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Contribution of acoustic modes to the density of vibrational states measured by inelastic scattering techniques

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We consider the contribution of acoustic modes to the density of vibrational states measured by nuclear inelastic, inelastic x-ray, and inelastic neutron scattering. In nuclear and x-ray scattering, the low-energy part of the density of states (DOS) is compared with the contribution of acoustic modes to the *generalized* density of states. Different to that, in neutron scattering the DOS is compared with the contribution of acoustic modes to the *true* density of states. We argue that in general this is not correct and that similar to nuclear and x-ray scattering, the neutron data in most cases must also be compared with the contribution of acoustic modes to the generalized DOS. For neutron scattering, this contribution usually is smaller than the contribution to the true DOS. Thus, the comparison of the neutron data with the contribution of acoustic modes to the true DOS systematically overestimates the level of acoustic modes. However, an extrapolation of the neutron DOS to zero energy often exceeds even this overestimated level. In our eyes, even for glasses the manifold excess of the extrapolation of the neutron DOS to zero energy over the expected level of acoustic modes seems to be unreasonable even though in this case one can still argue on existing of additional soft modes. However, a similar excess observed also for crystalline samples clearly indicates an uncertainty of the absolute scale of the DOS measured by neutron scattering.

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I. INTRODUCTION

Anomalies of low-energy vibrational modes in glasses remain the subject of intense studies. An important clarification of the nature of these modes can be achieved by comparison of the observed number of states with the expected contribution of acoustic modes, i.e., the so-called Debye level. For instance, the consistence of the measured states with the Debye level would favor ascribing of the glass anomalies to sound waves, whereas the excess of the measured states over the Debye level would support alternative hypothesis of localized vibrations.

Traditionally, these studies are performed using inelastic neutron scattering.[1–12] Recently, they became feasible also with nuclear inelastic scattering[13,14] and inelastic x-ray scattering. Revealing qualitatively similar effects, the results of the neutron and nuclear scattering techniques diverge specifically in the comparison of the measured density of states (DOS) with the calculated contribution of acoustic modes: while nuclear inelastic scattering shows that the extrapolation[15] of the derived DOS to zero energy is consistent with the Debye level,[13,14] inelastic neutron scattering, with few exceptions,[3,9,11] systematically shows that the zero-energy limit of the DOS significantly exceeds the level of acoustic modes.[1,2,5–7,10–12]

An appropriate comparison of the measured DOS with the contribution of acoustic modes obviously requires correct determination of the Debye level. On the other hand, the calculations of the Debye levels for various techniques follow different approaches: in nuclear and x-ray scattering, the low-energy part of the DOS is compared with the contribution of acoustic modes to the *generalized* density of states. In contrast, in neutron scattering the DOS is compared with the contribution of acoustic modes to the *true* density of states.

We argue that this is not correct and that similar to nuclear and x-ray scattering, the neutron data must also be compared with the generalized Debye level. For neutron scattering, this contribution is usually smaller than the contribution to the true DOS. Thus, the comparison of the neutron data with the true Debye level systematically overestimates the level of acoustic modes.

However, the extrapolation of the neutron DOS to zero energy often exceeds even this overestimated level.[1,2,5–7,10–12] Furthermore, when properly compared with the contribution of acoustic modes to the generalized density of states, the neutron DOS in some cases[12] exceeds the Debye level by a factor of 10. A similar excess has been also reported for crystalline samples.[12] This, in our eyes, indicates uncertainty of the absolute scale of the DOS measured by neutron scattering.

The paper is organized as follows. In Sec. II we consider general equations relating the true and the generalized DOS in the low-energy region. Section III analyzes these relations for particular cases of nuclear, x-ray, and neutron scattering. In Secs. IV and V we show that the DOS measured by nuclear and x-ray scattering is consistent with the generalized but not with the true Debye level. In Sec. VI we argue that the same should hold also for neutron scattering. Finally, Sec. VII analyzes the uncertainty of the absolute scale of the DOS measured by neutron scattering.

II. GENERAL EQUATIONS

We assume that the true DOS $g(E)$ [as well as discussed below, generalized and partial DOSs $\tilde{g}(E)$] is normalized to be the density of states per one degree of freedom,[16] i.e., that

$$\int_0^\infty g(E)dE = 1. \tag{1}$$

Then the true Debye level, i.e., the contribution of acoustic modes to the true DOS is given[17] by

$$\lim_{E\to 0} \frac{g(E)}{E^2} = \frac{1}{2\pi^2\hbar^3 n\langle v\rangle^3}, \tag{2}$$

where n is the number of atoms[18] per unit volume and $\langle v\rangle$ is the mean sound velocity defined by

$$\frac{1}{\langle v\rangle^3} = \frac{1}{12\pi}\sum_{j=1}^{3}\int \frac{d\Omega}{v_j^3}. \tag{3}$$

Here j numerates three acoustic modes, v_j is the directional-dependent sound velocity, and Ω is the solid angle variable of the sphere integral. For isotropic systems, Eq. (3) is reduced to

$$\frac{1}{\langle v\rangle^3} = \frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right). \tag{4}$$

The true DOS can be measured by inelastic scattering techniques only for monoatomic samples.[19] For polyatomic samples, the measured spectrum is a sum of spectra for various types of atoms weighted by unequal coefficients. Although each partial spectrum is directly related to the partial DOS of the given atoms, the measured "mixture" of spectra does not allow one to calculate the sum of the partial densities of states, i.e., the true DOS. In order to derive the true DOS, one has to use some additional information from, e.g., theory[20,21] or isotopic-contrast technique.[22]

A more common approach consists in processing data for polyatomic samples assuming that they are monoatomic substances. The function derived according to this procedure is called the generalized DOS in order to distinguish it from the true one.

