Excitons in bulk liquid ^{4}He

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(Received 14 February 2005; published 30 June 2005)

We present the first measurements of excitons in bulk liquid He, performed at several densities. Inelastic x-ray scattering was used to take these measurements of ^{4}He. The exciton measurements are very similar to those for solid ^{4}He, with the exciton excitations occurring at nearly the same energy transfers for the same pressure. This similarity suggests that excitons in solid helium rely mostly on short range order. The measured peaks for the liquid are asymmetric in nature and fit well to two Gaussians, suggesting that at least two exciton transitions are present in the signal peak.

DOI: 10.1103/PhysRevB.71.233107 PACS number(s): 71.35.−y, 67.20.+k, 67.90.+z, 61.10.Eq

Excitons can be formed in certain liquids despite the absence of long-range order. Only short-range atomic interaction at distances at least as large as an exciton radius is needed.[1] Condensed noble gases provide notable examples for study of electronic states in disordered insulators. Liquid Xe was a suggestive early case,[2] with subsequent work leading to report of an $n=1$ exciton, described to occur "in a small and loose momentary cluster of atoms."[3] Extensive work by many groups followed.[4] Using reflectivity spectra, "intermediate" excitons were found in liquid Kr and liquid Ar as well.[5] For Xe, Kr, and Ar, in which the electron affinities (ground-state energies relative to a vacuum) are positive, delocalized conduction electrons have been identified, in both the excited solids[6] and liquids.[7] Such electrons are weakly coupled to the medium. However, for the liquids Ne and He, the mobility of such electron states is limited because the electron affinity becomes negative.[4] In fact, it was not known whether liquid helium could support excitons.[8]

Helium is a particularly interesting subject for study because a very wide density range can be studied in both the liquid and solid states. For significant density changes, there are both electron-energy computations for liquid He[9] and limited linear combination of atomic orbitals (LCAO) work on the band structure of crystal He.[10] However, calculations directly relevant to the present measurements do not appear to have been published. For solid Ne, absorption and luminescence spectra have been extensively analyzed, and many details of exciton dynamics explained.[11] An early one-site calculation of $n=1$ exciton in solid Ne[12] examined, in particular, details of the spin-orbit interaction and *e-h* exchange on doublet structure and of the continuum spectrum above threshold. These were related to the calculated band structure, which shows a spin-orbit splitting of the valence band near the Γ point. We note that the LCAO work on the band structure of solid He shows a valence-band splitting at Γ, which increases as the atomic density is increased.

Electronic excitation measurements have previously been made for bulk liquid He, but none have measured excitons. Measurements of the $1s \rightarrow 2p$ and the "forbidden" $1s \rightarrow 2s$ transitions in superfluid ^{4}He were made by Surko *et al.* through reflectance measurements of VUV light,[13] with this method restricting measurements to those at saturated vapor pressure. The reason excitons were not observed is likely because a critical pressure is needed before excitons appear in noble gas liquids, taken to be near that of the triple point for the heavier noble gases.[3,4] Neither stable helium isotope has a traditional triple point where gas, solid, and liquid coexist; the most similar point for helium is that of the lower λ point (where gas, normal fluid, and superfluid coexist). Even then, the pressure of Surko's sample (83 Pa)[14] is 60 times less than the lower λ point (5.0 kPa) for ^{4}He. An inelastic x-ray scattering study of liquid He was made by Marra *et al.*, but the experimental conditions seem to be similar to those of Surko's, and only vague hints of the interband transition can be seen at their resolution of 9 eV.[15] The only previous measurements of excitons for He are of bulk solids[16,17] and liquid droplets.[18,19]

The technique used to make these measurements was nonresonant inelastic x-ray scattering (IXS), which is a bulk probe of the sample, unlike VUV reflectance measurements. The experiment was carried out at the 15-ID beamline of the Advanced Photon Source, which is operated by ChemMatCARS. The beamline uses a standard APS undulator A as its insertion device. A diamond (1 1 1) double-crystal monochromator (DCM) (reproducible for an absolute energy of ±40 meV) was used as the high-heat-load monochromator (HHLM). The high-energy-resolution monochromator (HERM) was a channel-cut pair of silicon (4 4 0) crystals. The analyzer was a germanium (1 1 1) crystal bent to a 1.0 m radius with an angular aperture of ±1.5°.

