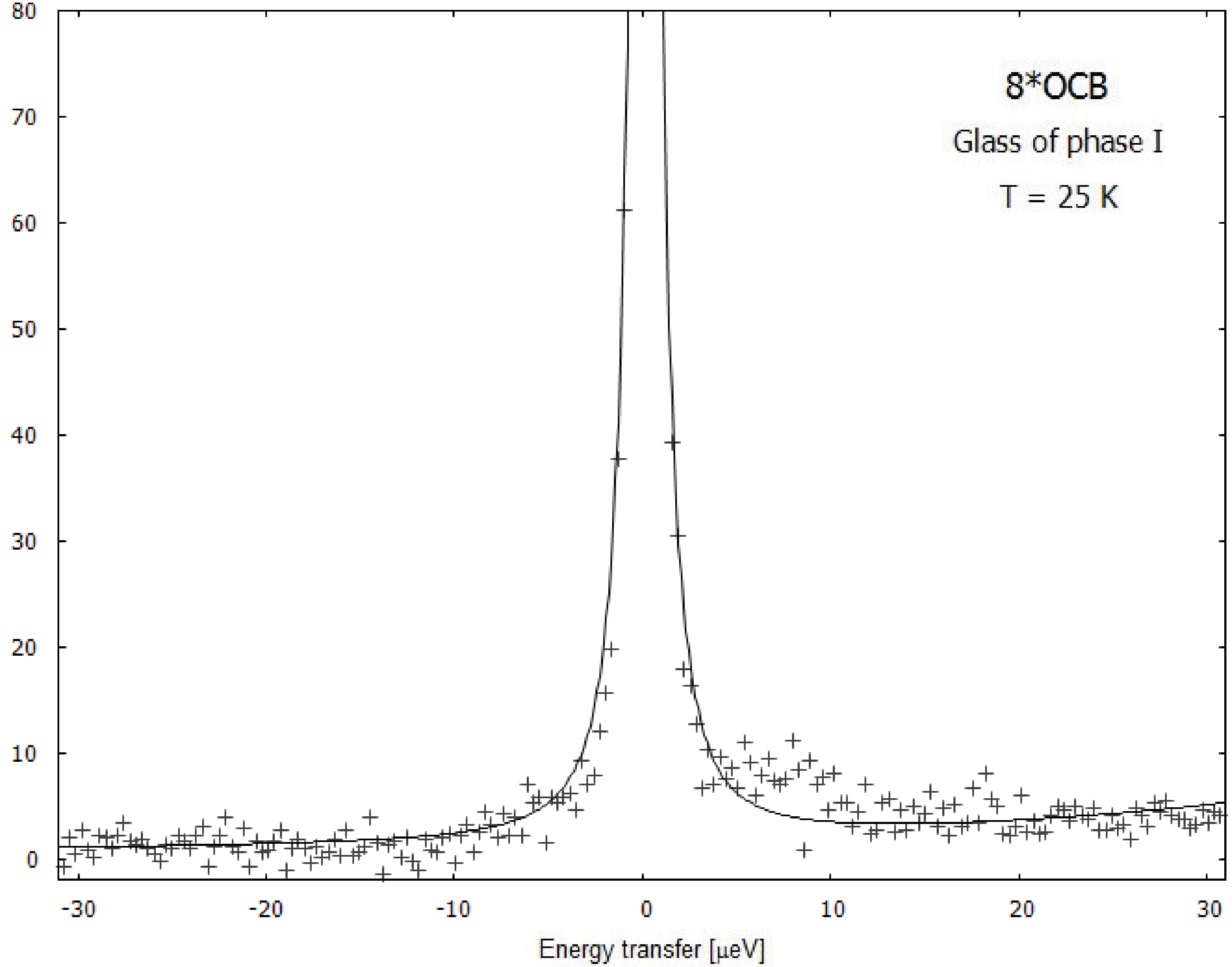
8*OCB,   glass of isotropic liquid, T = 25 K