Neglecting multiphonon terms of inelastic scattering and possibly small differences in the Debye-Waller factors of various types of atoms, the relative weight of a given atom in the spectrum of inelastic scattering is proportional to the ratio σ/m of its scattering cross section σ and mass m. Under these conditions, the generalized density of states $\tilde{g}(E)$ derived from the experimental data is a sum of the partial DOSs weighted by the same ratios σ/m.

In general, a relation between the true and the generalized DOSs can be obtained only knowing all eigenvectors for all vibrational states. However, in order to compare the measured density of state with the contribution of acoustic modes, only the low-energy approximation of the generalized DOS has to be considered.

For the low-energy acoustic vibrations with sufficiently long wavelengths one can assume identical displacements of various atoms. Then, at low energy all partial DOS should have identical functional dependence scaled by a coefficient proportional to the atomic mass m. Using this assumption, one arrives to the proportionality of the low-energy limits of the generalized and the true DOSs,[20,23–25]

$$\lim_{E\to 0} \frac{\tilde{g}(E)}{E^2} = \eta \lim_{E\to 0} \frac{g(E)}{E^2}, \tag{5}$$

where the scaling coefficient η can be expressed as the ratio of the effective probe mass m_p and the mean atomic mass $\langle m\rangle$,

$$\eta = \frac{m_p}{\langle m\rangle}, \quad m_p = \frac{\langle\sigma\rangle}{\langle\sigma m^{-1}\rangle}. \tag{6}$$

Here the averaging $\langle\cdots\rangle$ is performed over all atoms of the sample.

From Eqs. (2) and (5), the generalized Debye level, i.e., contribution of acoustic modes to the generalized DOS, is obtained as

$$\lim_{E\to 0} \frac{\tilde{g}(E)}{E^2} = \eta \frac{1}{2\pi^2\hbar^3 n\langle v\rangle^3}. \tag{7}$$

This result has been obtained independently for neutron scattering [compare Eqs. (29) and (34) in Ref. 20], x-ray scattering [Eq. (24) in Ref. 23], and nuclear scattering.[24,25]

III. PARTICULAR CASES

The contributions of acoustic modes to the generalized and to the true DOSs are the same only if all atoms of the system have identical masses. In this case, Eq. (6) gives $\eta = 1$. In contrast, equality of the cross sections does not give $\eta = 1$ but leads to

$$\eta = \frac{1}{\langle m\rangle\langle m^{-1}\rangle} \le 1. \tag{8}$$

For x-ray scattering, the square root of the scattering cross section is approximately proportional to the mass of the atom. Under this condition, Eq. (6) gives

$$\eta \approx \frac{\langle m^2\rangle}{\langle m\rangle^2} \ge 1. \tag{9}$$

Nuclear scattering occurs only for a particular type of atoms with low-energy nuclear transition. In this case, the coefficient η is reduced to the ratio of the mass m_r of the resonant atom and the mean atomic mass

$$\eta = \frac{m_r}{\langle m\rangle}. \tag{10}$$

For neutron scattering, a similar extreme is reached for many hydrogen-containing compounds, in particular, for polymers and proteins. For hydrogen, the ratio of the cross section to the mass is so large relative to all other atoms, which the effective probe mass m_p [Eq. (6)] is basically indistinguishable from the hydrogen mass m_H, and the coefficient η becomes

$$\eta \approx \frac{m_H}{\langle m\rangle}. \tag{11}$$

For nuclear scattering, which occurs only for a single type of atoms, the measured spectrum of inelastic scattering by

TABLE I. Mass-ratio coefficient η for samples used for comparison of the density of states measured by nuclear inelastic scattering with the contribution of acoustic modes.

Sample	Mass ratio η	Reference
Iron	1.00	25, this work
$Sn_{0.01}Pd_{0.99}$	1.12	25
Fe_2O_3	1.76	25
$FeBO_3$	2.46	This work
$NaFeSi_2O_6$	2.46	This work
$Na_2FeSi_3O_{8.5}$	2.56	14
Myoglobin	8.20	24

definition is a pure partial one and is directly related to the pure partial DOS of the given atoms. Thus, in this case there is no need to use any approximation estimating the weight of the given atoms in the spectrum of inelastic scattering. Therefore, for nuclear inelastic scattering Eqs. (7) and (10) are valid also beyond the single-phonon approximation: they can be obtained directly from the assumption of identical displacements of various atoms and the definition of the partial DOS.[26]

IV. NUCLEAR INELASTIC SCATTERING

Nuclear inelastic scattering provides direct evidences that the measured DOS must be compared with contribution of acoustic modes not to the true but to the generalized DOS. For nuclear scattering, the coefficient η is given by the ratio of the mass of the resonant atom and the mean atomic mass [Eq. (10)]. Frequently, the resonant isotope is the heaviest atom of the substance. In these cases, the mass-ratio coefficient η is bigger than unity (Table I). For proteins consisting of light atoms as myoglobin,[24] the mass-ratio coefficient is close to a factor of 10 (Table I).

