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Inelastic neutron and low-frequency Raman scattering in a niobium-phosphate glass for Raman gain applications

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ABSTRACT

We present measurements of the vibrational spectrum of a binary niobium-phosphate glass in the THz frequency range using inelastic neutron and Raman scattering. The spectra of these glasses show a low-frequency enhancement of the vibrational density of states ("boson peak"). Using a recently developed theory of vibrational excitations in disordered solids we are able to reconcile the measured neutron and Raman spectra using fluctuating elastic and Pockels constants as a model concept. As the spontaneous Raman susceptibility is a key parameter for Raman amplification our results suggest a significant gain profile for application of niobium-phosphate glasses in Raman amplifiers.

1. Introduction

The structural disorder of glasses leads to a spectral enhancement in the 1-THz (or 100 cm^{-1}) regime, which shows up both in inelastic neutron and Raman spectra. This enhancement, together with a strong light-strain (Pockels) coupling leads to a rather large Raman susceptibility in the class of niobium-phosphate glasses, which make them good candidates for Raman amplifyer materials. Both the enhancements of the Raman as well as the neutron spectra have been termed "boson peak", as the temperature dependence is just given by the boson function $n(\omega)+1=1/(1-e^{-\hbar\omega/k_BT})$. In reality this just demonstrates via the fluctuation–dissipation theorem that the underlying spectrum is temperature independent, i.e. the phenomenon is a harmonic one.

Concerning the boson peak an extended literature exists, in which the nature of the vibrational state in this frequency regime is investigated by experimental and simulational work, as well as by theoretical modelling [1–4]. However the light-vibrational coupling was hitherto discussed in terms of a phenomenological frequency-dependent function $C(\omega)$, and it was assumed that this function entered the prefactor of the Shuker–Gammon formula [5,6]

$$I(\omega) = [n(\omega) + 1]C(\omega)\frac{g(\omega)}{\omega}, \tag{1}$$

where $g(\omega)$ is the vibrational density of states (DOS). As the function $C(\omega)$ was unknown, researchers tried to determine it by comparing Raman data with DOS data, extracted from specific-heat or neutron scattering measurements [7,8]. Only very recently two of the present authors developed a theoretical model, in which the light-vibration coupling is modelled by spatially fluctuating Pockels constants, thereby allowing for the violation of the local momentum and angular-momentum selection rules [9]. The vibrational spectrum of the disordered solid was modelled by generalizing elasticity theory to allow for spatial fluctuations of the shear modulus [11–13]. This made it possible for the first time to treat inelastic X-ray, neutron and Raman scattering on the same footing. It was shown that the spectral shape of the "boson peak" seen by Raman scattering is not the same as that revealed by neutron scattering.

In the present contribution we report on a combined experimental and theoretical investigation of the low-frequency vibrational spectrum of 40 Nb_2O_5–60 $NaPO_3$ glass in order to explore its properties as candidate for Raman gain material. As spectroscopic methods we used inelastic neutron scattering and Raman scattering. The material shows a Raman scattering intensity ten times higher than that of a silica glass [14]. It is therefore indeed a promising candidate for all-optical Raman gain applications. By applying the theoretical framework of [9] we show, that the neutron and Raman spectra can be reconciled with each other using a model which involves a spatially fluctuating shear modulus and spatially fluctuating Pockels coefficients. By this procedure valuable structural information concerning the statistics of these fluctuations is obtained.

2. Theory

We briefly review our theoretical framework. We model the disordered solid as an elastic continuum, allowing for spatial

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fluctuations of the shear modulus G. The statistical properties of the fluctuations $\Delta G(\boldsymbol{r}) = G(\boldsymbol{r}) - \langle G \rangle$ are represented by the correlation function

$$C_G(\boldsymbol{r}) = \langle \Delta G(\boldsymbol{r} + \boldsymbol{r}_0)\Delta G(\boldsymbol{r}_0)\rangle \equiv \left\langle \Delta G^2 \right\rangle e^{-\frac{1}{2}r^2/\xi_G^2} \tag{2}$$

