

Observation of Umklapp processes in noncrystalline materials

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Inelastic X-ray scattering data have been measured in liquid lithium at 475 K as a function of momentum transfer Q ($2 < Q < 55 \text{ nm}^{-1}$), and at several constant energies transfer E in the range 15–40 meV. This data provide a direct experimental evidence that Umklapp-like processes can be identified in the dynamic structure factor of a disordered system. Generalizing a picture valid for a crystalline material, it is possible to relate the broadening of the Umklapp peaks to the width of the principal peak in the static structure factor of disordered materials and therefore to the topological disorder.

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Transport properties in a material determine the flow of characteristic quasiparticles induced by an external field (temperature gradient, electric field, etc.). In an ideal infinite perfect crystal, with no lattice imperfections, impurities and surface effects, the existence of a stationary flow is a consequence of interactions among quasiparticles and of Umklapp processes (U -processes). The interaction is necessary to exchange energy and momentum, and, in particular to allow scattering processes such as $k_1, k_2 \rightarrow k_3$, where $\hbar k$ is the quasiparticle momentum. However, as the total momentum is conserved ($k_1 + k_2 = k_3$), the interaction alone is not sufficient to reach equilibrium. This is possible thanks to the U -processes.¹ Their fundamental role is to open further scattering channels where the momentum of the quasiparticles in the initial state is different from that of the final state. The difference, necessary for the total momentum conservation in the scattering event, is supplied by the crystal periodicity via the reciprocal lattice vectors G : $k_1 + k_2 = k_3 + G$. Therefore, it is evident that the concept of U process is intimately related to the existence of a periodic lattice, via the vectors G , and to the periodic repetition of the crystal quasiparticles dispersion relation in successive Brillouin zones.

Phonon U processes are, for example, directly responsible for the thermal conductivity in insulators. It is firmly believed that also in *disordered systems* the thermal transport properties are determined by the excitation spectrum of the density fluctuations.² In particular, in glasses, the effect of the disorder on the collective dynamics is supposed to be responsible for the observed anomalies in the heat capacity and thermal conductivity behavior when compared to their crystalline counterpart. In this respect, recent experimental^{3–8} and numerical^{9–13} works have demonstrated that, in glasses and disordered systems in general, propagating acousticlike collective excitations exist up to a momentum ($\hbar Q$) region approaching the Q value of the main peak of $S(Q)$, G_{MP} . These excitations, with increasing Q , show clear effects due to the disorder as, for example, the increasing nonplane wave character of their spatial eigenfunctions. Nevertheless, one finds for these excitations a dispersion relation $E(Q)$ vs Q strikingly similar to that of crystals. Among others, a linear behavior of $E(Q)$ at small Q , and a bend down of $E(Q)$ evolving, in certain cases where these

excitations are particularly well defined, into a maximum around $G_{\text{MP}}/2$. The behavior of the excitations dispersion relation in disordered materials, with its similarity to the crystalline case, has induced to speculate that also in these systems it is possible to define a pseudo-Brillouin zone,² whose first replica covers the region $0 < Q < G_{\text{MP}}/2$. Pushing further this speculation into higher order Brillouin zones, one may expect that U -like processes also exist in disordered systems.

The previous concepts are pictorially illustrated in Fig. 1 for the one-dimensional case. Here, the dashed line sketches an acoustic phonon dispersion relation $E(Q)$ in a perfect chain with lattice constant a . This dispersion relation periodically repeats itself with a period $G = 2\pi/a$. In the same