Some data listed in Table I have been obtained with disordered solids, where the ascription of all low-energy vibrations solely to the acoustic modes is still debated and, thus, the validity of Eqs. (2) and (7) could be questioned. Therefore, here we present more data obtained with single crystals and polycrystalline samples, where Eqs. (2) and (7) *must* be fulfilled.

The measurements were performed at the Nuclear Resonance beamline[27] ID18 at the European Synchrotron Radiation Facility (ESRF). All data were taken at ambient conditions using the nuclear inelastic spectrometer with the energy resolution of 0.6 meV. Description of the experimental setup and data processing can be found elsewhere.[28,29]

Figure 1 demonstrates reliability of nuclear scattering data. Here and below all shown nuclear scattering and neutron DOSs are normalized to be the density of states per one degree of freedom [Eq. (1)].

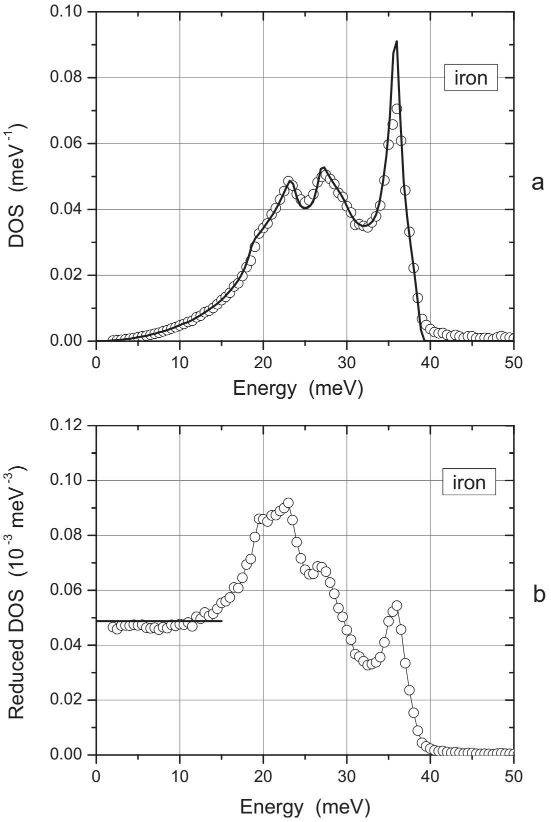

FIG. 1. (a) The density of phonon states $g(E)$ measured by nuclear inelastic scattering for polycrystalline ^{57}Fe. For comparison, the thick solid line shows the DOS calculated from dispersion relations obtained by neutron scattering (Ref. 30). (b) The corresponding reduced density of states $g(E)/E^2$. The thick horizontal line shows the expected contribution of acoustic modes calculated according to Eq. (2). The thin line is guide for the eyes.

Figure 1(a) shows the density of states of polycrystalline iron, i.e., of a monoatomic sample, where the measured DOS must coincide with the true one. The DOS measured by nuclear inelastic scattering is basically indistinguishable from the DOS calculated[30] from dispersion relations measured by neutron scattering. These particular neutron data are chosen for the comparison because the DOS *calculated* from dispersion relations is not affected by the discussed below uncertainty of the *measured* neutron DOS. For proper comparison, the neutron data have been convoluted with a Gaussian function of 0.6 meV width, which simulates the instrumental function of the inelastic spectrometer. Some disagreement of the two data sets near the sharp peak at ~36 meV is attributed to a broadening of the phonon states by the finite lifetime, which is not taken into account in calculations of the DOS from dispersion relations. Similar agreement of nuclear and neutron scattering data has been observed for nuclear data obtained at the Advance Photon Source.[28]

In order to check the agreement of the low-energy part of the DOS with sound velocity data according to Eq. (2), Fig. 1(b) shows the corresponding *reduced* density of states $g(E)/E^2$. In Debye approximation, this function should be a horizontal straight line. The reduced DOS of the polycrystalline iron follows the Debye approximation up to ~12 meV. It matches the contribution of acoustic modes, which was calculated according to Eq. (2) using the mean sound velocity of 3.50 km/s. The mean velocity was derived according to Eq. (3) assuming that the elastic constants and the lattice

