Electronic Excitations in hcp ^{4}He at 61.5 MPa and 4.3 K Studied by Inelastic X-Ray Scattering Spectroscopy

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The dynamic structure factor $S(\vec{q},\omega)$ of electrons in solid ^{4}He was measured with 1.6 eV energy resolution by means of inelastic scattering of synchrotron x rays from a hcp single crystal for $\vec{q}$ along the c axis and for $q = 0.45$, 0.97, and 1.24 a.u. The hcp crystal was grown *in situ* at 61.5 MPa and 4.3 K. A q-independent energy loss peak at 21.9 ± 0.3 eV could unambiguously be identified. These signals are the first directly measured electronic excitations in solid helium. They are discussed in terms of excitonic excitations.

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Even today we have practically no experimental data on the optical and electronic properties of solid helium, especially as far as band structure and electronic excitations are concerned. The reason for this lack of information is the remarkable quantum nature of the atomic constituents, which allows solidification only under externally applied pressure, even at zero temperature. Because of this a pressure cell is necessary for experiments with solid helium, which inhibits the application of such methods as vacuum ultraviolet (vuv) reflectivity, photoemission, photoconductivity, measurements of electron and hole mobility, cyclotron resonances, electron energy loss spectroscopy, magneto-optical investigations, etc., none of which have been tried so far.

The only method successfully applied to gain information about the dynamics of solid helium in its various modifications, bcc, hcp, and fcc, has been neutron scattering. And indeed, by fruitful theoretical and experimental effort, considerable knowledge has been gained during the last 25 years—but only knowledge about lattice [1] and single-particle [2] dynamics. The lack of experimental data about electronic properties is regrettable, because solid helium (with only two electrons per atom) is a case amenable to essentially first-principle theoretical studies.

Calculations of solid helium electronic structure are rare [3]. Recently, preliminary results for the hcp solid helium band structure were obtained [4] by using the code CRYSTAL 92 [5] together with the basis set of Kunz, which will be published separately elsewhere. All authors neglect the influence of nuclear motion, an effect of unknown magnitude. In low-density hcp ^{4}He, nuclear vibration amplitudes are 20% to 25% of nearest neighbor distances; but, on the other hand core radii are a similar fraction, so that the solid is maintained at the density concerned through (atomic) kinetic energy, not through overlap repulsion of atomic cores, as in usual crystals. At lower densities, pair interactions dominate the cohesion of solid helium. At extreme compressions, triplet interactions are significant [6]. These appear to include both triplet-dipole Axilrod-Teller-Muto (ATM) and triplet exchange. In the heavier noble gas solids Ar, Kr, and Xe, it seems that ATM interactions are more important than triple exchange and higher-order multipole interactions [7].

Indirect knowledge of electronic properties of solid helium could be gained by extrapolating the results of measurements on atoms according to relations found between atomic and bulk properties in other noble gases, presuming these relations also to be valid for helium. In the heavier gases Xe, Kr, Ar, and Ne, absorption spectra in the solid state are closely similar to those of the corresponding free atoms. Solid state effects show up (1) at the onset of transitions from inner shells, and (2) in weak structures superimposed upon the absorption continuum. Gross features in absorption and reflection can be explained using atomic theory (for liquid helium, e.g., see [8]). Band gaps in the heavier solids have been inferred from the limits of the Wannier exciton series [9,10]. For atomic He, the K-shell binding energy is 24.6 eV, and the $1s\,^2S_{1/2}$ series limit is at 24.580 eV [9].

A more direct way of obtaining information about optical properties and electronic excitations in the solid state is the detailed study of clusters prepared in a supersonic beam. While there is good agreement between calculated and observed thresholds for fragmentation, which has been attributed to precursor excitonic excitations caused by electron bombardment of small He clusters [11], it has recently been called in doubt whether the concept of excitons can be applied to helium clusters [12]. These doubts are mainly supported by inconsistencies coming up when the results of fluorescence spectroscopy on helium clusters containing between 50 and 10^6 atoms/particle were evaluated. Those inconsistencies are in strange contrast to quite similar investigations on, e.g., argon clusters with the same method [13].

The highest atomic ionization energy of 24.6 eV among all elements of the periodic table will lead to a presumed band gap of larger than 25 eV between essentially flat conduction and valence bands in solid helium. The information about optical and electronic properties is therefore expected to arise from the visible and the vuv region of the electromagnetic spectrum. Because no window material is available which both is transparent in this spectral range and can withstand the high pressure necessary for solidification, the only direct method for investigating those properties is inelastic x-ray scattering spectroscopy (IXSS). Progress in this field is mainly due to the development of better x-ray sources as insertion devices at various synchrotron radiation facilities [14].