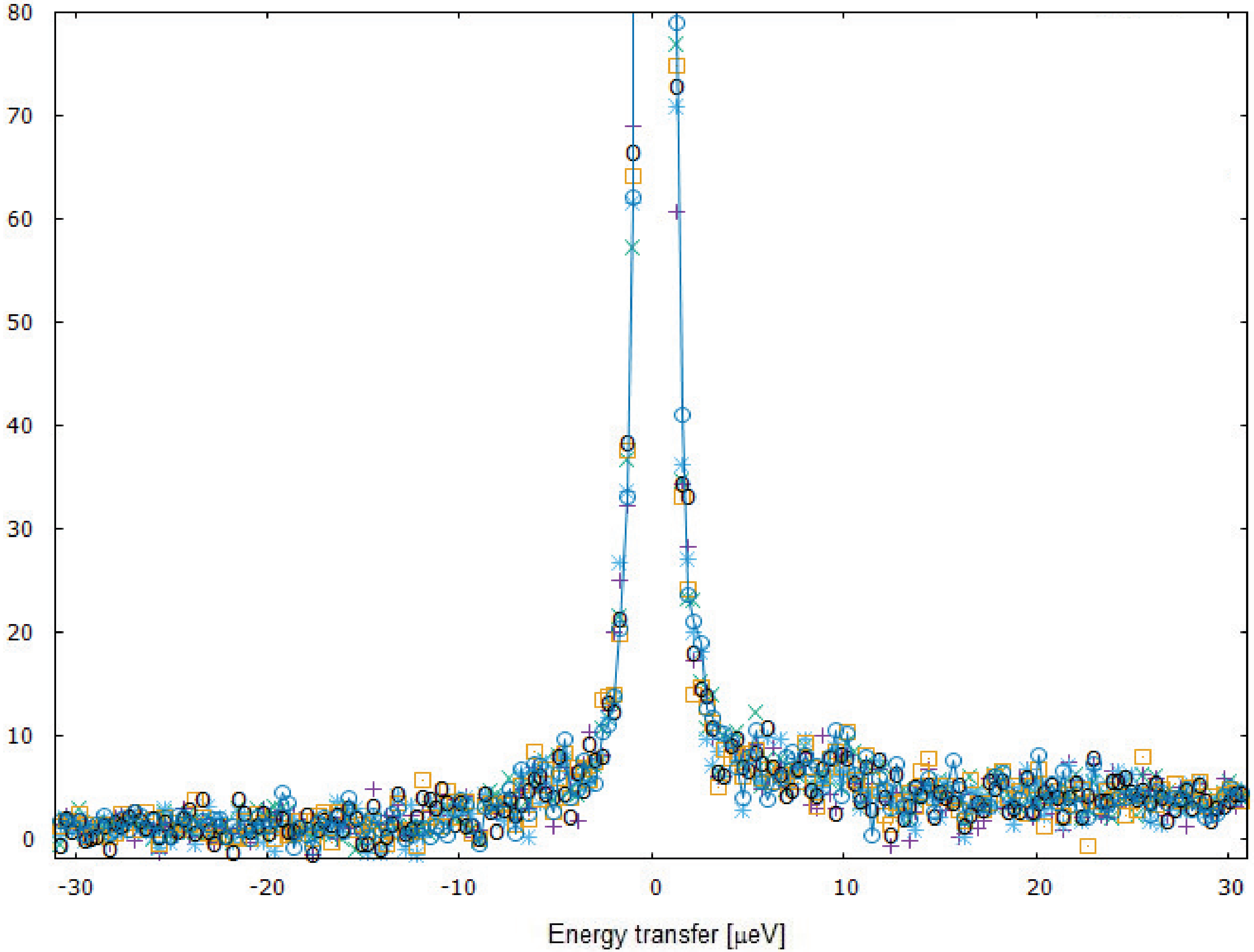
8*OCB, phase II, T = 25 K



8*OCB, glass of phase