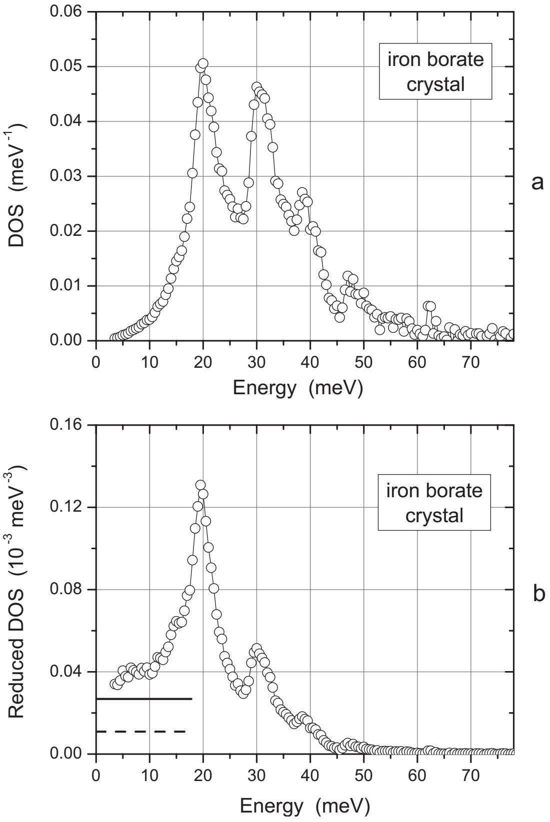

FIG. 2. (a) The iron-partial density of phonon states $\tilde{g}(E)$ measured by nuclear inelastic scattering for iron borate ^{57}FeBO$_3$ single crystal with x-ray beam along the {111} crystallographic axis. (b) The corresponding reduced density of states $\tilde{g}(E)/E^2$. The solid and dashed horizontal lines show the expected contributions of acoustic modes to the partial [Eq. (7)] and the true [Eq. (2)] DOSs, respectively. The thin solid lines on both panels are guides for the eyes.

constant of the ^{57}Fe sample are the same as those[31] of the natural iron.

Figures 2 and 3 demonstrate nuclear scattering data for polyatomic samples, where the measured generalized (in this case, the iron-partial) DOS must differ from the true one. Figure 2(a) shows the DOS measured for the single crystal of iron borate ^{57}FeBO$_3$ with the incident x-ray beam directed along the {111} crystallographic axis (quoted for a rhombohedral lattice). In this case, one obtains the iron-partial DOS "projected"[32] on this particular direction of the crystal. Figure 3(a) shows the DOS of the polycrystalline aegirine Na ^{57}FeSi$_2$O$_6$.

Figures 2(b) and 3(b) serve to verify whether the corresponding reduced densities of states $\tilde{g}(E)/E^2$ are consistent with the contribution of the acoustic modes to the generalized [Eq. (7)] or to the true [Eq. (2)] DOS. The two contributions are shown by the solid and dashed horizontal lines, respectively. The Debye behavior of the reduced DOS for these samples is not pronounced, in particular, because of the larger unit cells and, consequently, smaller Brillouin zones. Nevertheless, the extrapolation of the reduced densities of states to zero energy is clearly consistent with the contributions of acoustic modes to the generalized DOS (solid lines) and not to the true one (dashed lines).

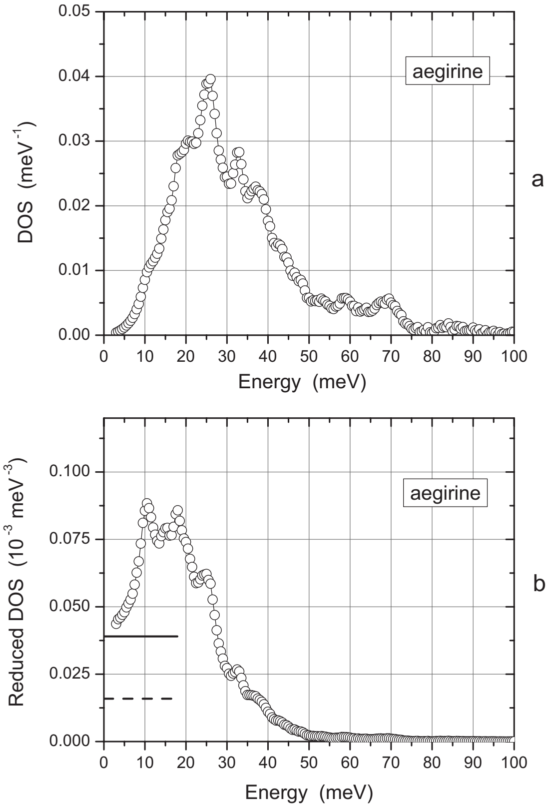

FIG. 3. (a) The iron-partial density of phonon states $\tilde{g}(E)$ measured by nuclear inelastic scattering for aegirine Na ^{57}FeSi$_2$O$_6$ polycrystalline sample. (b) The corresponding reduced density of states $\tilde{g}(E)/E^2$. The solid and dashed horizontal lines show the expected contributions of acoustic modes to the partial [Eq. (7)] and the true [Eq. (2)] DOSs, respectively. The thin solid lines on both panels are guides for the eyes.

The mean sound velocities required for the calculations of the contributions of acoustic modes were determined as follows: for the iron borate single crystal, it was calculated using reported elastic constants[33] with the expression

$$\frac{1}{\langle v\rangle^3} = \frac{1}{4\pi}\sum_{j=1}^{3}\int\frac{(\mathbf{n}\cdot\mathbf{u}_j)^2}{v_j^3}d\Omega, \tag{12}$$

which accounts for the projected[32] character of the measured DOS. Here $\mathbf{n}$ is the unit vector directed in accordance with the experimental geometry along the {111} crystallographic axis and $\mathbf{u_j}$ is the unit polarization vector of the jth acoustic mode. The obtained value of 5.27 km/s is close to the mean sound velocity of 5.23 km/s calculated according to Eq. (4) from longitudinal (8.44 km/s) and transverse (4.70 km/s) sound velocities[33] measured along the {111} axis.

For the aegirine, the sound velocities and elastic constants are available from early ultrasound measurements.[34] Based on these data, the mean sound velocity calculated according to Eq. (3) is 4.51 km/s. However, recent publications indicate that the data in Ref. 34 obtained for a natural mineral seem to understate the sound velocities. For instance, two independent studies of the equation of state gave the *isothermic* bulk modulus of 117(1) (Ref. 35) and 116.1(5) GPa.[36] Since the

TABLE II. Mass-ratio coefficient η for samples used for comparison of the density of states measured by inelastic x-ray scattering with the contribution of acoustic modes.

