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Dynamics in Liquids Studied by Inelastic X-Ray Scattering[1]

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Inelastic X-ray scattering with an energy resolution of the order of milli-electron volts is a relatively new tool to investigate collective excitations in condensed matter. A high energy resolution can be achieved by extreme backreflection (Bragg angle close to 90°) from perfect crystals. This technique is used with the spectrometer INELAX for inelastic scattering experiments at DESY, Hamburg. Energy transfers from a few milli-electron volts up to 5 eV at any wavevector between 0.3 and 14 $Å^{-1}$ are accessible. One of the successful applications of this method is the investigation of the dynamical structure factor of liquids. Results on liquid lithium are presented and compared with neutron data and molecular dynamics.

KEY WORDS: backscattering; dynamical structure factor; inelastic X-ray scattering; liquid lithium; NPA potential.

1. INTRODUCTION

The high intensity of X-rays emitted by synchrotron radiation provides the possibility of performing new types of X-ray experiments. In the area of inelastic X-ray scattering, a sufficiently high energy resolution, of the order of 10 meV (15 ps^{-1}), could be achieved for the direct measurement of phonons [1]. Up to now, this was possible only by means of inelastic neutron scattering.

In the case of X rays, the dominant process for coherent scattering is Thomson scattering from the core and valence electrons. The performance of X-ray scattering experiments with a high resolution in energy and

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momentum transfers allows us to determine the dynamical structure factor $S(Q, \omega)$. This is the Fourier transform in time and space of the electron density–density correlation function $n_e(r, t)$:

$$S(Q, \omega) = \int d^3r \int dt \, \langle n_e(r, t) \rangle \, e^{i(\mathbf{k} \cdot \mathbf{r} - \omega \cdot t)}$$

Assuming the validity of the adiabatic approximation, the electron density–density correlation function is proportional to the ion density–density correlation function. Therefore, peaks in $S(Q, \omega)$ can be interpreted either as localized density fluctuations around $\omega = 0$ or as propagating sound modes for $\omega \neq 0$. The latter excitations correspond to the well-known phonon excitations in single crystals.

Since coupling of the energy to the momentum transfer is negligible, inelastic X-ray scattering has almost no restrictions in the accessible (Q, ω)-space. Hence this method is extremely attractive for investigation of the coherent part of the dynamical structure factor for liquids and amorphous solids with high sound velocities. In contrast to this, inelastic neutron scattering is strongly limited by the mass of the neutron itself just in this part of the (Q, ω)-space. Moreover, in cases where neutron scattering cannot be used because of the lack of a coherent neutron cross section, an inelastic X-ray scattering experiment provides complementary information.

2. EXPERIMENTAL SETUP

The high-energy resolution of several milli-electron volts can be obtained by Bragg scattering from perfect single crystals in extreme back-scattering geometry. With this technique the inelastic X-ray spectrometer

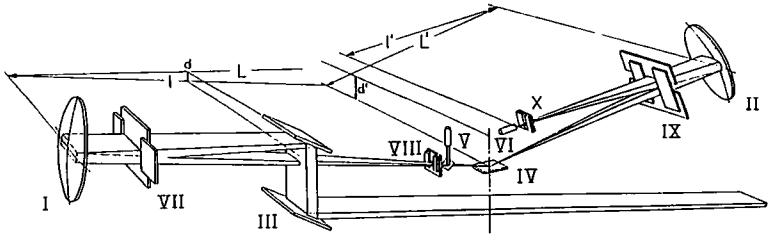

Fig. 1. The instrument INELAX at the HARWI wiggler line of HASYLAB. The beam passes the premonochromator (III) and the monochromator (I) before it illuminates the sample (IV). The scattered intensity is focused by the analyzer (II) into the detector (VI). The primary intensity is controlled by a monitor unit (V). VII–X indicate slit systems. For lengths of the labeled distances see Table I.