The energy change of the photons was measured by means of a fixed energy at the detector and a varied incident energy to obtain Stokes-shifted spectra. The beamline was set to the energy required for a germanium analyzer employing the (5 5 5) Bragg reflection at near backscattering. The energy selected by the analyzer was measured, using the main monochromator (±40 meV), as 9.487 keV (1.307 Å). The incident energy was varied by changing the angles of the

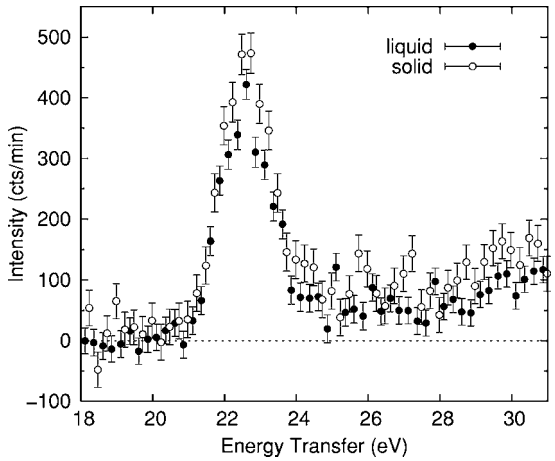

FIG. 1. The exciton peaks for an hcp solid (Ref. 17) and liquid samples of ^{4}He at equal pressure, measured during the previous experiment with only the temperature changed (from 14.0 K to 25.0 K). This was our initial observation of an exciton in liquid ^{4}He. The strong similarity of the signals shows that the exciton continues to exist in the liquid phase. The solid measurement is of the Γ point.

synchronized HHLM and HERM crystals. The measured instrument resolution was 350 meV.

The ^{4}He sample gas is contained in a high-pressure system and liquefied into a cylindrical sintered Be cell (0.8 mm ID) using a cryostat. This system has been fully described elsewhere.[20–22] Pressures in the fluid samples were measured using a resistance strain-gauge cell, calibrated against a precise Bourdon pressure gauge. The corresponding molar volume (density) values for the samples were interpolated from existing *PVT* measurements for liquid ^{4}He.[23]

With samples of varying densities being measured, they have varying numbers of x-ray scatterers in the beam. In order to make a relative intensity comparison between samples, the measured x-ray intensities need to be scaled to a common density using the fact that the scattered x-ray intensity is linearly proportional to density. For all figures in this paper, the measurements have been scaled to a density that is central to those shown, leaving the count rates shown approximately correct.

Using a similar setup to the one described here, although with lower energy resolution, excitons were previously measured in a crystal of solid hcp ^{4}He, where the molar volume was 10.72 cm^3 and the temperature 14.0 K.[17] During the same experiment, after those measurements of the solid, the temperature was raised to melt the crystal (at constant pressure), and a measurement of electronic excitations in liquid helium was taken, with a molar volume of 11.23 cm^3 and temperature of 25.0 K; this measurement, shown in Fig. 1, has not been published before. The instrumental energy resolution of this previous experiment (1.1 eV) is several times coarser than that of the experiment presented in this paper. From Fig. 1, one can see that an excitonic state does exist for liquid helium, and that there is a strong similarity of the exciton peaks in the solid and liquid signals, as well as in the high-energy tails. After adjusting for the density difference, the exciton peak in liquid is only slightly smaller than the exciton peak in solid. Since excitons in liquids depend only on short-range order, this similarity suggests that the excitons measured in solid helium are largely dependent on short-range order.

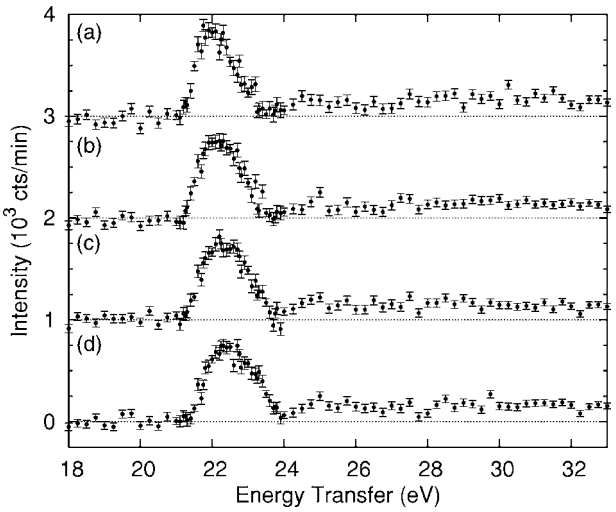

FIG. 2. The full measurements for the four molar volumes: (A) 14.39 cm^3, (B) 13.10 cm^3, (C) 12.24 cm^3, and (D) 11.61 cm^3. Note the asymmetric shape of the peaks, as well as the narrowing of the peak with increasing molar volume (decreasing pressure).