This can be shown [9,11–13] to lead to frequency-dependent complex sound velocities $v_{L,T}^2(\omega) = v_{L,T,0}^2 - \Sigma_{L,T}(\omega)$, where $\omega = 2\pi\nu$, and $\Sigma_T(\omega) = \frac{1}{2}\Sigma_L(\omega) \equiv \Sigma(\omega)$ is the so-called self energy. The latter obeys the self-consistent equation (self-consistent Born approximation, SCBA)

$$\Sigma(\omega) = \gamma \int\limits_{|\boldsymbol{k}|<k_D} \frac{d^3\boldsymbol{k}}{(2\pi)^3} \tilde{C}G(k)[\chi_L(\boldsymbol{k},\omega) + \chi_T(\boldsymbol{k},\omega)] \tag{3}$$

where we have put $C_G(k) = f_G\tilde{C}_G(k)$ with $\frac{1}{8\pi^3}\int_{|\boldsymbol{k}|<k_D} d^3\boldsymbol{k}\tilde{C}_G(\boldsymbol{k}) = 1$ and $\gamma \propto f_G \propto \langle \Delta G^2 \rangle$. The longitudinal and transverse strain susceptibilities $\chi_{L,T}$ are

$$\chi_{L,T}(\boldsymbol{k},\omega) = k^2 G_{L,T}(\boldsymbol{k},\omega) = \frac{k^2}{-\omega^2 + k^2\left[v_{L,T}^2(\omega)\right]} \tag{4}$$

The DOS is given by

$$g(\omega) = \frac{2\omega}{3\pi} \int\limits_{|\boldsymbol{k}|<k_D} \frac{d^3\boldsymbol{k}}{(2\pi)^3} \operatorname{Im}\{G_L(\boldsymbol{k},\omega) + 2G_T(\boldsymbol{k},\omega)\} \tag{5}$$

For the description of the light-vibration coupling the dielectric tensor is expanded with respect to the strain tensor $u_{ij} = (1/2)[\partial_i u_j + \partial_j u_i]$ as $\Delta\varepsilon_{ij}(\boldsymbol{r},t) = a_1(\boldsymbol{r})\sum_\ell u_{\ell\ell}(\boldsymbol{r},t)\delta_{ij} + a_2(\boldsymbol{r})v_{ij}(\boldsymbol{r},t)$ with $v_{ij} = u_{ij} - (1/3)\delta_{ij}\sum_\ell u_{\ell\ell}$ [15]. a_i are the opto-elastic or Pockels constants. They are now assumed [16] to have disorder-induced fluctuations $a_{1,2}(\boldsymbol{r}) = a_{1,2}^{(0)} + \Delta a_{1,2}(\boldsymbol{r})$ with correlation functions $C_{1,2}(\boldsymbol{r}) = \langle \Delta a_{1,2}(\boldsymbol{r}_0 + \mathrm{r})\Delta a_{1,2}(\boldsymbol{r}_0)\rangle$. The constant (average) terms $a_{1,2}^{(0)}$ produce the usual formulae for Brillouin scattering and Raman scattering. From the fluctuating terms one obtains

$$\begin{aligned} I_{VH}(\omega) &= [n(\omega) + 1]\frac{\alpha}{15}\left(\chi_{2,L}(\omega) + \frac{3}{2}\chi_{2,T}(\omega)\right) \\ I_{VV}(\omega) &= \frac{4}{3}I_{VH}(\omega) + \alpha[n(\omega) + 1]\chi_{1,L}(\omega) \end{aligned} \tag{6}$$

with the partial Raman susceptibilities ($i = 1,2$)

$$\chi_{i,L,T}(\omega) = \operatorname{Im}\left\{\int \frac{d^3\boldsymbol{k}}{(2\pi)^3} C_i(\boldsymbol{k})\chi_{L,T}(\boldsymbol{k},\omega)\right\} \tag{7}$$

where α is a proportionality constant which involves the incident intensity, divided by the 4th power of the wavelength of the scattered light [9]. We assume that the Pockels correlation functions are of Gaussian form (Eq. (2)) and introduce correlation lengths ξ_i and prefactors f_i as $C_i(k) = f_i\tilde{C}_i(k)$ with $\frac{1}{8\pi^3}\int_{|\boldsymbol{k}|<k_D} d^3\boldsymbol{k}\tilde{C}_i(k) = 1$.