Sample	Mass ratio η	Reference
Diamond	1.00	23
BN	1.03	38
MgO	1.10	23

adiabatic bulk modulus is usually few percent higher than the isothermic modulus, one could expect it to be about ~120 GPa. However, the adiabatic bulk modulus calculated[35] from the ultrasound data[34] is 107 GPa, i.e., *smaller* than the isothermic one. In order to clarify this discrepancy, we verified some sound velocities by inelastic x-ray scattering. The measurements of the acoustic phonon dispersions were performed at the Inelastic Scattering II beamline[37] ID28 at the ESRF. The values of 7.80 and 4.47 km/s were obtained for the longitudinal velocity along {100} direction and for the transverse velocity along {010} direction with atomic displacements along {100} axis, respectively. The fit of the measured velocities using scaling of elastic constants from Ref. 34 gave a reasonable adiabatic modulus of 125 GPa and the mean sound velocity of 4.94 km/s. This value was used to calculate the contributions of acoustic modes shown in Fig. 3(b).

V. INELASTIC X-RAY SCATTERING

For inelastic x-ray scattering, the possibility to measure the density of vibrational state has been demonstrated quite recently.[23,38] Thus, the list of the investigated samples for the moment is relatively short (Table II). Nevertheless, inelastic x-ray scattering data also show that the measured DOS must be compared with contribution of acoustic modes not to the true but to the generalized DOS.

For inelastic x-ray scattering, the coefficient η can be approximated by Eq. (9). Thus, it should be bigger than unity. Table II shows that this is indeed the case. For monoatomic diamond, an agreement of the low-energy part of the DOS with the calculated contribution of acoustic modes confirms reliability of the data.[23] For biatomic MgO, the mass-ratio coefficient η differs from unity not too much. Nevertheless, the measured DOS agrees with contribution of acoustic modes to the generalized but not to the true DOS.[23]

VI. INELASTIC NEUTRON SCATTERING

Different to nuclear and x-ray scattering, the density of states measured by inelastic neutron scattering is always compared with the contribution of acoustic modes not to the generalized [Eq. (7)] but to the true DOS [Eq. (2)]. To the best of our knowledge, this approach is not explicitly argued for but followed as the self-evident one in all relevant publications.[2–12] Moreover, the experimental reports on inelastic neutron scattering most often even do not distinguish the true and the generalized DOSs.

Derivations of the DOS from inelastic neutron scattering data follow various approaches. Here we analyze three of them, which appear to be the main trends.

According to the first approach,[2,12,39] the obtained DOS is normalized to be the density of states per one degree of freedom. This means that the area of the derived DOS is forced to be equal to unity. When the DOS is measured in a sufficiently broad energy region, the normalization is done explicitly.[2] For measurements performed within a limited energy range, the same normalization is attempted[40] by estimation of the number of vibrational modes in the studied energy region.[12,39]

This approach is clearly identical to that discussed for nuclear inelastic and inelastic x-ray scattering. Therefore, in our eyes, the low-energy part of the DOS must be compared with the contribution of acoustic modes to the generalized DOS. The comparison of the derived DOS with the contribution of acoustic modes to the true DOS[2,12] in this case is clearly unjustified.

The second approach[3,7,11,12,41] is based on the procedure described by Carpenter and Pelizzari.[42] The neutron scattering data are normalized so that the static structure factor $S(Q)$ is equal to unity at the infinite wave vector Q. Then, assuming that a sample is composed by atoms with the masses equal to the mean atomic mass, one can derive the density of states so that it is equal to the true DOS exactly at zero energy.[20,42,43] The total area of this DOS is equal not to unity but to $1/\eta$ (Ref. 20).

When following this approach strictly, it indeed would require the comparison of the derived density of states with the contribution of acoustic modes not to the generalized but to the true DOS. In practice, however, this procedure is appended by a subsequent renormalization of the DOS in order to fit the calculated specific heat to the experimental data. Below we show that in most cases this leads to the normalization of the DOS according to the first approach, i.e., with the area equal to unity.

For instance, comparison of the density of states of orthoterphenil glass reported in Refs. 12 and 41 shows that the DOS derived in Ref. 41 using the Carpenter-Pelizzari procedure does not fit the specific heat data. In order to obtain the acceptable fit, in Ref. 12 the DOS has been additionally renormalized, i.e., divided by a factor of about 2. This renormalization factor has been evaluated by matching the area of the DOS to the estimated number of vibrational modes in the studied energy region. This is identical to forcing of the entire area of the DOS to unity. Similar procedure has been also followed in Ref. 39. Thus, the fit to the specific heat data caused in these cases the renormalization of the DOS according to the first approach.

Similarly, in Ref. 7 the density of states of vitreous silica was derived according to the Carpenter-Pelizzari procedure and then renormalized. The renormalization factor of 1.27 has been derived by fitting the calculated specific heat to the experimental data. According to Table III, it is close to the inverse mass-ratio coefficient $1/\eta$. Because at zero energy the initial Carpenter-Pelizzari DOS is equal to the true one, this procedure makes the zero-energy limit of the renormalized DOS close to the generalized Debye level defined by Eq. (7). Thus, the extrapolation of the DOS to zero energy in

TABLE III. Mass-ratio coefficient η for samples used for comparison of the density of states measured by inelastic neutron scattering with the contribution of acoustic modes.

