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Electronic Structure of Crystalline ^4He at High Pressures

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Abstract

Using inelastic x-ray scattering techniques, we have succeeded in probing the high-pressure electronic structure of helium at 300 K. Helium has the widest known valence-conduction band gap of all materials a property whose high-pressure response has been inaccessible to direct measurements. We observed a rich electron excitation spectrum, including a cutoff edge above 23 eV, a sharp exciton peak showing linear volume dependence, and a series of excitations and continuum at 26 to 45 eV. We determined the electronic dispersion along the Γ - M direction over two Brillouin zones, and provided a quantitative picture of the helium exciton beyond the simplified Wannier-Frenkel description.

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As an archetypal quantum solid that exhibits numerous singular properties, including the lowest freezing temperature [1], highest solidification pressure [2], extraordinary quantum effects [3,4], and largest band gap energy, condensed helium has been the focus of extensive recent studies (e.g., Refs. [3–9]). Helium under high-pressure-temperature conditions is also of great current interest to astrophysicists, as helium makes up a quarter of the mass of baryonic matter in the Universe [10]; the electron band gap closure and metallization of

helium may occur within planets of Jupiter's mass and larger [11–14]. Our knowledge of high-pressure electronic structures of solid helium, however, is solely based on theoretical calculations; experimental determination has not been previously possible. Here we report the first direct measurement of electron excitations of single-crystal helium above 11 GPa, and *ab initio* calculations for comparison.

Helium has the highest ionization energy of all materials. The energies of the valence-conduction band gap and associated excitations of solid helium are higher than 20 eV and far beyond the range of typical optical measurements. Probing helium's electronic structure by one-photon optical absorbance, reflectance [15], or fluorescence [16] spectroscopy requires vacuum ultraviolet photons at 20–40 eV that would be completely blocked by the high-pressure chamber and the bulk helium sample itself. Only the surface of condensed helium can be sampled in near vacuum conditions [15], precluding high-pressure studies of bulk helium. This energy range can be accessed by the newly advanced, two-photon, inelastic x-ray scattering (IXS) spectroscopy [17] which uses high-energy x rays ($\sim 10^4$ eV) to enter (with energy E) and exit (with energy E_0) the pressure vessel and sample. The electronic spectra in the 20–40 eV range are revealed by analyzing the x-ray energy loss between the two photons, $\hbar\omega = E - E_0$. High-energy x ray has an additional advantage in probing momentum transfer ($\mathbf{q}$), while the optical ultraviolet photons can only probe the Brillouin zone center ($\mathbf{q} \approx 0$). The IXS double differential cross section is proportional to the dynamic structure factor

$$S(\mathbf{q}, \omega) = \sum_f |\langle f | e^{i\mathbf{q} \cdot \mathbf{r}} | I \rangle|^2 \delta(\hbar\omega - E_f + E_I) \quad (1)$$

where I and f label the initial and final electronic states and their energies. As the second lightest element, however, helium has a very low x-ray scattering cross section, and its IXS signals are very weak even using a high-brilliance synchrotron x-ray source. Previous IXS measurements of solid helium are therefore limited to relatively large samples (10 mm^3) in a beryllium cell at low pressures ($< 0.22 \text{ GPa}$) and temperatures ($< 22 \text{ K}$) [5,6,17,18].

At ambient temperature, diamond anvil cell (DAC) is the only apparatus to pressurize ^4He to solidification at 11 GPa and beyond [2]. The maximum sample size in DAC is small, i.e., 10^{-4} times smaller than that in the beryllium cell [17]. Although high-pressure electronic IXS spectroscopy in DAC has been developed for studying second-row elements [19–21], measurement of the weak signal from ^4He has proven challenging. We optimized the IXS-DAC technique at three third-generation synchrotron beam lines: 13ID-C [19] of the GeoSoilEnvironCARS (GSECARS) and 16ID-D [21] of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS), and the Taiwan Beamline BL12XU [20] at SPring-8, Japan. To get sufficient counting statistics, we accumulated the signal and background for a total of one month of beam time.

We used a panoramic DAC [22] and maximized the helium sample volume (10^{-3} mm^3) for the 10–20 GPa range using large diamond anvils of 630 μm culet diameter. A high-strength beryllium gasket with 5 mm outer diameter and 1 mm thickness [22] was fabricated to

match the diamond culets and to form a sample chamber of 180 μm inner diameter and 25 μm thickness. Research-grade helium with natural isotopic abundance of ^4He (99.986%) was loaded in the DAC at 0.2 GPa [23]. Pressure was calibrated by ruby fluorescence.