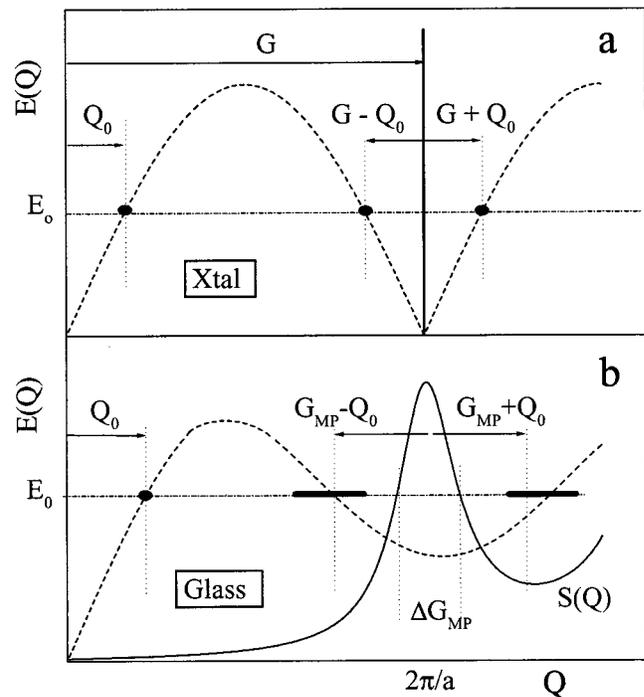


FIG. 1. Sketch of the dispersion relation $E(Q)$ (dashed lines) and of the static structure factor $S(Q)$ (full lines) of a one-dimensional system. (a) reports the case of an ordered chain; (b) that of a disordered chain.

plot, we also sketch the static structure factor $S(Q)$, which in such a periodic system corresponds to Bragg peaks at Q values $G_n = 2\pi n/a$ (full vertical line). Let us imagine now performing the following scattering experiment in such a perfect chain: as shown by the dash-dotted line in Fig. 1(a), we scan the exchanged momentum at the fixed energy E_0 . We will observe a sharp peak, the Brillouin peak, at $Q = Q_0 \approx \hbar E_0/\nu$, where ν is the sound velocity and Q is low enough to be in the linear dispersion region. This peak will also be observed at $Q = G \pm Q_0$, where G is any of the reciprocal lattice vectors. The presence of these other peaks, the Umklapp peaks, is due to the fact that the phonon momentum is defined to within a reciprocal lattice vector. Naively, one can say that the phonon of momentum Q_0 is “reflected” by the lattice (or by the Bragg peak at $Q = G$) and its signature in the spectrum is the appearance of peaks not only at Q_0 but also on the two sides of the Bragg peak, i.e., at $G \pm Q_0$. In Fig. 1(b), we report an attempt to translate the discussed scattering experiment from a periodic array into a disordered system. Supposing for the time being that the excitations in such “glassy” system were phononlike plane waves, one still observes a sharp Brillouin peak at $Q = Q_0$. However, the absence of periodicity destroys the sharp Bragg peaks, and the static structure factor is characterized by a main peak centered at $Q = G_{\text{MP}} \equiv 2\pi/a$ (a is the average nearest-neighbor distance). This feature has a finite width ΔG_{MP} determined by the distribution of this nearest-neighbor distances that typically is an important fraction of G_{MP} . In analogy to the crystal case, one then expects that this MP is also capable to “reflect” phonons. However, with respect to the peak at Q_0 , the peaks at $Q = G_{\text{MP}} \pm Q_0$ will have a width increased at least by ΔG_{MP} (a broadening contribution from the topological disorder will always be present). In this scenario, the initial working hypothesis that the excitation at $Q = Q_0$ is a plane wave is not really necessary. In fact, taking into account that in a glass the disorder induces a width of the Brillouin line, one expects that also the Umklapp peaks widths will increase accordingly. Finally, one expects that the simple description sketched in Fig. 1(b), although more complicated, is still valid in a real three-dimensional system, at least for longitudinal phonons, on a qualitative ground. A quantitative description has been derived by Carpenter and Pellizzar,¹⁴ under the assumption of pure plane wave excitations, and further refined by Ribeiro, Wilson, and Madden.¹³

On the experimental side the search for U processes in disordered systems has been attempted in the past by Inelastic Neutron Scattering,¹⁵ and, in particular, scattering experiments such as the one sketched in Fig. 1(b) have been performed in glasses.¹⁶ However, these experiments has not been able to cover the whole interesting Q - E region, going at least from Q_0 up to the main peak (MP).