I, T = 25 K

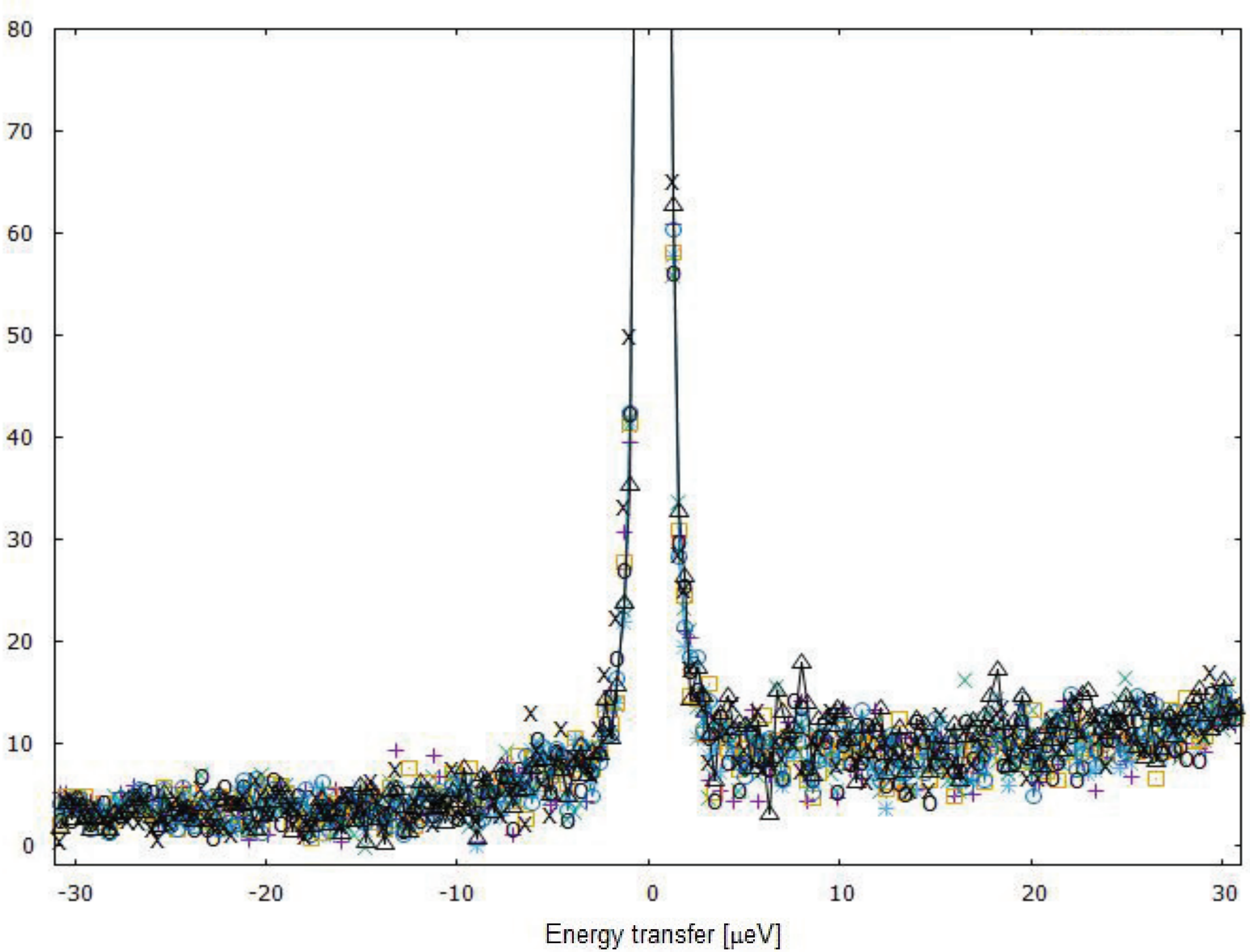


5*CB, glass of cholesteric phase