Sample	Mass ratio η	Reference
Germanium	1.00	1
Boron oxide	0.94	2 and 3
Silica	0.88	4–7
Germania	0.77	7
Polyisobutylene	0.22	8
Polybutadiene	0.19	9 and 10
Glycerol	0.16	11
Orthoterphenyl	0.15	12

this case also must be compared with the contribution of acoustic modes to the generalized and not to the true DOS.

The observed reduction of the Carpenter-Pelizzari DOS to the DOS defined according to the first approach by fitting specific heat data is not surprising. The vibrational part of specific heat per one atom is related to the true DOS $g(E)$ according to the relation[44]

$$c_V(T) = 3k_B \int_0^{\infty} g(E,T) \frac{x^2 \exp(x)}{[\exp(x) - 1]^2} dE, \qquad (13)$$

where $x=E/(k_BT)$, k_B is the Boltzmann constant, and T is the temperature. It shows that the contribution of the relatively flat reduced density of states $g(E)/E^2$ to specific heat is weighted by the factor $x^4 \exp(x)/[\exp(x)-1]^2$, which has a maximum at about $x=4$. Then, because the Carpenter-Pelizzari DOS is equal to the true one only at low energies, let us say, below 1 meV, the calculated specific heat should be equal to the experimental data only below 1 $\mathrm{meV}/(4k_B)=3$ K. Therefore, the specific heat calculated from the Carpenter-Pelizzari DOS could fit only *zero-temperature extrapolation* of specific heat. In practice, however, this is hardly possible because at low temperatures the vibrational part of specific heat is shadowed by tunneling processes.

At higher temperatures, the calculated specific heat is determined by vibrational states at higher energies, where the DOS derived according to the Carpenter-Pelizzari procedure is bigger that the true one.[20] Therefore, the fit to the specific heat data requires the corresponding renormalization of the DOS. Furthermore, at higher temperatures the calculated specific heat looses the sensitivity to the shape of the DOS and is determined mainly by the DOS normalization. Because the area of the Carpenter-Pelizzari DOS is equal to $1/\eta$, (Ref. 20) the fit of the calculated specific heat to the experimental data inevitably requires the division of the initially derived DOS by the factor of $1/\eta$, i.e., the renormalization of the DOS to unit area. This explains the experimental observations,[7,12,39] where the fit to the specific heat data effectively reduces the Carpenter-Pelizzari DOS to the density of states defined according to the first approach.

Finally, the third approach[1,4–6] consists in calculations of the DOS according to models of atomic motions. For monoatomic samples, the derived DOS is reported to be not much sensitive to the chosen model.[1] For polyatomic samples, however, the choice of the model can change the absolute scale of the derived DOS by a big factor.[4] Our limited expertise in inelastic neutron scattering does not allow us to judge how the contribution of acoustic modes could be *a priori* determined in this case. However, the published results show that the density of states derived according to this approach[5,6] coincides with the DOS obtained according to the Carpenter-Pelizzari procedure and additionally divided by the coefficient close to $1/\eta$ (Ref. 7). Thus, the model-dependent calculations of the DOS also appear to provide the density of states defined according to the first approach. Therefore, the low-energy part of the DOS in this case must also be compared with the contribution of acoustic modes not to the true but to the generalized DOS.

VII. IMPLICATIONS

As discussed above, the most common approaches to treat the data of inelastic neutron scattering lead to the density of states, which the low-energy limit should be compared with the contribution of acoustic modes not to the true but to the generalized density of states.

Unlike nuclear and x-ray scattering, for neutron scattering the contribution of acoustic modes to the generalized DOS [Eq. (7)] is usually smaller than that to the true one [Eq. (2)]. Indeed, Table III shows that the mass-ratio coefficients η for samples used in relevant inelastic neutron scattering experiments are smaller than unity. For substances composed of atoms with comparable cross sections, this could be expected from Eq. (8). For hydrogen-containing compounds, this follows from Eq. (11).

Therefore, the comparison of the density of states measured by inelastic neutron scattering with the contribution of acoustic modes to the true and not to the generalized DOS systematically overestimates the Debye level. Table III shows that while in case of boron oxide the error is relatively small, for hydrogen-containing orthoterphenil the overestimation of the Debye level is bigger than a *factor* of 6.

However, an extrapolation of the neutron DOS to zero energy as a rule exceeds even this overestimated level. Usually the reported value of the excess over the contribution of acoustic modes to the true DOS reaches a factor of 2 or 3 depending on samples.[2,5–7,10–12] The proper comparison of the DOS with the contribution of acoustic modes not to the true but to the generalized DOS shows that in some cases[12] the excess surpasses a factor of 10. In our eyes, even for glasses this manifold excess of the zero-energy limit of the DOS over the Debye level seems to be unreasonable even though in this case one can still argue on existing of additional soft modes.