INELAX [2] was built at the synchrotron radiation laboratory at DESY, Hamburg. The setup of this instrument is shown schematically in Fig. 1. The primary parts of the instrument are the monochromator (I) and the analyzer (II) units. Both components consist of spherically bent silicon crystal disks and operate with deviations less than 0.8 mrad from perfect backreflection.

The photon beam from the storage ring passes the premonochromator (III) on its way to the monochromator. This premonochromator acts essentially as a heat filter to protect the monochromator against the integrated power of the synchrotron beam, which is in the range of several kilowatts.

The monochromator defines the desired small energy bandwidth of the photon beam focused onto the sample (IV). The beam intensity is monitored by a scintillation counter (V).

The analyzer crystal collects the radiation scattered by the sample from a variable solid angle and focuses it onto the detector (VI), which is an ion-implanted Si diode working just below room temperature. Various slit systems (VII–X) help to define the beam cross section and the scattering geometry and to reject radiation at unwanted energies, arising due to imperfections of the focusing elements. The sample is mounted on a vertical diffractometer with a 2.5-m-long arm which serves as a mount for the analyzer unit.

Most parts of the beam line are enclosed in vacuum tubes to reduce the intensity losses due to absorption along a distance of 51 m. The relevant geometrical distances of the instrument INELAX are given in Table I.

The energy transfer in an inelastic scattering experiment is established by an energy shift between the monochromator and the analyzer crystal. This is done by thermal tuning of the lattice parameter of the analyzer crystal. Using the (8 8 8) Bragg reflection of silicon with a primary energy

Table I. Geometric Distances of INELAX (Fig. 1) at the HARWI Wiggler at DORIS: The Source for the Beam to the Analyzer is Slit VIII

Distance	Monochromator	Analyzer
Source to crystal, L (m)	38	2.6
Crystal to image, l (m)	8	2.5
Bending radius, R (m)	13	2.55
Distance between both beams, d (mm)	6	4
Beam size at crystal		
D_{hor} (mm)	90	80
D_{ver} (mm)	8	80

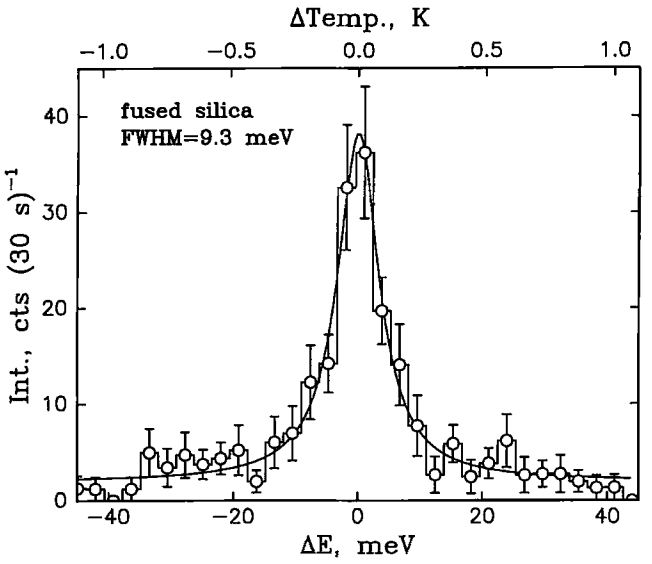

Fig. 2. Intensity elastically scattered from fused silica as a function of the temperature difference between the monochromator and the analyzer and the corresponding energy transfer.

of 15.8 keV, a temperature difference of 1 K between both crystals corresponds to an energy transfer of 41 meV.

The resolution function can be directly measured by recording the elastically scattered intensity from fused silica as a function of the energy transfer (Fig. 2).

3. MEASUREMENTS ON LIQUID LITHIUM

Investigations of the collective density modes in liquid lithium at the instrument INELAX were started with an energy resolution of 30 meV and later continued with an improved resolution of 12 meV [2–4]. Figure 3 shows the energy-resolved X-ray scattering intensity of liquid lithium observed at $Q = 1.25$ Å^{-1} as a function of the energy transfer. The collective excitation peak is clearly visible and well separated from the quasielastic scattering contribution around zero energy. By fitting the spectra with Lorentzians [2, 4], the dispersion of the sound mode can be determined. The result is shown in Fig. 4. At small wavevectors Q the dispersion reveals a linear behavior, which corresponds to a constant macroscopic sound velocity. Beyond 1 Å^{-1} one can observe a maximum of the dispersion curve, similar to the shape of phonon dispersions in single crystals.