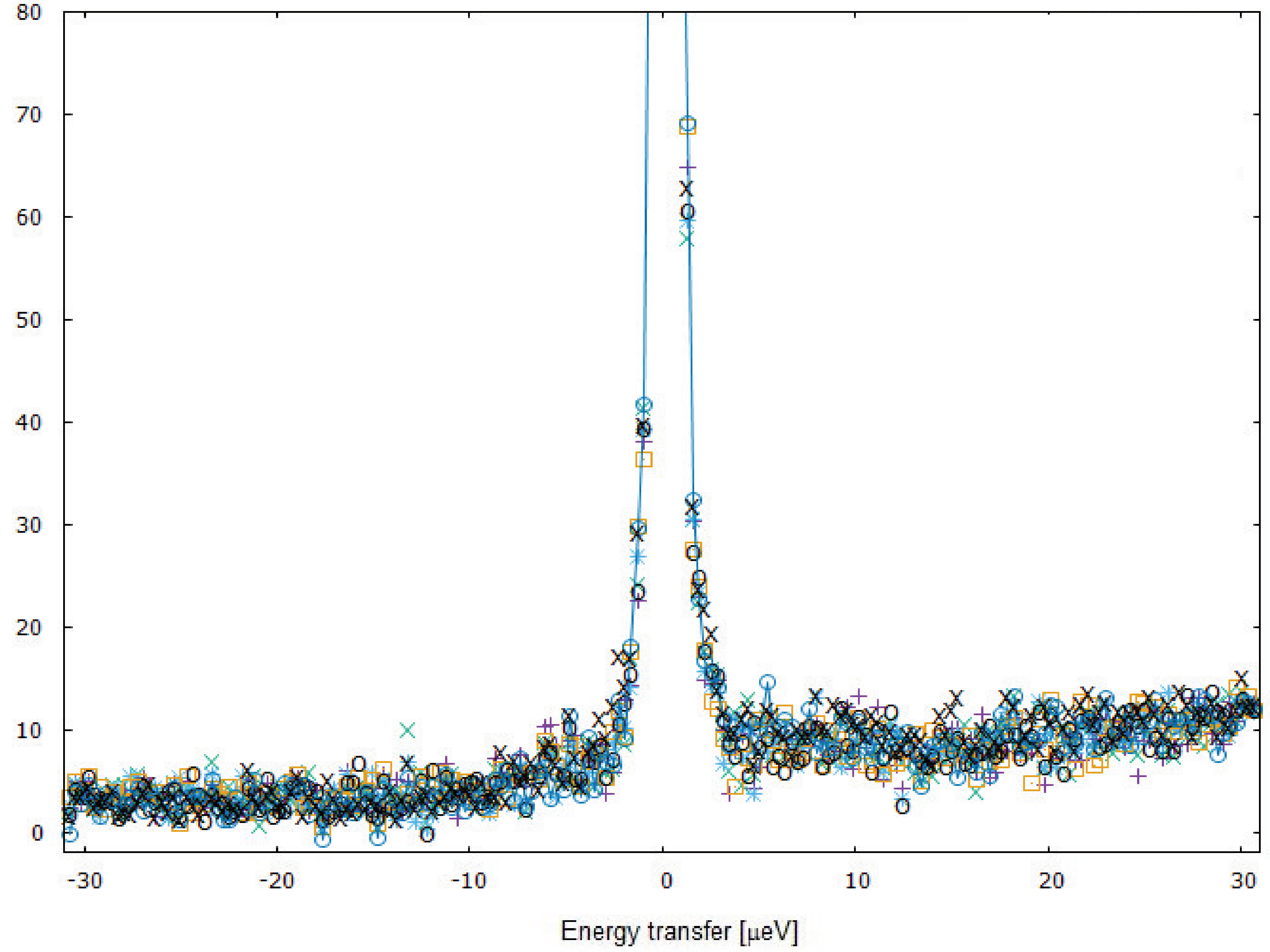
T = 4.4 K
8.4 K
12.3 K
16.3 K
20.9 K
25.4 K