Liquid lithium is a disordered system that has been already thoroughly investigated using the inelastic x-ray scattering (IXS) technique.¹⁷ Compared to prototypical glassy systems (vitreous silica for example) it shows a particularly favorable contrast between inelastic and elastic signals. This property makes liquid lithium a very good candidate to search for Umklapp features in the Q region around G_{MP} ,

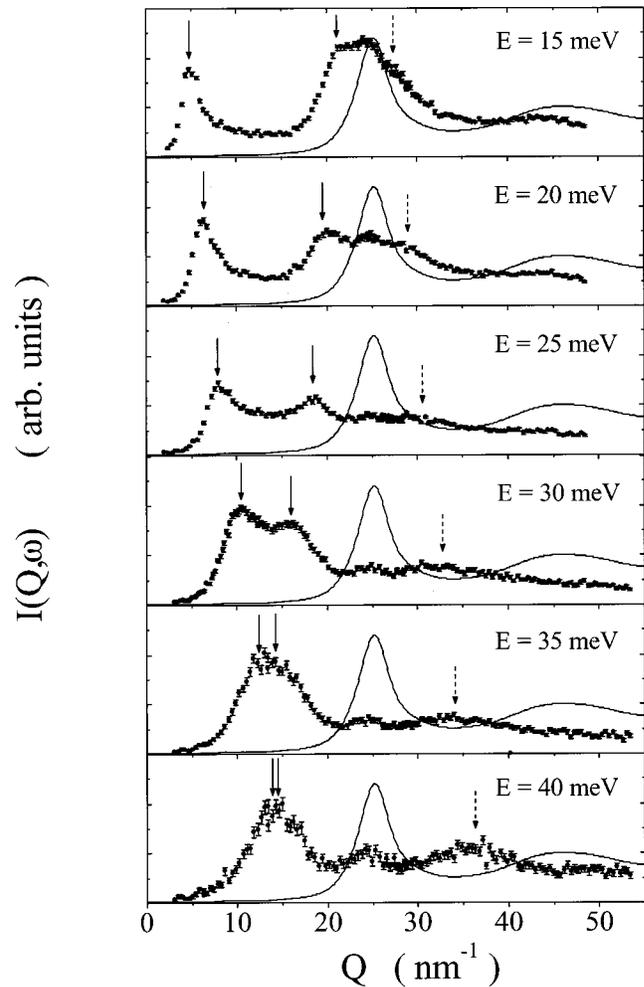


FIG. 2. IXS spectra of liquid lithium at $T=475$ K (full circles) taken at the indicated constant energy as a function of Q . The arrows mark the position of the main spectral features (Brillouin peaks at low Q and Umklapp peaks around the MP). The full line in each panels is the $S(Q)$ reported on an arbitrary intensity scale, calculated at the melting point ($T_m=450$ K) by molecular dynamics simulations.

where the elastic contribution to the spectra has its maximum intensity and where the first Umklapp peaks are expected to be.

The IXS experiment has been carried out at the very high-energy resolution IXS beam-line (ID28) at the European Synchrotron Radiation Facility. The instrument consists of a back-scattering monochromator and five independent analyser systems, held one next to each other with a constant angular offset on a 7 m long analyzer arm. We utilized the Si(9 9 9) configuration, giving a total instrumental energy resolution of 3.0 meV full width at half maximum (FWHM),¹⁸ and an offset of 2.4 nm^{-1} between two neighbor analyzers. The spectra have been measured as a function of Q transfer and at different constant E transfers by setting a constant temperature difference between the monochromator and analysers crystals and by rotating the analyzer arm. The measured Q range is $1\text{--}55 \text{ nm}^{-1}$, and the Q resolution is 0.3 nm^{-1} FWHM. The spectra were normalized to the incoming