The measurements presented here have been made feasible by further progress in instrumentation for IXSS using synchrotron radiation from the HARWI wiggler at DESY/HASYLAB, Hamburg. The instrumental details are outlined in Ref. [15]. The principle of the setup is as follows. Synchrotron radiation from the "hard x-ray wiggler" HARWI is monochromatized and sagittally focused on the sample position by the cylindrically bent second crystal of a fixed-exit (511) Si double-crystal monochromator in a nondispersive setting. The inelastically scattered radiation is collected by a spherically bent (12 0 0) Si analyzer crystal, Bragg reflected at 86°, and focussed on a Ge solid state detector. The scattering sample and the detector are placed on the Rowland circle of the analyzer. The spectrometer works in the so-called inverse geometry: The primary energy (around 13.8 keV) is changed by the monochromator in order to analyze the spectral distribution of the scattered radiation, while the analyzer's Bragg angle is kept fixed. Vertical dispersion compensation [16] enhances the spectral throughput appreciably.

We installed a modified liquid helium flow cryostat, with a high-pressure polycrystalline Be cell inside, at the sample position in the scattering chamber of the IXSS spectrometer. The helium crystal was grown within this Be cell by pressurizing it through a stainless steel capillary to 61.5 MPa. This pressure was generated by a thermal pump consisting of a pressure vessel that was alternately cooled down and warmed up between 77 and 300 K. The sample cell had an accessible height of approximately 10 mm, an outer diameter of 2.1 mm, and an inner diameter of 1.2 mm; it was rated to 270 MPa. A heater block, a RhFe resistor, two Si diodes, and two Manganin heating wires were attached near the top and the bottom of the cell, so that the temperature distribution could be controlled, and, especially, a temperature gradient along the cell axis could be maintained. This high-pressure handling system including Be cell and cryostat will be described elsewhere [17].

During solidification, the pressure in the cell was maintained constant by keeping the capillary open using the heating wires. When the whole cell was filled with solid, the capillary was allowed to cool to approximately 5 K, thereby sealing off the cell and allowing constant-volume conditions. At 61.5 MPa, ^{4}He solidifies to the hcp modification with its c axis (within about 20°) normal to the long axis of the cell, i.e., normal to the growth direction, due to the large anisotropy of the thermal conductivity in hcp ^{4}He. Structurally the c/a ratio is "ideal." The crystal parameters were $V_{\mathrm{mol}} = 13.5 \pm 0.1$ cm^3, $c = 5.17 \pm 0.1$ Å, and $T_{\mathrm{melt}} = 10.2 \pm 0.1$ K. The crystal orientation was controlled by (002) Bragg reflection. Fortunately, the c axis had grown directly in the scattering plane of the instrument.

For each scattering vector $\vec{q}$, up to five single spectra were taken and processed as described in [18]: scanning of the primary energy corresponding to an energy loss from -40 to 100 eV in steps of 0.7 eV; renormalization of the scattered intensity to the readout of a second Ge detector, monitoring the quasielastic signal of the scattering sample under $\theta = 70°$; subtraction of a linear background; adding of the single spectra with respect to the Rayleigh line position; and subtraction of the quasielastic scattered line, where this procedure makes the spectral range between 0 and 5 eV energy loss less reliable, so that this range was not used for serious evaluation. In this way, for each $\vec{q}$, about 12 000 counts were collected at a peak position of the inelastically scattered spectra.

After having measured the solid helium within the Be cell, the solid was melted by heating the cryostat to 20 K, so that the helium vented to atmospheric pressure. Then the cryostat again was cooled down to 4.3 K. In order to obtain the pure IXSS spectrum of solid helium, one has to measure the contribution of the empty Be cell (with He residual gas) separately and has to subtract it from the spectrum of the Be cell filled with solid helium. Because of sample geometry, focus dimension, and the low density of solid helium the contribution of solid helium to the total spectrum is only about 15%. Since small shifts in the beam position can change the solid helium contribution appreciably and since it is difficult to estimate the sample absorption for the two cases (empty and the filled Be cell), we normalized the spectra for these two cases to arbitrary units in the following way: By multiplying the spectrum of the empty Be cell by a scaling factor x (given in Figs. 2–4) we forced the difference of both spectra to be, on the average, zero between 5 and 15 eV; the peak value of the "filled" spectrum was normalized to 1. This kind of normalization was chosen for physical reasons: It is extremely unlikely that there could exist contributions to the solid helium spectra at energy losses smaller than 15 eV, since the lowest free atomic excitation $1\,^1S_0 \rightarrow 2\,^3S_1$ is at 20.6 eV [9].