5*CB, glass of phase II



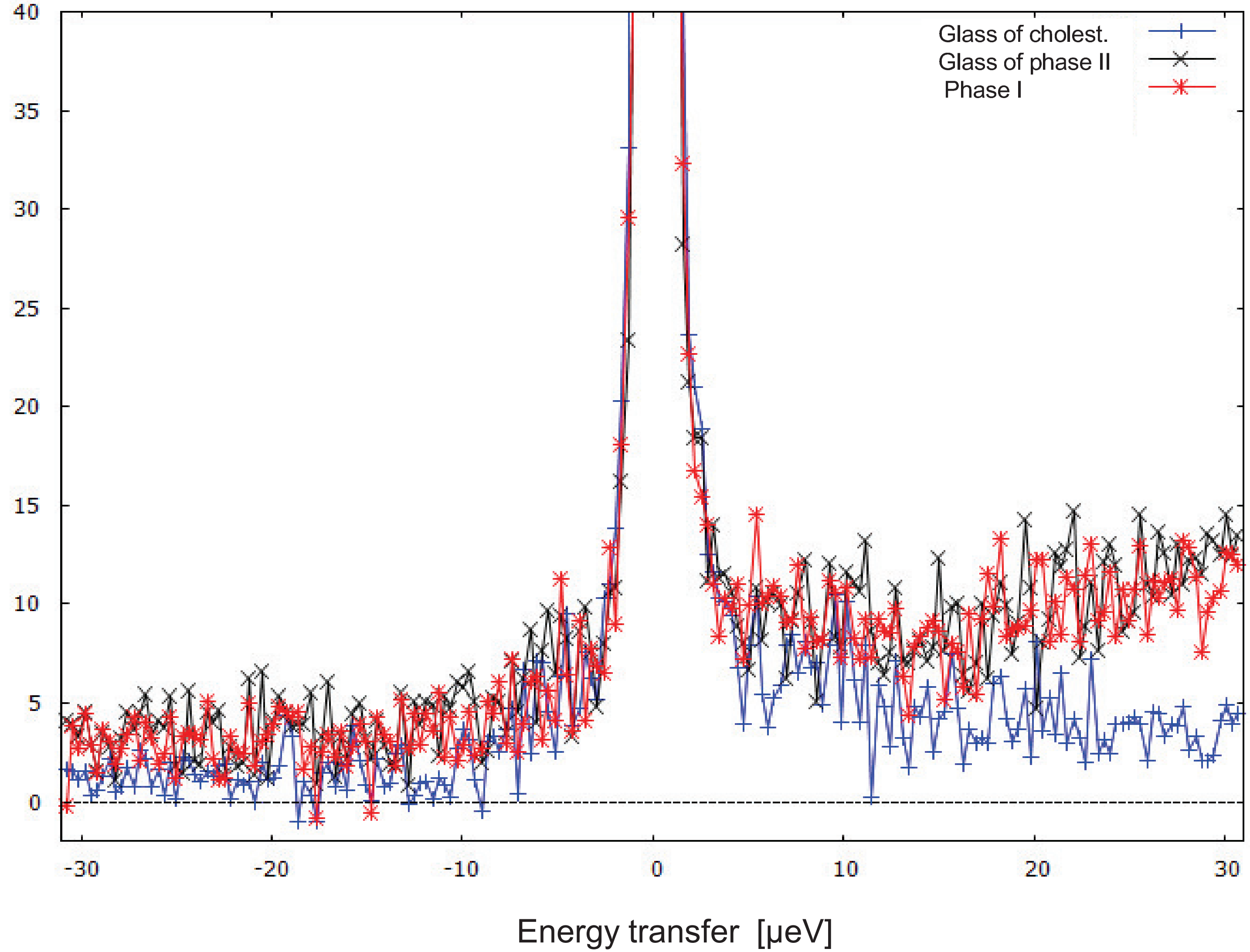
T = 3.5 K
7.7 K
9.7 K
14.6 K
19.2 K
24.7 K
29.8 K
35.0 K