photon flux, and, for improved statistical accuracy, the signals from different analysers in overlapping Q regions were averaged together. Each scan took about 150 min, and each spectrum was obtained by the typical average of five scans. The liquid lithium sample was in an uncapped container made of austenitic stainless steel. A resistance heater was used to keep the liquid at 475 K, i.e., slightly above the melting point at 453 K. The 20 mm long sample was loaded in an argon glove box and kept in a 10^{-6} mbar vacuum. Empty vacuum chamber measurements were also performed. They gave either the flat electronic detector background of 0.6 counts/min at $Q > 8 \text{ nm}^{-1}$, or, for $Q < 8 \text{ nm}^{-1}$, a small elastic signal due to the vacuum chamber Kapton windows (50 μm thick), whose intensity gives a negligible contribution to the inelastic spectra reported here.

The IXS spectra measured at the constant E values of 15, 20, 25, 30, 35, and 40 meV are reported in Fig. 2 (full circles). In the same figure the static structure factor $S(Q)$ is also shown as a full line, and the MP is found at $G_{\text{MP}} \approx 25 \text{ nm}^{-1}$ with a width of $\Delta G_{\text{MP}} \approx 4 \text{ nm}^{-1}$. The value of $G_{\text{MP}} = 2\pi/a$ is consistent with the average nearest-neighbor distance $a \approx 0.24 \text{ nm}$.

The inelastic spectra, $I(Q, E)$, reported in Fig. 2, normalized only to the incident photon flux, could be reduced to the dynamic structure factor $S(Q, E)$ by correcting for the lithium atomic scattering form factor $f(Q)$ and for a coefficient $g(Q)$ that takes into account the Q -dependent response function of the IXS spectrometer: $S(Q, E) = I(Q, E) / [f(Q)g(Q)]$. Both $f(Q)$ and $g(Q)$ are smooth functions which decrease monotonically with increasing Q . However, independently of the specific knowledge of the functions $f(Q)$ and $g(Q)$, the spectra $I(Q, E)$ can be put on an absolute scale—thus deriving the $S(Q, E)$ —using the well known sum rules of the dynamic structure factor.¹⁹ This procedure has been exploited elsewhere.¹⁷ In the present work, as preliminary results, we report the raw data to emphasise the direct observation of the peak shifts without any manipulation. In Fig. 2 the spectra have been normalized to an arbitrary value such that their intensity is comparable to that of

the $S(Q)$ in the high Q region.

The spectra in Fig. 2 show in the small Q region a Brillouin peak that increases its Q position and width with increasing energy. More importantly, the spectra show also other inelastic peaks at higher Q values (marked by the arrows). This ensemble of inelastic features can be interpreted within the same framework as the one sketched in Fig. 1(b). In fact, one observes, at low energy transfer E , not only the Brillouin peak at $Q_0(E)$, but also a second peak at approximately $G_{\text{MP}} - Q_0(E)$. Moreover, one clearly observes that, with increasing E , the peaks at $Q_0(E)$ and $G_{\text{MP}} - Q_0(E)$ get closer and, at the energy $E \approx 40 \text{ meV}$, they merge together at a Q value close to $G_{\text{MP}}/2$ (this is the ideal value that one would expect in the crystalline case). This behavior, as previously emphasised in Fig. 1(b), is precisely the one expected in presence of Umklapp peaks. These data, therefore, provide compelling evidence that the U processes are active also in disordered systems and show that the effect of disorder can be framed within the qualitative model presented in Fig. 1(b). In this respect, in fact, the Umklapp peak at $G_{\text{MP}} - Q_0$ is considerably broader than the Brillouin peak at Q_0 . This broadening is also responsible for the even more reduced visibility of the Umklapp process in the third pseudo-Brillouin zone that is expected at $G_{\text{MP}} + Q_0$. We notice however that this second family of Umklapp peaks at $G_{\text{MP}} + Q_0$ is nevertheless observable in the limit of large E as emphasised by the dashed arrows.

