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Exciton Dispersion and Electronic Excitations in hcp ^{4}He

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We present first measurements of the dispersion of excitons in solid helium, taken on a single hcp ^{4}He crystal along the c axis. In agreement with studies on helium clusters, the major energy-loss peak can be interpreted as an intermediate molecular-type exciton, as we do not observe Wannier-like excitations. The measurements are in the (0 0 2) periodic zone, with the exciton energy dispersing along the c axis with a minimum at the Γ point. A calculated conduction band minimum at 31.0 eV above the valence band at Γ is supported by our data at energies above the exciton energy, leading to an exciton binding energy of 8.4 eV.

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We report on new measurements of electronic excitations in crystalline hcp ^{4}He. The inelastic x-ray scattering measurements clearly reveal an excitation that we interpret as an exciton. The measurements extend previous such measurements by Schell *et al.* [1], and demonstrate that despite extremely flat valence and conduction bands, exciton dispersion along Γ-A is observable.

Excitons in insulators and semiconductors are generally classified as being either of a Wannier type, with a wave function extending over many atomic sites, or of a Frenkel type, with a more localized wave function, although intermediate cases are also possible [2]. The Wannier type is evidenced by a series of excitations corresponding to different Bohr atom radii scaled by the dielectric constant and the reduced mass obtained from the effective masses. Without a clearly observed Wannier spectrum Frenkel excitons are deduced which are delocalized in reciprocal space.

Excitons in solid helium must be considered a special case for several reasons. First, since there are only two electrons for each atom one cannot make the usual separation between core and valence electrons. Second, the quantum nature of the crystal comes into play in determining the range of the exciton wave functions. That helium is a special case is also manifested in the fact that the density of the solid is determined through kinetic energy of the atoms and not through overlap repulsion of atomic cores, as is the case for other noble gas solids. There is a simplification compared to the more massive noble gases in that one-electron binding is substantially stronger than electron-electron interactions. This makes ^{4}He amenable to essentially *a priori* theoretical studies. However, in spite of the fact that atomic motion is known to be large compared to nonquantum crystals, practically all calculations to date of the electron structure have ignored nuclear motions (or simply have as an *ad hoc* input parameter the observed lattice parameter). A review of this subject has been done by Aziz *et al.* [3]. For the above reasons precise measurements are desirable.

At lower densities, pair interatomic interactions in helium are dominant, and are thoroughly characterized by exhaustive analysis and experiment [3]. Compared to the more massive noble gases, ^{4}He has the largest ionization potential and therefore the largest band separation. The band separation of the more massive noble gases has been ascertained from measurements of excitons, so the present results can be viewed as the first precise information concerning the band separation of hcp ^{4}He. All previous experimental studies of solid state effects related to band structure of noble gas solids have been limited to measurements which yield only frequency-dependent information, such as dielectric constants, joint densities of states folded with transition probabilities, or core spectra (commonly compared to atomic values) [4–6]. Studying solid helium requires applied pressure, even at very low temperatures, because otherwise the zero-point internal pressure keeps it liquid. To date, there are very few measurements of electronic properties. Direct absorption and emission spectra would lie in the EUV, a spectral range in which beryllium pressure cells are opaque. Up to now, optical studies have only been made on systems, liquid helium and helium clusters, which have a free surface [7–9].

A few calculations of the electronic structure in solid helium have been made [10,11]. These calculations were performed neglecting the large zero-point energy of helium. Nuclear vibration amplitudes can amount to 20% of the nearest neighbor distance [11–13]. No calculations of excitonic excitations in solid helium exist. Based on their work on helium clusters Joppien *et al.* provide a detailed picture of the electronic structure of helium clusters of various size. The absorption spectrum of large clusters resembles the one of liquid helium measured by Surko *et al.* The significant difference to absorption spectra for clusters of the more massive noble gases is that in the case of helium one does not observe the Wannier series. Joppien *et al.* conclude that the Wannier and Frenkel exciton models work well in the case of the more massive noble gases but fail with respect to helium. Assuming a dielectric constant of 1.055 and a heavy-hole approach, $\mu = m_e$ [14], the calculated exciton radius for the Wannier exciton, $n = 2$, is smaller than the nearest neighbor distance of 3.5 Å in the liquid. Moreover, the radial distributions of the $3p$ and $4p$ wave functions of the excited helium molecule approach the nearest neighbor distance, thus the traditional Frenkel model is also not appropriate. However, based on helium excimer potentials, Joppien *et al.* successfully fit their data (which were excitation spectra of helium clusters) [8,9,15].