5*CB, phase I



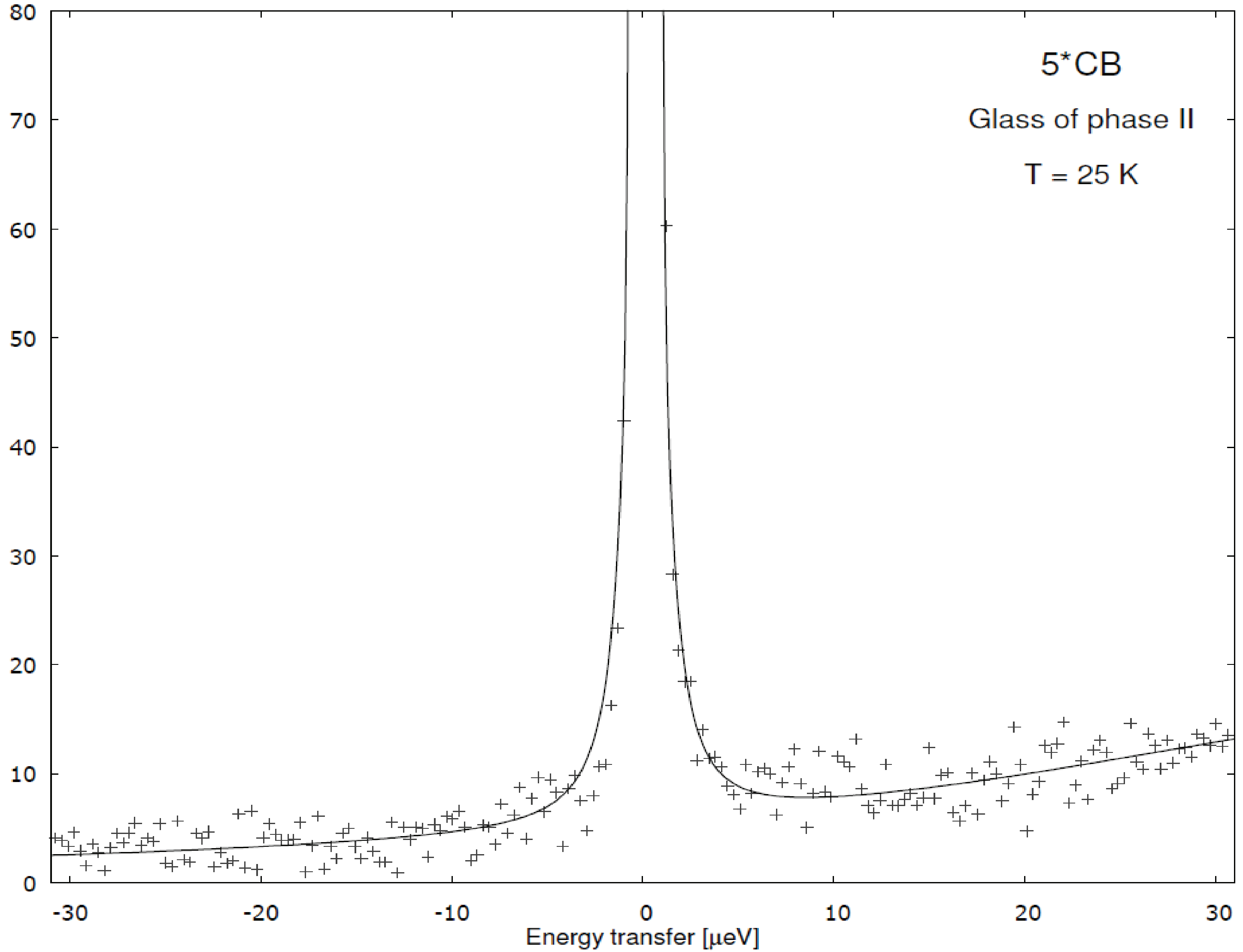
T = 4.5 K
8.8 K
13.0 K
17.5 K
22.3 K
27.3 K
32.5 K