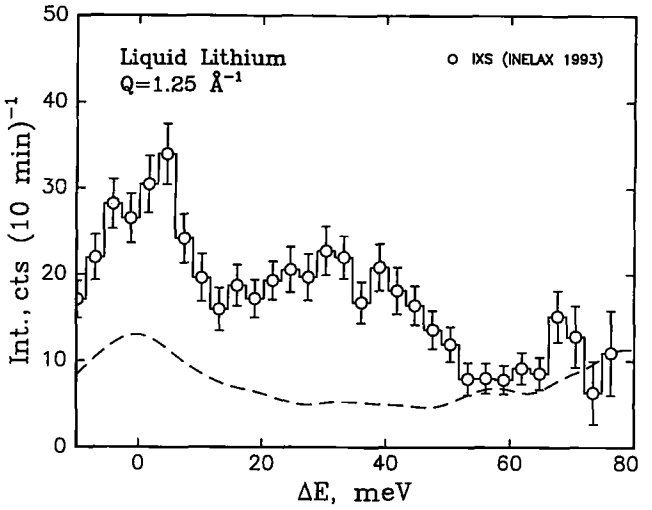

Fig. 3. Inelastic X-ray scattering intensity of liquid lithium at $Q = 1.25$ Å^{-1} as a function of the energy transfer.

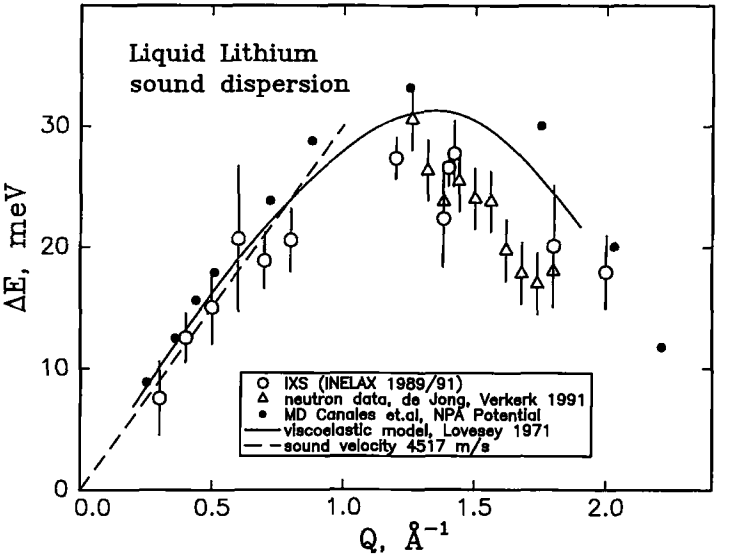

Fig. 4. Dispersion of collective modes in liquid lithium. The results from inelastic X-ray scattering are shown together with neutron data [8] and molecular dynamical results [9].