However, a similar excess is observed also for *crystalline* samples. For instance, Fig. 4 shows the reduced density of states from Ref. 12 measured by inelastic neutron scattering for the orthoterphenyl (OTP) polycrystalline powder. For compatibility, we converted the original data from THz to meV units and divided the DOS by a factor of 3 in order to come to the density of states per one degree of freedom. The contributions of acoustic modes were calculated using the

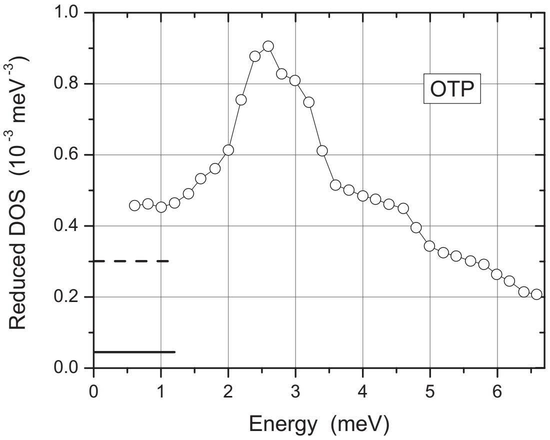

FIG. 4. The reduced density of states $\tilde{g}(E)/E^2$ measured by inelastic neutron scattering (Ref. 12) for orthoterphenyl polycrystalline powder at 200 K. The solid and dashed horizontal lines show the expected contributions of acoustic modes to the generalized [Eq. (7)] and the true [Eq. (2)] DOSs, respectively. The thin line is guide for the eyes. From Ref. 12.

mean sound velocity of 1.90 km/s derived from the average of the reported $\langle v\rangle^{-3}$ values[45] for three lattice directions of the OTP crystal.[12]

The solid and dashed horizontal lines, as above, show the expected contributions of acoustic modes to the generalized [Eq. (7)] and the true DOSs [Eq. (2)], respectively. Different to Figs. 2 and 3, however, the relative positions of the lines are the opposite: the contribution of the acoustic modes to the generalized DOS (solid line) is lower than that to the true one (dashed line). As discussed above, this turnover originates from $\eta \geq 1$ for nuclear scattering (Table I) and $\eta \leq 1$ for neutron scattering (Table III).

Figure 4 shows that extrapolation of the derived DOS to zero energy exceeds even the overestimated contribution of acoustic modes to the true DOS (dashed line). The proper comparison, however, has to be done with the contribution of acoustic modes to the generalized DOS (solid line) because the reported DOS has been normalized by authors so that its area is equal to the estimated number of vibrational modes within the studied energy region.[12] Figure 4 shows that the zero-energy limit of the DOS of a crystalline sample is bigger than the properly estimated Debye level (solid line) by about a factor of 10. This clearly indicates uncertainty of the absolute scale of the DOS measured by neutron scattering.

VIII. SUMMARY

We argue that the low-energy part of the density of vibrational states measured by inelastic neutron scattering has to be compared with the contribution of acoustic modes to the generalized DOS and that the commonly accepted comparison of neutron data with the contribution of acoustic modes to the true DOS systematically overestimates the level of acoustic modes. The degree of the overestimation is given by the ratio of the mean atomic mass to the effective probe mass. It is especially noticeable for hydrogen-containing compounds, where the effective probe mass is small because scattering proceeds mainly via the light hydrogen atoms.

However, an extrapolation of the neutron DOS to zero energy often exceeds even this overestimated level. In our eyes, even for glasses the observed manifold excess of the zero-energy limit of the DOS over the expected level of acoustic modes seems to be unreasonable even though in this case one can still argue on existing of additional soft modes. However, an existing of similar observations also for crystalline samples clearly indicates uncertainty of the absolute scale of the DOS measured by neutron scattering.

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[1] U. Buchenau, M. Prager, W. Kamitakahara, H. R. Shanks, and N. Nucker, Europhys. Lett. **6**, 695 (1988).

[2] A. C. Hannon, R. N. Sinclair, and A. C. Wright, Physica A **201**, 375 (1993).

[3] D. Engberg, A. Wischnewski, U. Buchenau, L. Börjesson, A. J. Dianoux, A. P. Sokolov, and L. M. Torell, Phys. Rev. B **58**, 9087 (1998).

[4] U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, Phys. Rev. B **34**, 5665 (1986).

[5] A. Wischnewski, U. Buchenau, A. J. Dianoux, W. A. Kamitakahara, and J. L. Zarestky, Phys. Rev. B **57**, 2663 (1998).

[6] A. Wischnewski, U. Buchenau, A. J. Dianoux, W. A. Kamitakahara, and J. L. Zarestky, Philos. Mag. B **77**, 579 (1998).

[7] E. Fabiani, A. Fontana, and U. Buchenau, J. Chem. Phys. **128**, 244507 (2008).

[8] K. Niss, B. Begen, B. Frick, J. Ollivier, A. Beraud, A. Sokolov, V. N. Novikov, and C. Alba-Simionesco, Phys. Rev. Lett. **99**, 055502 (2007).

[9] R. Zorn, A. Arbe, J. Colmenero, B. Frick, D. Richter, and U. Buchenau, Phys. Rev. E **52**, 781 (1995).

[10] U. Buchenau, A. Wischnewski, D. Richter, and B. Frick, Phys. Rev. Lett. **77**, 4035 (1996).

[11] J. Wuttke, W. Petry, G. Coddens, and F. Fujara, Phys. Rev. E **52**, 4026 (1995).

[12] A. Tölle, H. Zimmermann, F. Fujara, W. Petry, W. Schmidt, H. Schober, and J. Wuttke, Eur. Phys. J. B **16**, 73 (2000).