5*CB, T ≈ 25 K

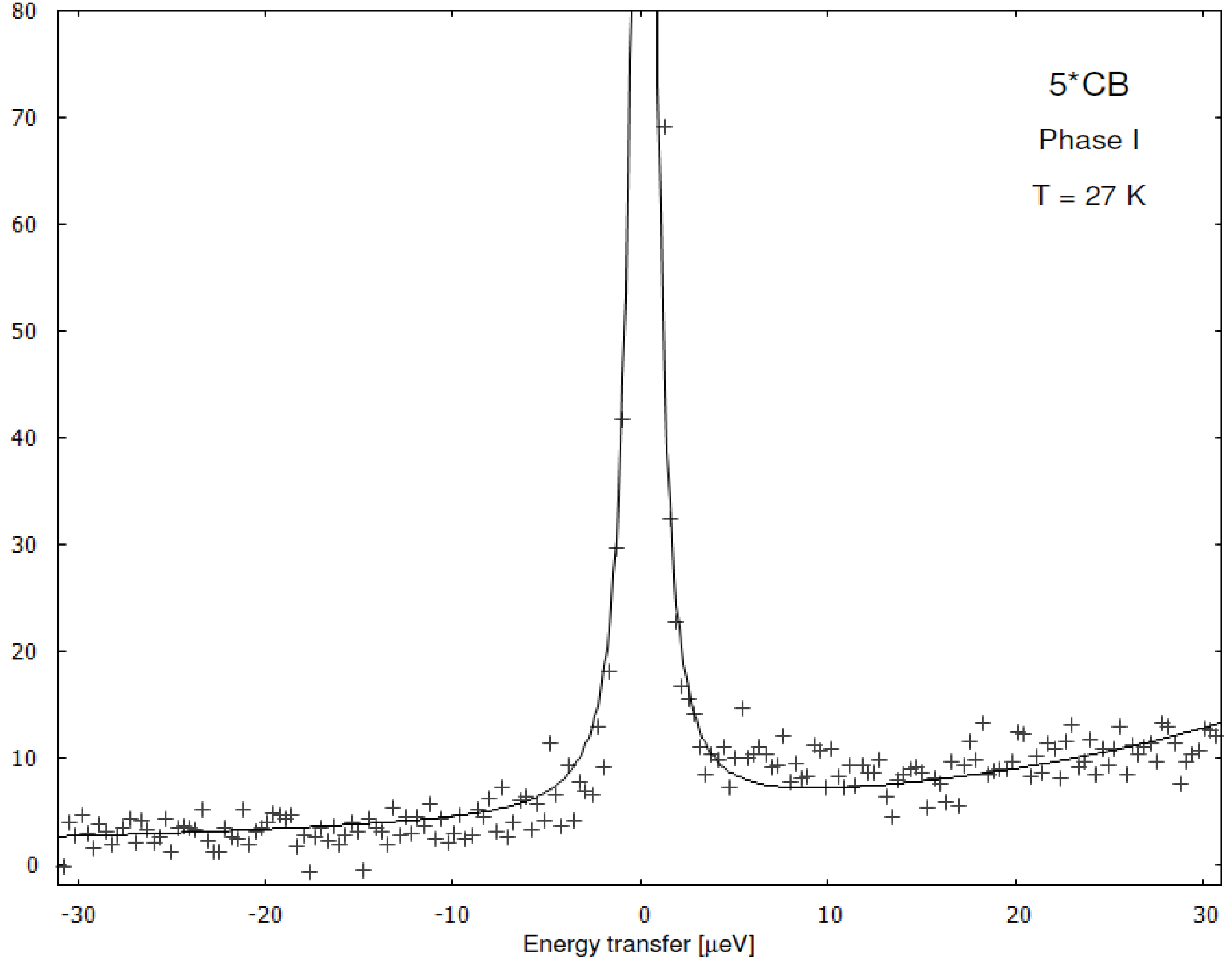


40
35
30
25
20
15
10
5
0
-30
-20
-10
0
10
20
30
Energy transfer [μeV]
Glass of cholest.
Glass of phase II
Phase I