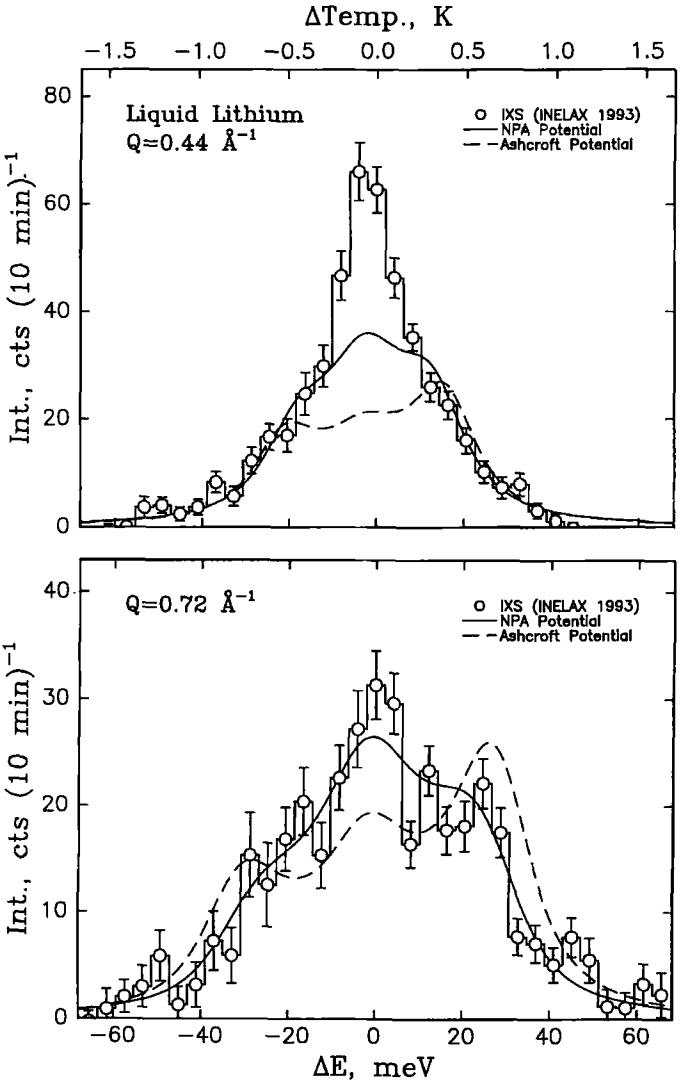

Fig. 5. Inelastic X-ray scattering intensity scattered of liquid lithium 40 K above the melting point at 0.48 and 0.72 Å^{-1}. The solid and dashed lines are molecular dynamical calculations performed by Canales et al. [5] for two potentials. For details see the text.

At low Q values the data are in good agreement with results from molecular dynamics [5] and with model calculations based on the viscoelastic approximation of Lovesey [7]. At higher Q values neutron data are also available [8]. In this region, the predictions from the viscoelastic approximation and the molecular dynamics seem to differ from the neutron scattering results. However, the statistical accuracy of the inelastic X-ray data is not yet sufficient for definite conclusions.

Figure 5 displays a more detailed comparison between the molecular dynamical calculations and recent INELAX measurements. The X-ray spectra are normalized and corrected for background and container scattering. The molecular dynamical calculations were performed by [5] using two pseudo-potentials for the interatomic forces, the Ashcroft pseudopotential and the NPA potential [6]. For comparison the results of these simulations were convoluted with the INELAX resolution function.

At $Q = 0.72$ Å^{-1} the NPA curve fits the experimental data ($\chi^2_{\text{NPA}} = 1.6$) quite well, whereas the Ashcroft potential with its broad and flat spectrum ($\chi^2_{\text{Ash}} = 5.1$) shows discrepances. However, at $Q = 0.44$ Å^{-1} neither of the potentials can explain the observed strong elastic intensity. Nevertheless, the NPA result shows less deviation, as evident from the values of χ^2, $\chi^2_{\text{NPA}} = 4.7$ and $\chi^2_{\text{Ash}} = 11.8$.

There is an overall agreement between the experimental data and the theoretical approaches shown. In any case, these experiments are the base of a detailed study of liquids with this new technique. A major concern is the study of strong elastic scattering intensity at small wavevectors, which might reveal interesting information on the electron correlations.

The present results are a demonstration of the actual capabilities of inelastic scattering of X rays with meV resolution. Certainly, this new method of spectroscopy is complementary to inelastic neutron scattering. But it also reveals additional information, which is inaccessible for neutron scattering. The attractiveness of the method and the ease of handling will increase with higher photon fluxes at the sample. The instrument INELAX at an undulator at the ESRF or at the high-energy ring PETRA, Hamburg, will increase the number of applications.

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