Beam lines 13ID-C uses a Si(220) and 16ID-D uses a diamond (111) incident x-ray monochromator, and both beam lines use an array of six spherical Si(660) analyzers (50 mm diameter) on a Rowland circle of 87 cm diameter focusing to a single detector in back-scattering geometry (Bragg angle of 89°) at a fixed energy of $E_0 = 9.6865$ keV, achieving 1 eV (FWHM) energy resolution [19]. Beam line BL12XU at SPring-8 uses a Si(400) incident x-ray monochromator and two Si(555) spherical analyzers on a Rowland circle of 2 m diameter at 9.8992 keV, achieving 175 meV energy resolution [20].

At 11 GPa the ^4He sample was compressed to form a hexagonal close-packed (hcp) single crystal [8,23,24], whose orientation was determined by x-ray diffraction [23,24]. For comparison with optical spectroscopy, which samples the Brillouin-zone center, we measured IXS spectra near the 3 point of the first repetitive Brillouin zone. To minimize the background signals, we focused the incident x-ray beam to restrict the beam cross section within the ^4He sample volume. To block the background signals along the x-ray beam path before and after the ^4He sample, we aligned a 150 μm -width receiving slit close to the gasket. The residual background signals from the diamond anvils and Be gasket are significantly below the sample signals and can be fully subtracted based on the control measurements of the diamond and Be. With the improved measurements, we are able to observe many more features in the electronic structure of helium than previously possible [5,6,18]. Our IXS spectrum of ^4He at 13.4 GPa [Fig. 1] shows a wealth of information. In addition to the sharp exciton peak at 24.4 eV and the steep edge below 23.7 eV, for the first time we have observed a second broad, unresolved series of peaks around 27.5 eV, and a continuum at higher energy.

The sharp exciton peak was the only feature previously observed in helium at low pressure [5,6,18]. Two limiting cases have been used to describe excitons in noble-gas solids: the Wannier exciton with a freely mobile, weakly bound electron and hole, or the Frenkel exciton with a more localized wave function that is tightly bound together. Unable to see the $n = 2$ Wannier exciton, Arms *et al.* [5] suggested it was a Frenkel exciton. Now with the clear presence of the series of unresolved peaks at 26–45 eV in our experiment, the possibility of Wannier series excitons mixing with interband transitions can no longer be dismissed. In any case, the Frenkel-Wannier distinction is somewhat artificial, and the onset of the continuum should have a smooth transition from the upper Rydberg-like excitons to unbound states. High pressures change the length scales of both exciton radii and the nearest neighbor atomic distance. Description of the system requires the full electronic spectrum, its dispersion, and its change under pressure.

We measured the electronic IXS spectra over a range of pressure and momentum space. The ^4He IXS spectra along the Γ - M ($h00$) branch were measured at 11.9, 13.4, and 17.0 GPa, corresponding to molar volumes of 4.170, 4.000, and 3.696 cm^3/mol , and d_{100} spacing of 1.853, 1.827, and 1.780 $\text{\AA}$, respectively. The momentum transfer (q) was calculated from the scattering angle (2θ) and the x-ray wavelength (λ_0) by $q = (4\pi/\lambda_0) \sin\theta$; the reduced

momentum transfer along Γ - M is $q^* = q(d_{100}/2\pi)$. Figure 2 shows the change of the $q^* = 1$, zone-center spectra as a function of pressure. The inset of Fig. 2 shows the shift of the zone-center exciton as a function of the molar volume (V):

$$E(\text{eV}) - E_0(\text{eV}) = 17.0(2) + 1.85(4)V(\text{cm}^3/\text{mol}). \quad (2)$$

The 11.9 and 17.0 GPa spectra were obtained with a 1 eV instrumental resolution at beam lines 13ID-C and 16ID-D, and the 13.4 GPa spectrum, with 175 meV resolution at beam line BL12XU [20]. The higher resolution of the latter showed a narrower exciton peak and improved resolution of features above 26 eV [Fig. 1], at the expense of a six-fold reduction in count rate. The 1 eV resolution is adequate for revealing many major features, including the cutoff edge, the sharp exciton, the series of additional excitations, and their shifts as a function of pressure and momentum transfer. We used the 1 eV resolution to cover the wide range of pressure and momentum space, and the 175 meV resolution for verification of key points.

We investigated the electron dynamics of hcp ^4He along the Γ - M ($h00$) direction at 11.9 GPa. Figure 3 (left) shows a series of 16 IXS measurements for 2θ ranging from 25° to 130° corresponding to the q^* range 0.628 to 2.628. The series was collected with the vertical-scattering spectrometer at 13ID-C, APS [19], as the horizontal-scattering spectrometers at 16ID-D and BL12XU are incompatible with the horizontally polarized synchrotron sources for $2\theta > 60^\circ$. The data quality was at its best near the $q^* = 1$ at $30^\circ < 2\theta < 50^\circ$. At lower angles, the background from Be and diamond increased rapidly. At higher angles, the IXS intensity diminished, and the collection time became exceedingly long.