Figure 1 shows, as a representative example, the processed and normalized sum spectra both of He in Be and of the empty cell for $q = 0.97$ a.u. Notice that the spectrum of the "empty" Be cell has the typical one-peak-one-shoulder structure of Be, as found in Ref. [19]. Figures 2–4 show the normalized difference spectra for

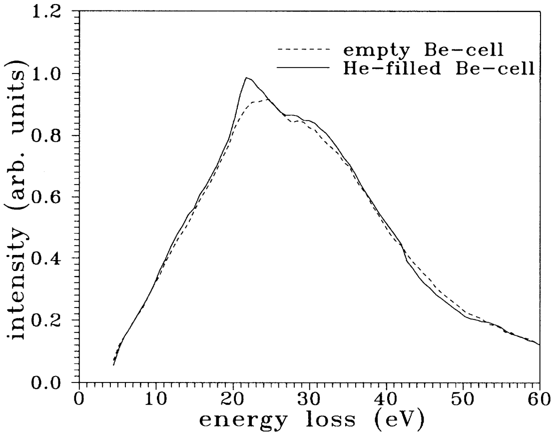

FIG. 1. Processed and normalized IXSS spectra for $q = 0.97$ a.u., intensity in arbitrary units. Solid line: spectrum of solid helium within a high-pressure Be cell; peak is normalized to 1. Dashed line: spectrum of the Be cell filled with helium residual gas. The normalization procedure is described in the text.

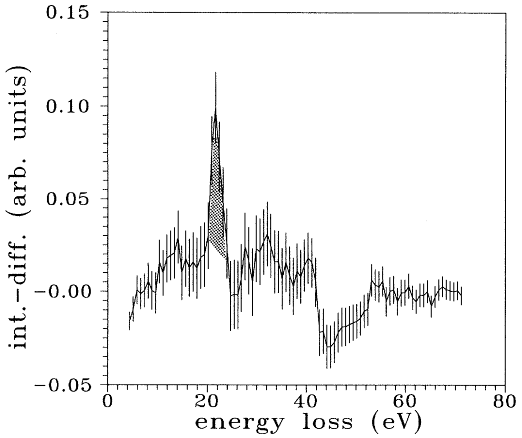

FIG. 3. IXSS difference spectrum for $q = 0.97$ a.u. Definition of the intensity difference as in Fig. 2. The peak at 21.7 ± 0.4 eV is screened. $x = 0.92$.

$q = 0.45$, 0.97, and 1.24 a.u. The error bars are related to the pure statistical errors. It cannot be excluded that longterm beam instabilities during the measurements produced some of the distinct oscillations, which in most cases are within the statistical error, so that it is inappropriate to relate the apparent differences between the spectra above 27 eV at different q values to details of the calculated helium band structure. Therefore we based all further discussion of the data only on those features which were common for all spectra with different $\vec{q}$.

For all three q values one finds unambiguously an energy loss signal, namely, a sharp peak. The position of this peak is, within the experimental error, independent of the q value, found at 21.9 ± 0.3 eV energy loss by taking the average of the three measurements. The width of this peak seems to be resolution limited. Furthermore, a steep rise at 27.0 ± 0.3 eV is visible in all three spectra.

A natural interpretation for the excitation at 21.9 eV is a Frenkel-type exciton of atomic parentage related to the free atomic $1\,^1S_0 \rightarrow 2\,^1P_1$ transition, which is at 21.2 eV, and has been found in liquid helium at 21.6 eV [8], where this shift to higher energies has been interpreted to be due to the relative large extension of the wave function of an atom in the excited state. This extension gives rise to a significant overlap of this wave function with the ground state wave function of the nearest neighbors. Moreover, fluorescence excitation spectroscopy results on He clusters and/or droplets [12] have established this shift to higher excitation energy with an increasing number of atoms and/or clusters. The steep rise of the IXSS spectrum at 27.0 eV might be attributed to the onset of a (nonresolved) Wannier-exciton series at $n = 2$, according

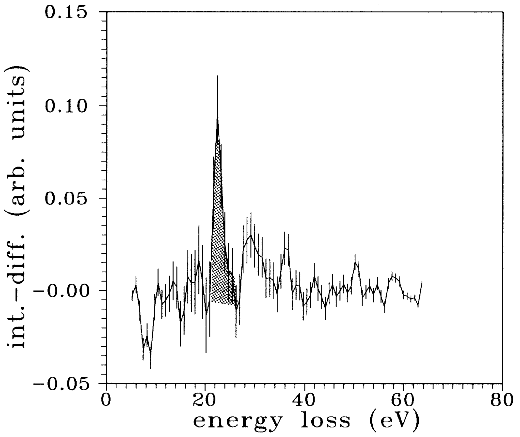

FIG. 2. IXSS difference spectrum for $q = 0.45$ a.u.: Solid-helium-filled Be-cell spectrum minus empty Be-cell spectrum. The peak at 22.3 ± 0.4 eV is screened. $x = 1.02$.