For the current experiment, measurements (signal and empty cell background) were done at a temperature of 26.17 ± 0.02 K and an angle of 2θ equal to $20.0 \pm 1.5°$, which corresponds to a momentum transfer $Q = 1.67 \pm 0.12$ Å^{-1}. Both elastic and inelastic scans were made for each measurement. The center of a fitted Gaussian to the elastic peak defined the zero of energy loss was found to be the same throughout the experiment. There was no scaling of the empty cell background before it was subtracted, as there was

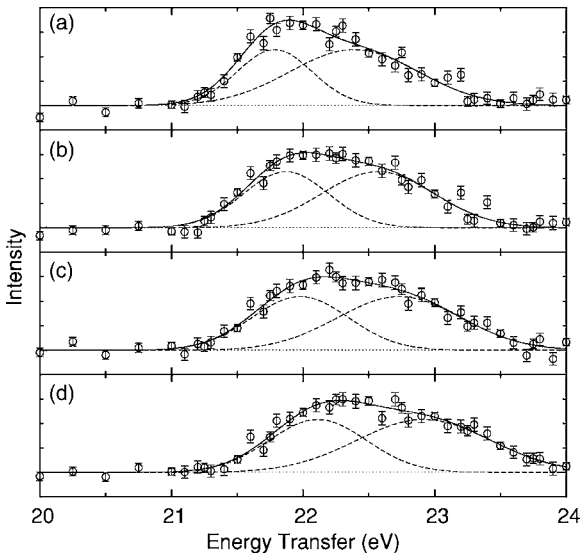

FIG. 3. Shown are the best fits to a sum of two Gaussians (with amplitudes constrained to be equal) for the four molar volumes: (A) 14.39 cm^3, (B) 13.10 cm^3, (C) 12.24 cm^3, and (D) 11.61 cm^3. The range of data shown is the range used for fitting.

TABLE I. Exciton measurements.

		One-Gaussian fit		Two-Gaussian fit				
Pressure (MPa)	Molar volume (cm^3)	Energy (eV)	FWHM (eV)	Energy 1 (eV)	FWHM 1 (eV)	Energy 2 (eV)	FWHM 2 (eV)	E_2-E_1 (eV)
186.15	11.61±0.01	22.53	1.52	22.11	0.87	22.92	1.20	0.81
150.85	12.24±0.01	22.37	1.43	21.98	0.87	22.73	1.11	0.75
116.25	13.10±0.01	22.24	1.30	21.87	0.76	22.57	1.01	0.70
81.85	14.39±0.01	22.10	1.23	21.78	0.67	22.39	1.15	0.61

excellent agreement at energies below the excitation signal. Shown in Fig. 2 are the full sets of data for the four molar volume measurements. In the vicinity of the peaks, data were collected at finer intervals.

Looking at Fig. 2, one can again see the exciton peak for each sample density, as well as the high energy tail. However, there appears to be an asymmetry to the peaks, unlike in Fig. 1 where there is less energy resolution. The elastic peaks were measured to be very symmetric, so the asymmetry could not have been caused by instrumental error. This asymmetry of the exciton peak suggests that there is more than one peak.

The measurements (dropping the higher energy signal) were fit two different ways. The first fit to the data is to a single Gaussian. This ignores the asymmetry of the peaks, and is useful for comparing to previous measurements with lower energy resolution. The second fit is to a sum of two Gaussians. With the six variables in this model, there is too much fit error associated with the peak amplitudes, causing the measurements to fit inconsistently. Constraining the amplitudes to be equal brought all the fit errors below 10%. This constrained fit works well and is shown in Fig. 3. The calculated Gaussian positions for both fits are shown in Table I.