[13] A. Monaco, A. I. Chumakov, Y.-Z. Yue, G. Monaco, L. Comez, D. Fioretto, W. A. Crichton, and R. Rüffer, Phys. Rev. Lett. **96**, 205502 (2006).

[14] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki, and R. Rüffer, Phys.

Rev. Lett. **97**, 135501 (2006).

[15] To avoid misunderstanding, we stress that the so-called "boson peak" is not a subject of the present discussion. Here we consider the exact zero-energy limit of the DOS.

[16] An alternative option of the density of states per one atom, i.e., per three degrees of freedom (Refs. 11 and 12), requires an additional factor of 3 for the right parts of Eqs. (1), (2), and (7) and for the left part of Eq. (13).

[17] See, e.g., A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Theory of Lattice Dynamics in the Harmonic Approximation*, Solid State Physics Vol. 3, edited by F. Seitz and D. Turnball (Academic, New York, 1963).

[18] An alternative use of a number of the molecules but not the atoms per unit volume (Refs. 9, 10, and 12) would require the area of the DOS to be equal to a number of atoms in the molecule.

[19] Although not for all of them, some more conditions as, e.g., equality of the Debye-Waller factors for all atoms are required.

[20] S. N. Taraskin and S. R. Elliott, Phys. Rev. B **55**, 117 (1997).

[21] S. N. Taraskin and S. R. Elliott, Phys. Rev. B **56**, 8605 (1997).

[22] M. G. Zemlyanov, I. V. Krylov, P. P. Parshin, and P. I. Soldatov, Sov. Phys. JETP **77**, 148 (1993) [Zh. Eksp. Teor. Fiz. **104**, 2538 (1993)].

[23] A. Bosak and M. Krisch, Phys. Rev. B **72**, 224305 (2005).

[24] K. Achterhold, C. Keppler, A. Ostermann, U. van Bürck, W. Sturhahn, E. E. Alp, and F. G. Parak, Phys. Rev. E **65**, 051916 (2002).

[25] M. Y. Hu, W. Sturhahn, T. S. Toellner, P. D. Mannheim, D. E. Brown, J. Zhao, and E. E. Alp, Phys. Rev. B **67**, 094304 (2003).

[26] J. T. Sage, C. Paxon, G. R. A. Wyllie, W. Sturhahn, S. M. Durbin, P. M. Champion, E. E. Alp, and W. R. Scheidt, J. Phys.: Condens. Matter **13**, 7707 (2001).

[27] R. Rüffer and A. I. Chumakov, Hyperfine Interact. **97-98**, 589 (1996).

[28] A. I. Chumakov and W. Sturhahn, Hyperfine Interact. **123-124**, 781 (1999).

[29] V. G. Kohn and A. I. Chumakov, Hyperfine Interact. **125**, 205 (2000).

[30] H. R. Schober and P. H. Dederichs, in *Phonon States of Elements: Electron States and Fermi Surfaces of Alloys*, Landolt-Börnstein, New Series, Group 13, Pt. A, Vol. III, edited by K.-H. Hellwege and J. L. Olsen (Springer, Berlin, 1981), p. 56.

[31] M. M. Choy, W. R. Cook, R. F. S. Hearmon, H. Jaffe, J. Jerphagnon, S. K. Kurtz, S. T. Liu, and D. F. Nelson, in *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börnstein, New Series, Vol. 11, edited by K.-H. Hellwege and A. M. Hellwege (Springer Verlag, Berlin, 1979), p. 10.

[32] V. G. Kohn, A. I. Chumakov, and R. Rüffer, Phys. Rev. B **58**, 8437 (1998).

[33] R. Diehl, W. Jantz, B. I. Noläng, and W. Wettling, Curr. Top. Mater. Sci. **11**, 241 (1984).

[34] K. S. Aleksandrov, T. V. Ryzhova, and B. P. Belikov, Sov. Phys. Crystallogr. **8**, 589 (1964) [Kristallografiya **8**, 738 (1963)].

[35] R. T. Downs and A. K. Singh, J. Phys. Chem. Solids **67**, 1995 (2006).

[36] F. Nestola, T. B. Ballaran, C. Liebske, M. Bruno, and M. Tribaudino, Phys. Chem. Miner. **33**, 417 (2006).

[37] M. Krisch and F. Sette, *Light Scattering in Solids, Novel Materials and Techniques: Inelastic X-ray Scattering from Phonons*, Topics in Applied Physics Vol. 108 (Springer-Verlag, Berlin, 2007).

[38] A. Bosak and M. Krisch, Radiat. Phys. Chem. **75**, 1661 (2006).

[39] A. Criado, F. J. Bermejo, A. de Anres, and J. L. Martinez, Mol. Phys. **82**, 787 (1994).

[40] Strictly speaking, this estimation can be performed only for the true DOS. It seems to be unjustified for the experimentally measured generalized DOS.

[41] J. Wuttke, M. Kiebel, E. Bartsch, F. Fugara, W. Petry, and H. Sillescu, Z. Phys. B: Condens. Matter **91**, 357 (1993).

[42] J. M. Carpenter and C. A. Pelizzari, Phys. Rev. B **12**, 2391 (1975).

[43] U. Buchenau, Z. Phys. B: Condens. Matter **58**, 181 (1985).

[44] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1967).

[45] This is more appropriate than averaging of $\langle v \rangle$ values in Ref. 12. Also, this gives better agreement with the measured DOS.