For comparison to our results we now list the reported excitation energies for condensed ^{4}He so far as we know them. As expected, the single most important scaling variable for this energy is the atomic density. Excitation energies for the ($n = 1$) exciton have been reported for liquid by Surko *et al.* [7], clusters by Joppien *et al.* [8,15], and hcp single crystals by Schell *et al.* [1]. These measurements are summarized in Table I. The measurements by Schell *et al.* are along the c axis, where the c lattice parameter is 5.17 ± 0.1 Å.

The experiment was carried out at the 15-ID beam line of the Advanced Photon Source, which is operated by ChemMatCARS. The beam line uses a standard APS undulator *A* as its insertion device. The beam line was set to the energy required for a silicon analyzer employing the (5 5 5) Bragg reflection. The analyzer's backscattering angle of $\theta = 89.31°$ corresponds to a photon energy of 9.8865 keV (1.2541 Å).

The sample is contained in a beryllium cell. The material of which the cell is made was first a finely ground powder (97.5% Be and 2.5% BeO) which was then hot press sintered into a solid form, giving very uniform diffraction rings when exposed to x rays. Detailed inelastic x-ray studies of Be have been made by Schülke *et al.* [16]. The cell is cylindrical, having an inner diameter of 0.81 mm and an outer diameter of 2.1 mm. After the measurements were finished and the helium was removed from the cell, background measurements were done with the same scan parameters and cell orientation as the signal measurements at a temperature of 25.0 ± 0.2 K.

Nearly the same system was used by Venkataraman for various x-ray measurements [11], with the system being described by Venkataraman and Simmons [17]. This particular setup has been used for measuring the Debye-Waller factor of helium and is described in detail by Arms [12].

The energy transfer of the photons was measured by means of a fixed scattered energy and a varied incident energy. The incident energy was varied using the beam line's high-heat load diamond (1 1 1) double-crystal monochromator (DCM). The reproducibility of the DCM is ±40 meV, determined by repeated measurements of the position of a peak in the copper absorption spectrum during a 24-h period [18]. In addition, the energy bandpass of the DCM is 1.1 eV FWHM, with a flux at the sample (after slitting down) of $\sim 10^{12}$ photons/sec. The analyzer was a spherically bent crystal of 1 m radius. The angular resolution of the analyzer in 2θ was ±1.5°.

The determination of the molar volume for the crystal was made by a precise measurement of its freezing temperature. The freezing temperature is found during a cooling of the helium liquid, where the measured temperature momentarily pauses as the sample freezes. This is simultaneously seen in the pressure measured by strain gauges mounted on a cylindrical cell, as there is a small drop in the pressure during the temperature pause. The value of the temperature where it stops decreasing is the freezing temperature. Once the melting temperature is measured, previous measurements of liquid-solid phase transitions for helium [19,20] can be employed in order to find the pressure of the liquid at freezing and the molar volume of either the liquid or the solid at freezing.

The freezing temperature for the sample measured was 22.335 ± 0.005 K, resulting in a molar volume of 10.720 ± 0.005 cm^3/mole and a freezing pressure of 211.15 MPa. From previous measurements of hcp ^{4}He crystals [12], the c lattice parameter is known to be $c = 4.7821 \pm 0.0008$ Å. A 2θ measurement of the (0 0 2) reflection with an angular resolution of ±0.2° yields a direct value of $c = 4.81 \pm 0.04$ Å, agreeing with the previous value.

For the measurements, both elastic and inelastic scans were done at each value of 2θ. The temperature of the

TABLE I. Previous measurements.