Although the two-Gaussian fit to the data works well, there may be more than two peaks involved than can be currently resolved due to the current statistics and resolution. This uncertainty makes drawing many conclusions from the fit parameters premature, although a few things can be noted. From Table I, one can see that the peak positions from both fits move to higher energy values as the pressure is increased, as expected. The FWHM values also become larger as pressure is increased. For the two-Gaussian fit, the peak centers become more separated as pressure is increased.

The source of the structure in the liquid is not currently clear, although we infer that there are at least two excitons present. We have already noted the splitting of the valence band near Γ in an LCAO calculation.[10] Shirley did computations of excitons for hcp solid ^{4}He with a molar volume of 10.8 cm^3, which predicted two peaks for certain values of Q roughly 0.3 eV apart, corresponding to different parity states of the exciton.[24] This argument is more easily made for an hcp solid (where there are two atoms per unit cell and long-range order) but not for a liquid. It has been suggested that the second peak could be a member of a second exciton series.[25]

In liquid helium clusters, a peak corresponding to the forbidden $1s \rightarrow 2s$ atomic transition was measured.[18] There is no sign of any peak in the roughly constant signal at energies above the exciton peak, seen in Fig. 2, where the peak for the forbidden transition would exist. If it exists at this pressure, the peak is still very weak and cannot currently be resolved.

We now list the previously reported excitation energies of excitons in helium for all phases (summarized in Table II), which have been of the $n=1$ exciton in ^{4}He. Clusters of varying sizes have been studied by Joppien *et al.*,[18,19] with the highest pressure of 2.25 bars and size of $N=5000$ shown here. An hcp single crystal was studied by Schell *et al.*[16] along the c axis, yielding measurements with large uncertainties due to low statistics. Another hcp single crystal was measured with better statistics at three points along the c axis in the (0 0 2) periodic zone (at 14.0 K) by Arms *et al.*,[17] showing dispersion across the zone; the measurement shown in the table corresponds to the Γ point. From these helium samples of various types, one can qualitatively see that the exciton energy for helium rises as the density increases, as expected.

Pyper *et al.* have made calculations for the density dependence of the $1s \rightarrow 2p$ transition for a model of liquid helium that included a delocalized electron over shells of atoms surrounding a central atom.[26] They find an excitation energy that is shifted from that of the atomic transition energy (21.22 eV) by an amount that increases with increasing atomic density. The peak position of the exciton excitation extracted from the fit using one Gaussian for the liquid (and for the solid) has a density dependence in good agreement with the calculated values reported by Pyper *et al.*

From the hcp solid and liquid He measurements at identical measurement conditions except for temperature (fixed pressure), one can see that the electronic excitation measurements in liquid helium are very similar to those for solid helium, with no significant change in exciton energy through the solid-liquid transition. This is not the case for Xe, where a more noticeable difference was seen due to larger peak widths in the liquid, as well as the sharp attenuation of the $n=2$ excitons for the liquid.[2] This sharp similarity for helium

TABLE II. Previous measurements.

Sample	Molar volume (cm^3)	Exciton Energy (eV)
Cluster ($N=5000$) (Ref. 18)		21.64±0.02
hcp crystal (Ref. 16)	13.5±0.1	21.9±0.3
hcp crystal (Γ point) (Ref. 17)	10.720±0.005	22.60±0.04

suggests that excitons in solid helium rely mostly on short range order, which is all that exists for liquid helium.

We have measured excitons in bulk liquid ^{4}He, where the measurements seem to contain two or more exciton peaks. Four densities were measured, and the expected increase in energy with decreasing molar volume was seen (in both one- and two-Gaussian fits). Future measurements need to be made, where more care is taken when measuring the excitons in liquid helium, in order to try to better resolve the apparent multiple exciton peaks. Accompanying theoretical work will be needed to ascribe the observed multiple peaks to specific origins.

We are grateful to E. Shirley and S. A. Rice for very useful discussions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. ChemMatCARS Sector 15 is principally supported by the NSF/DOE under grant number CHE0087817 and by the Illinois Board of Higher Education. We wish to thank NSF and Professor S. M. Mini for the use of the HERM Monochromator under grant number CHE9871246. Work supported by U.S. Department of Energy, Division of Materials Sciences, under contract DOE-DE-FG02-91ER45439.

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