3. Inelastic neutron and Raman scattering

The $40Nb_2O_5$–$60NaPO_3$ glass was prepared according to the procedure described in Ref. [18]. For neutron scattering experiments the samples powder form was filled in Nb double-cylinders with 0.1 mm wall thickness.

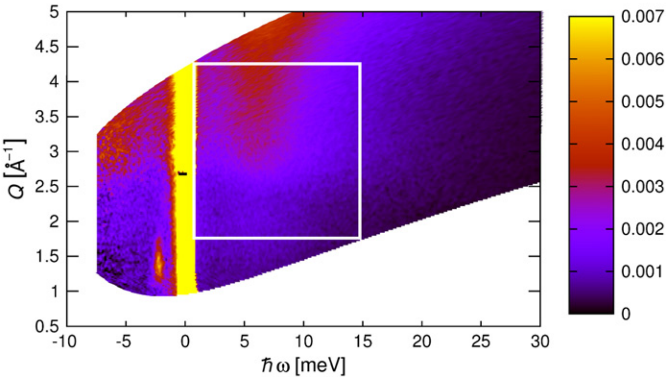

Fig. 1. Color plot of the scattering function $S(Q,\omega)$ of $40Nb_2O_5$–$60NaPO_4$ as measured by INS at the TOFTOF spectrometer. The boson peak is clearly visible on both the Stokes and the anti-Stokes side. For the calculation of the reduced DOS the region marked by the white rectangle was averaged with respect to Q (cf. text).

Inelastic neutron scattering experiment were carried out with the multi chopper time-of-flight spectrometer (TOFTOF) of the FRM II in Garching [10]. The direct geometry spectrometer is fed with neutrons of the cold source of the reactor which is operated with liquid D_2 at about 25 K. The neutrons are guided to the primary part of the spectrometer by an s-shaped curved neutron guide serving as gamma ray dump and wavelength filter with a cutting edge of 1.38 Å. Using a system of 7 rotating high speed chopper discs a pulsed monochromatic beam is extracted in the primary spectrometer and focused to the sample position. The time-of-flight the neutrons scattered by the sample need to travel to the detector is measured. Corresponding time-of-flight (*tof*) spectra are collected for all of the 600 individual detectors with an effective area of about 3 cm × 40 cm each. The detectors are arranged at 4 m distance from the sample tangentially to the intersection line of the Debye–Scherrer cones and a virtual sphere of 4 m radius around the sample position. Thus each detector collects a *tof*-spectrum at a well defined scattering angle 2θ despite its extended length.

From the intensity measured as a function of 2θ and *tof* the calculation of the scattering function weighted by the scattering lengths of the atoms of the sample $S(Q,\omega)$ can easily be evaluated. For this procedure the program 'ida' available at the spectrometer was used. The data was corrected for detector efficiencies using the elastic intensity of a vanadium measurement but also by taking the wavelength dependent sensitivity of the detectors and absorption of relevant spectrometer components into account. The data was furthermore corrected for background by subtraction of the empty can scattering. The density of states was obtained by an iterative procedure after correcting for the Debye–Waller factor and multi-phonon contributions.

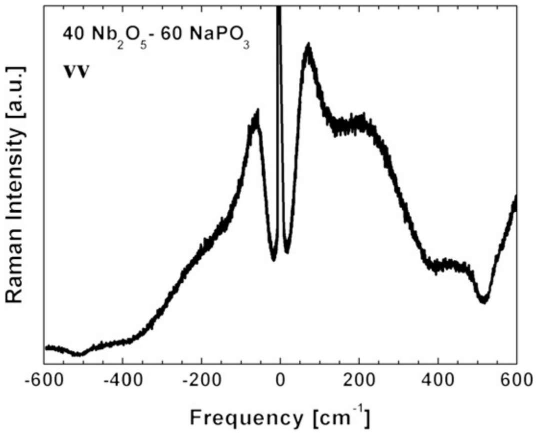

Fig. 2. Raman spectrum of $40Nb_2O_5$–$60NaPO_3$ glass excited at a wavelength of 514.5 nm. Shown is the vv polarized spectrum on both the Stokes (positive frequencies) and anti-Stokes sides.