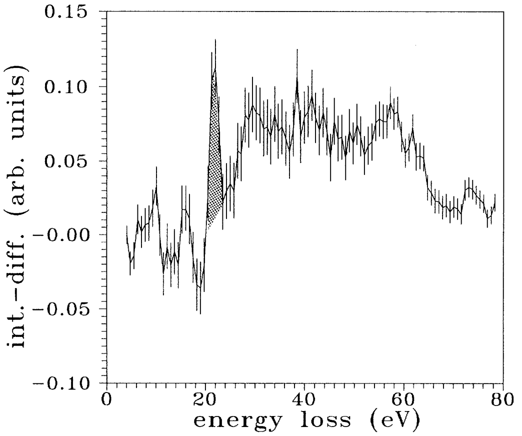

FIG. 4. IXSS difference spectrum for $q = 1.24$ a.u. Definition of the intensity difference as in Fig. 2. The peak at 21.8 ± 0.4 eV is screened. $x = 0.92$.

to the well-known relation for the exciton binding energy

$$E_n = \frac{\mu e^4}{2(\varepsilon \hbar n)^2}, \qquad (1)$$

where μ stands for the effective mass and ε for the dielectric constant. With $\mu = 0.8-1.0$ (following the assumptions of Ref. [12]) and $\varepsilon = 1.035$, the value for liquid helium one obtains is $E_n = 1.58-1.27$ eV, so that the energy gap would be 28.6–28.3 eV, not that far from 30.0 eV, the result of our above mentioned band structure calculation.

These results have proved the capability of IXSS to provide information about electronic excitations and the band structure of solid helium, so that a direct experimental method has been established, which, after some improvement of statistical accuracy, could enable detailed investigation of the density dependent influence of zero-point motion on *electronic properties.*

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[1] H. R. Glyde and E. C. Svensson, *Methods of Experimental Physics* (Academic Press, New York, 1987), p. 303.

[2] R. C. Blasdell, D. M. Ceperley, and R. O. Simmons, Z. Naturforsch. A **48**, 433 (1993).

[3] R. Colle, F. Bassani, and T. O. Woodruff, Nuovo Cimento Soc. Ital. Fis. **9D**, 1145 (1987).

[4] C. T. Venkataraman (private communication).

[5] R. Dovesi, V. R. Saunders, and C. Roetti, computer code CRYSTAL 92, user documentation, University of Torino, Torino, 1992.

[6] P. Loubeyre, R. LeToullec, J. P. Pineaux, H. K. Mao, J. Hu, and R. J. Hemley, Phys. Rev. Lett. **71**, 2272 (1993); M. Boninsegni, C. Pierleoni, and D. M. Ceperley, Phys. Rev. Lett. **72**, 1854 (1994).

[7] J. A. Barker, in *Simple Molecular Systems at High Density,* edited by A. Polian, P. Loubeyre, and N. Boccara (Plenum, New York, 1989), p. 341.

[8] C. M. Surko, G. J. Dick, F. Reif, and W. C. Walker, Phys. Rev. Lett. **23**, 842 (1969).

[9] B. Sonntag, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic Press, New York, 1977), Vol. II, p. 1021.

[10] N. Schwentner, E.-E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases* (Springer, Berlin, 1985).

[11] H. Buchenau, J. P. Tönnies, and J. A. Northby, J. Chem. Phys. **95**, 8134 (1991).

[12] M. Joppien, R. Karnbach, and T. Möller, Phys. Rev. Lett. **71**, 2654 (1993).

[13] J. Wörmer, M. Joppien, G. Zimmerer, and T. Möller, Phys. Rev. Lett. **67**, 2053 (1991).

[14] W. Schülke, in *Handbook on Synchrotron Radiation,* edited by G. Brown and D. E. Moncton (Elsevier, Amsterdam, 1991), Vol. III, p. 565.

[15] A. Berthold, S. Mourikis, J. R. Schmitz, W. Schülke, and H. Schulte-Schrepping, Nucl. Instrum. Methods Phys. Res., Sect. A **317**, 373 (1992).

[16] W. Schülke, H. Nagasawa, S. Mourikis, and P. Lanzki, Phys. Rev. B **33**, 6744 (1986).

[17] C. T. Venkataraman, N. Schell, and R. O. Simmons (unpublished).

[18] W. Schülke, Nucl. Instrum. Methods Phys. Res., Sect. A **246**, 491 (1986).

[19] W. Schülke, H. Nagasawa, S. Mourikis, and A. Kaprolat, Phys. Rev. B **40**, 12215 (1989).