Sample	Molar Volume (cm^3)	Exciton Energy (eV)	Exciton FWHM (eV)
Low density liquid		21.60 ± 0.02	0.58
Cluster ($N = 5000$)		21.64 ± 0.02	0.55
hcp single crystal	13.5 ± 0.1	21.9 ± 0.3	

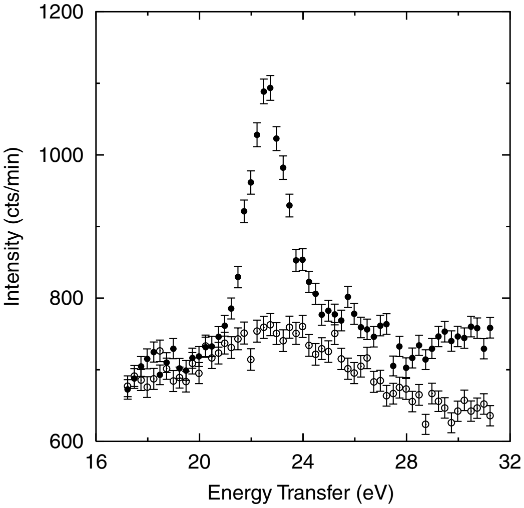

FIG. 1. Shown are the data (filled circles) and empty cell background (open circles) scans for $2\theta = 30.0°$. They are shown after being normalized to the monitor.

crystal during measurement was 14.0 ± 1.0 K. The empty cell background scan was subtracted directly from the signal scan, with no scaling. These scans for the 30.0° measurement are shown in Fig. 1. The resultant data have a peak with a rising baseline, which was fit to a Gaussian plus a linear function. The resultant peaks and their fits are shown in Fig. 2. The energy position of the Gaussian corresponds to that of the exciton, and the value for the full width at half maximum (FWHM) is also noted from the Gaussian parameters. The measured values for the samples are shown in Table II, along with the momentum transfer of the photons, Q, and the reduced momentum transfer in terms of the c axis, Q^*. With respect to earlier work at lower density, the energy shift of the exciton to higher energies indicates an increased repulsive contribution in the excited state, due to increased overlap with the nearest neighbor ground state. This also is reflected in the FWHM of the exciton peak where, after correcting for the instrument's bandpass, the value of 1.1 eV is double the value observed in the cluster and the liquid.

TABLE II. Exciton measurements.

2θ (°) ± 1.5	Q (Å^{-1}) ± 0.13	Q^* ($2\pi/c$) ± 0.1	Energy (eV) ± 0.04	FWHM (eV)
22.0	1.91	1.5	23.24	1.94
30.0	2.59	2.0	22.60	1.57
35.0	3.01	2.3	23.02	1.62

The measurements were taken along the c axis in the (0 0 2) periodic zone, at -1.0 A, Γ, and 0.6 A. The table and Fig. 2 show that there is dispersion of the exciton, with a minimum at Γ. There is broadening of the exciton peaks also. Shown in Fig. 3 is the rising baseline of the excitation spectrum (also seen in Fig. 2). In the figure, there is an onset of excitations at about 21 eV, where the data rise somewhat linearly.

We do not observe the steep rise at 27.0 eV previously reported by Schell [1]. This rise had been suggested as a Wannier exciton series at $n = 2$. We infer from the absence of any steep rise in the excitation spectrum that the Frenkel exciton model is favorable over the Wannier exciton model for hcp ^{4}He.

Calculations similar to those done by Venkataraman [11] have been made for electronic band structure using CRYSTAL98 [21]. Venkataraman used CRYSTAL92 to generate band structures using a set of trial electronic wave functions given by Kunz (although no band structure values were shown). As with CRYSTAL92, CRYSTAL98 neglects the large zero-point energy of helium. However, since typical

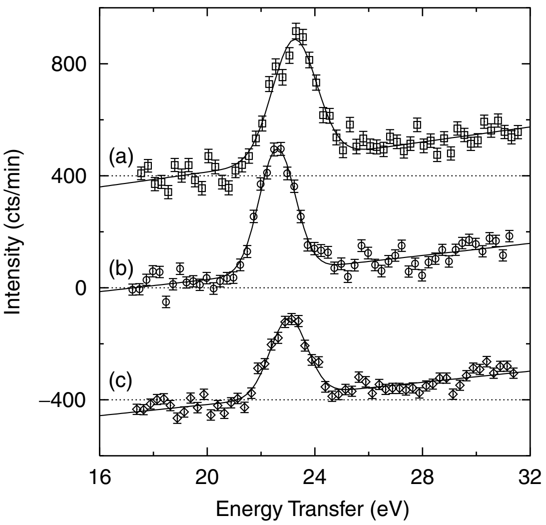

FIG. 2. Shown are the excitation peaks for 2θ values of 22.0° (a), 30.0° (b), and 35.0° (c). A dispersion among the peaks can be seen. The empty cell background has been subtracted. Values for the fitted Gaussians are in Table II.