With its closed $1s$ shell, ^4He is particularly amenable to theoretical calculations. We simulated the IXS spectra using *ab initio* treatments of separate electron and hole dynamics and electron-hole interactions [25,26] for the same volume, Brillouin zone, and 2θ range as the experimental measurements. We calculated theoretical IXS spectra based on calculating the loss function. This relied on a solution of the Bethe-Salpeter equation following the method of Benedict *et al.* [27], extended to finite momentum as by Caliebe *et al.* [28], and density-functional calculations carried out within the local-density approximation using the plane-wave pseudopotential approach, mimicking the methodology of earlier work [25]. We used a cutoff radius of 0.015 nm for the s -wave pseudo-potential and a 400 Ry cutoff to ensure a realistic calculation. The band structure was corrected using Hedin's GW approximation for the electron self-energy [29] using the method of Hybertsen and Louie [30] for fcc He with a 64-point Monkhorst-Pack grid [31] and 45 bands included in the electron Green's function—cutoffs that have proven adequate for such wide-gap insulators with small unit cells. (In the GW approximation, the self-energy is the electron Green's function G times the screened Coulomb interaction W .) In fcc He at the same atomic volume, the correction was a 7% stretch of the occupied bands and 2% stretch of the unoccupied bands, with a widening of the band gap from about 17.1 eV to about 27.1 eV at all pressures considered here, and we safely extrapolated such effects to the similarly close-packed hcp structure. Over the same pressure range, the dielectric constant calculated in the GW calculations varied between 1.44 and 1.49, a reasonable value for the atomic density,

and consistent with the values obtained from the Bethe-Salpeter calculations, in which we included 2 valence bands, 18 unoccupied bands, and up to 256 Brillouin zone sampling points, which proved to be well converged.

Since volume is a more fundamental variable than pressure the experimental results [Fig. 3, left] at 11.9 GPa are compared with the theoretical calculations (left) at the same volume of $4.170 \text{ cm}^3/\text{mol}$. Both show a similar general spectral shape, relative intensity, and dispersion. The calculations resolve the multiple peaks revealed by the experiments and provide more details of the exciton beyond the simplified categorization of Frenkel and Wannier types. Agreement between theory and experiment also provides confidence for calculations at higher pressures and temperatures beyond the current experimental range. We identify the first peak that is strongest near $2\theta = 45^\circ$ as an energetically isolated bound state. Core hole-excitonic effects are often very strong in wide-gap insulators, so that other excitonic features appear merged with the continuum spectrum. As in other systems [32], a broad, structured feature appears to straddle the continuum threshold.

The experimental and theoretical dispersions of the first excitonic peak as a function of the momentum transfer in the Γ - M branch are plotted in Fig. 4. Our experiment clearly identifies the energy minimum at the zone center (Γ point) and maximum at the zone edge (M point). The large dispersion amplitude (about 1.5–2 eV) for $q^* = 0.628$ to 1.0 is in good agreement with the calculation. The information from the first Brillouin zone is accurate and sufficient to show the amplitude of the repetitive periodic dispersion. The 0.5 eV offset between theory and experiment reflects the calculation uncertainty which is dwarfed by the correlation and excitonic binding effects on the excitation energy (about 4.5 eV and 3.5 eV, respectively). For $q^* > 1.3$ due to the diminishing exciton peak intensity and overlapping with the rising edge of features at higher energy [Fig. 3], the exciton peak is increasingly difficult to resolve and its position is uncertain. Nevertheless, the maximum and minimum are still visible qualitatively.

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FIG. 1.

^4He zone-center IXS spectra and background at 13.4 GPa. The raw spectrum contains a background contribution from Be and diamond. The Be gasket spectrum shows a typical metallic character with the initial slope taking off from zero energy loss. The diamond spectrum shows a gap with initial slope taking off above 10 eV. The backgrounds are subtracted by matching slopes of the raw spectrum at zero and 10 eV with a fraction of the Be and diamond spectra to obtain the net ^4He IXS spectrum.

FIG. 2.

⁴He zone-center IXS spectra at high pressures. To avoid the intense elastic scattering from the 100 Bragg diffraction, our measurements were taken slightly off the 3 point at $2\theta = 40^\circ$, corresponding to $q^* = 0.992, 0.998$, and 0.972 for 11.9, 13.4, and 17 GPa, respectively. Inset: exciton peak position as a function of volume.

FIG. 3. Experimental (left) and theoretical (right) IXS spectra of ^4He at the volume of $4.170 \text{ cm}^3/\text{mol}$. Dispersion along the $h00$ direction, IXS spectra are shown with scattering angle from 25° to 90° in 5° steps and 90° to 130° in steps of 20° . Dotted gray lines are a guide for the eye.

FIG. 4.

Dispersion of the ^4He exciton along periodic Brillouin zone Γ ($q^* = 1$ and 2) to M ($q^* = 0.5$ and 1.5) at the volume of $4.170 \text{ cm}^3/\text{mol}$.