5*CB, glass of phase II

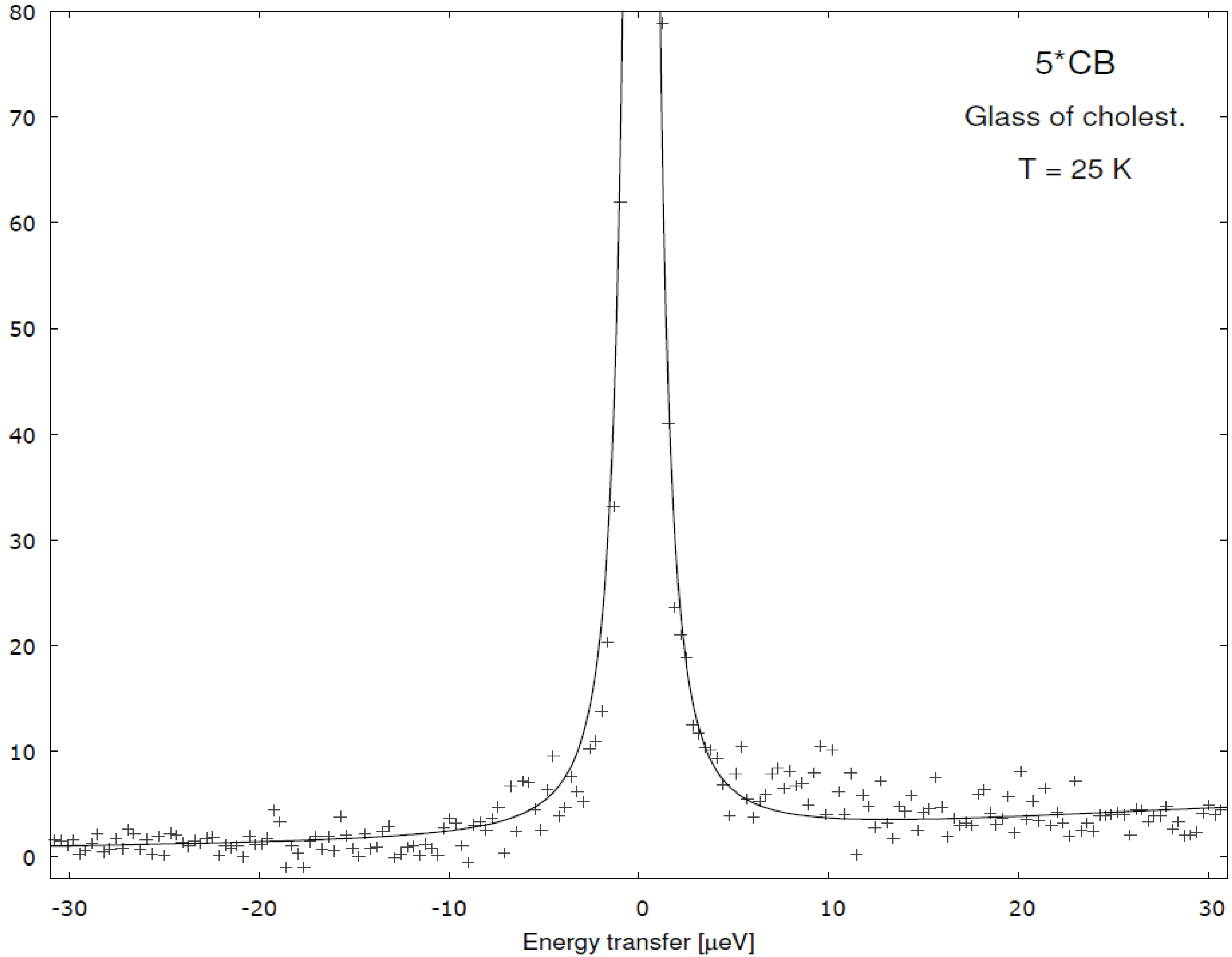


5*CB, phase I



80
70
60
50
40
30
20
10
0
-30
-20
-10
0
10
20
30
Energy transfer [µeV]
5*CB
Phase I
T = 27 K

5*CB, glass of cholesteric phase



- „Tail" of Boson peak visible for glass of isotropic liquid for 8*OCB and for glass of phase II and for phase I for 5*CB
  - some disorder in the most stable phase I

  A. Inaba, M. Massalska-Arodź, H. Suzuki, J. Krawczyk, Mol. Cryst. Liq. Cryst., **540** (2011) 102

- Fitted value of $\Gamma_{QENS} \approx 0.4 - 0.6\ \mu eV$ $(\tau \approx 1\ ns)$

  A little slower reorientation for glass of cholesteric of 5*CB,

  a little faster for isotropic phase of 8*OCB

- Both motions: stochastic (QENS) and „anharmonic” (localized) modes (Boson peak) are observed in both meV (ps) and μev (ns) scale

Acknowledgments

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Dr Hal Suzuki

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Thank you!