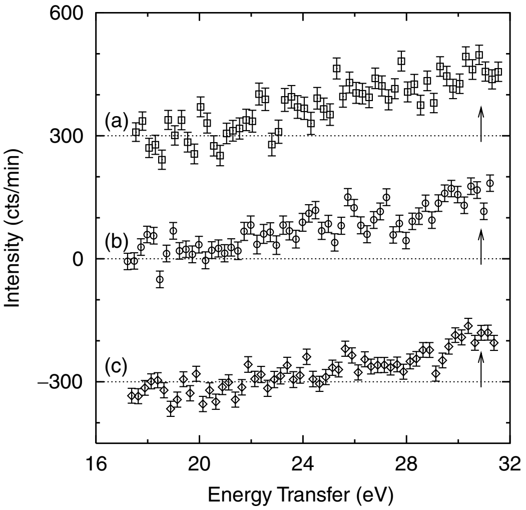

FIG. 3. Shown are plots of the data when the exciton peak has been subtracted. The plots correspond to 2θ values of 22.0° (a), 30.0° (b), and 35.0° (c). The empty cell background has been subtracted, and the exciton peak was removed by subtracting the Gaussian fit. The arrows denote the positions of the calculated 31.0 eV band separations.

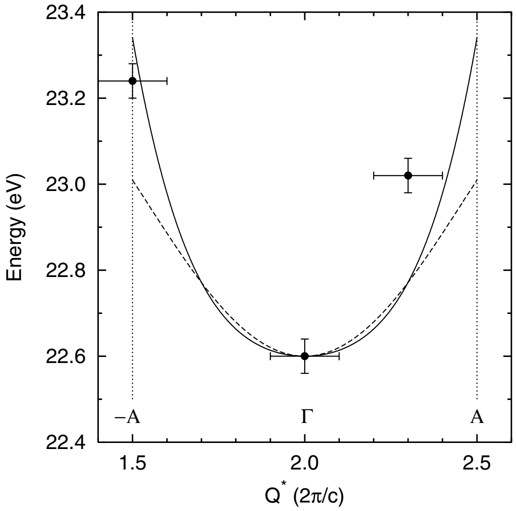

FIG. 4. The measured dispersion of the exciton is shown, along with curves corresponding to the calculated band bending for the valence band (dashed line) and conduction band (solid line) in the (0 0 2) periodic zone.

phonon energies are less than 10 meV compared to more than 20 eV for electronic excitations, we assume that the Born-Oppenheimer approximation is applicable, i.e., the nuclei are regarded as fixed at their atomic mean positions. We note that within this approximation the electrons move adiabatically with the nuclei, and it would not be inconsistent for exciton wave functions to have a range determined by atomic motion and to be influenced by quantum effects.

For our crystal parameters, the calculated band structure shows that along Γ-*A* there is a minimum separation between conduction and valence bands at Γ, with a band separation of 31.0 eV. At the *A* point, the conduction and valence bands are dispersed relative to Γ so that the conduction band is 32.2 eV above the valence band, with 0.8 of the 1.2 eV difference coming from the conduction band dispersion and 0.4 eV coming from the valence band dispersion. Our energy measurements at Q^* values of 1.5 and 2.0 have a difference of 0.64 eV (see Table II). In Fig. 3, an arrow shows the calculated result of 31.0 eV. The comparison of this value to the data shown in Fig. 3 suggests that the slow rise observed with increasing energy is due to the creation of electron-hole pairs, and that the exciton binding energy is 8.4 eV at Γ.

Figure 4 shows the measured exciton dispersion, as well as the calculated band bending of the conduction and valence bands. We note that the exciton dispersion is closer to the conduction band bending than it is to the valence band bending.

We have made precise measurements of helium excitons, showing dispersion along the *c* axis of the (0 0 2) periodic zone with a minimum at Γ. We see no evidence of an $n = 2$ Wannier exciton, suggesting that the exciton measured is more similar to a Frenkel exciton. The rise seen in Fig. 3 may be related to direct interband transitions, as suggested by our calculations showing a band separation of 31.0 eV.

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