In conclusion we have shown that in a system without any periodic order such as a monatomic liquid, one observes inelastic excitations that can be interpreted as the noncrystalline counterpart of Umklapp peaks. These peaks are no longer sustained by the periodicity of the lattice—as in crystals—but are due to the “reflection” of the wavelike (Brillouin) excitations from the short range order that still exists in the disordered material. Contrary to the crystalline case, however, the presence of disorder is responsible for an increasingly large broadening of these Umklapp peaks with increasing momentum. As in crystals, on the other hand, the present observation allows one to speculate that the Umklapp processes play an important role in the transport properties of disordered materials.

¹N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, Winston, Philadelphia, 1976).

²S. R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman, London, 1998).

³C. Masciovecchio, G. Ruocco, F. Sette, M. Krisch, R. Verbeni, U. Bergmann, and M. Soltwisch, *Phys. Rev. Lett.* **76**, 3356 (1996).

⁴P. Benassi, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Monaco, G. Ruocco, F. Sette, and R. Verbeni, *Phys. Rev. Lett.* **77**, 3835 (1996).

⁵F. Sette, M. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco, *Science* **280**, 1550 (1998).

⁶G. Ruocco, F. Sette, R. Di Leonardo, D. Fioretto, M. Lorentzen, M. Krisch, C. Masciovecchio, G. Monaco, F. Pignon, and T. Scopigno, *Phys. Rev. Lett.* **83**, 5583 (1999).

⁷C. Masciovecchio, A. Mermet, G. Ruocco, and F. Sette, *Phys.*

Rev. Lett. **85**, 1266 (2000).

⁸O. Pilla, A. Cunsolo, A. Fontana, C. Masciovecchio, G. Monaco, M. Montagna, G. Ruocco, T. Scopigno, and F. Sette, *Phys. Rev. Lett.* **85**, 2136 (2000).

⁹S. N. Taraskin and S. R. Elliott, *Phys. Rev. B* **56**, 8605 (1997).

¹⁰R. Dell’Anna, G. Ruocco, M. Sampoli, and G. Viliani, *Phys. Rev. Lett.* **80**, 1236 (1998).

¹¹J. L. Feldman, P. B. Allen, and S. R. Bickham, *Phys. Rev. B* **59**, 3551 (1999).

¹²G. Ruocco, F. Sette, R. Di Leonardo, G. Monaco, M. Sampoli, T. Scopigno, and G. Viliani, *Phys. Rev. Lett.* **84**, 5788 (2000).

¹³M. C. C. Ribeiro, M. Wilson, and P. Madden, *J. Chem. Phys.* **108**, 9027 (1998).

¹⁴J. M. Carpenter and C. A. Pelizzari, *Phys. Rev. B* **12**, 2391 (1975); U. Buchenau, A. Wischnewski, M. Monkenbusch, and

- W. Schmidt, *Philos. Mag. B* **79**, 2021 (1999).
- ¹⁵J. B. Suck, H. Rudin, H.-J. Guentherodt, and H. Beck, *J. Phys. C* **13**, L1045 (1980); M. Foret, B. Hehlen, G. Taillades, E. Courtens, R. Vacher, H. Casalta, and B. Dorner, *Phys. Rev. Lett.* **81**, 2100 (1998).
- ¹⁶U. Buchenau, A. Wischnewski, D. Richter, and B. Frick, *Phys. Rev. Lett.* **77**, 4035 (1996); L. Borjesson, U. Buchenau, A. J. Dianoux, D. Engberg, A. P. Sokolov, and A. Wischenewski, *Physica B* **234–236**, 383 (1997); A. P. Sokolov, U. Buchenau, D. Richter, C. Masciovecchio, F. Sette, A. Mermet, D. Fioretto, G. Ruocco, L. Willner, and B. Frick, *Phys. Rev. E* **60**, R2464 (1999).
- ¹⁷T. Scopigno, U. Balucani, A. Cunsolo, C. Masciovecchio, G. Ruocco, F. Sette, and R. Verbeni, *Europhys. Lett.* **50**, 189 (2000).
- ¹⁸C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni, *Nucl. Instrum. Methods Phys. Res. B* **117**, 339 (1996).
- ¹⁹U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).