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Free electron gas under high pressure

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We have carried out Compton scattering studies on metallic sodium under various pressures up to 42 kbar utilizing high-energy x rays from a third generation synchrotron source. The high pressure was applied using a large volume cell with a boron gasket. The induced change of free electron density ($\Delta V/V = 27\%$) is clearly detectable in the measured Compton profiles. The observed pressure effects are due to the change of the Fermi momentum, electron-ion, and electron-electron correlations as the average distance between electrons is reduced. The observed differences in the Compton profiles are well explained by a RPA calculation.

The free electron theory successfully explains a wide range of metallic properties. Several important macroscopic quantities can be calculated by simply assuming electrons to obey the Fermi-Dirac distribution. The free electron theory serves for metals in most cases as a first order approximation and with suitable extensions and corrections it can be applied to more complicated solid-state systems. Therefore, the theoretical and experimental study of free electron gas systems accounts one of the cornerstones in solid-state physics.[1] It is worthwhile to notice that for the simple free electron theory the free electron density is the only system dependent quantity (together with the temperature) affecting the electron gas response. This is the reason why different solid-state theories produce predictions for various measurable physical quantities as a function of $r_s = (3/4\pi n)^{1/3}$, where n is the free electron density.

Traditionally, the free electron gas behavior has been studied by various free electron-like systems available in nature, mainly alkali metals like Li, Na, K, Rb, and Cs.[2] They all have different free electron densities and measurements can be done for comparison between different r_s. However, in the majority of the experiments the solid-state effects (long-range order, for example) modify the free electron behavior and it is generally difficult to separate these contributions. Therefore it would be most appealing to perform a study of the same solid-state system with varying the free-electron density. This can be done by compressing the solid metal by applying high pressure which simply reduces the lattice constant and r_s. Similar (but smaller) effects can be also induced by changing the temperature but in this case the electron-ion interaction is modified.[3] In the extreme case one can utilize solid-to-liquid phase transition in order to exclude effects due to the long range order.[4]

Sodium is an excellent choice for this type of study for several reasons. Na 3*s* electrons form within a very good approximation a free electron gas and its Fermi surface is known to be isotropic within very good precision, which verifies minimal solid-state effects.[5] Furthermore, it does not have any structural phase transitions within the pressure range of the present study. However, being an alkali metal it is very reactive and great concern should be taken to prepare and treat the sample properly. In order to induce high pressure the sample must be closed within a pressure gasket. Therefore, hard x rays are a natural choice to probe the system properties. Specifically, inelastic scattering at high momentum transfer, usually referred to as Compton scattering, is a unique tool to probe directly the electron ground-state properties utilizing hard x rays.[6] The Compton profile $J(p_z)$ is defined as a one-dimensional projection of momentum density on to the scattering vector. For example, the measured Compton profile gives the momentum density of the scattering electrons, which is related to charge density, band structure, and wave functions.

Furthermore, in many solid-state systems the electron-electron correlation effects can play a crucial role in determining the system behavior.[7] Separating these effects from the other overlapping solid-state contributions experimentally via a direct measurement is not that simple a task. However, Compton scattering can in principle be utilized to directly produce correlation related parameters, like the quasiparticle renormalization constant Z_F which is given by the jump of momentum density at the Fermi break.[7] Obviously, the correlation effects depend on the free electron density but different theories predict significantly different r_s dependencies.[8] Figure 1 shows the calculated momentum densities for sodium at various pressures based on the model by Daniel and Vosko.[9] The corresponding changes of other relevant parameters are summarized in Table I. Only few experiments have been done to access different electron densities using different elements (typically Li, Be, and Na (Ref. 10). However, using different sample materials it is very difficult to separate the band-structure effects, for example, from the correlation effects. Therefore, we have studied sodium at different pressures to directly modify the free-electron density without a major change of the atomic structure. In addition for sodium, the so called high momentum components in the Compton profile due to the electron-ion interaction are very weak.

During the last decade there has been a vast development of inelastic scattering techniques.[11] The advent of synchrotron radiation has made it possible to use crystal analyzers to significantly improve the momentum resolution which has opened up new possibilities to study fine structures related to Fermi-surface topology.[12] Recently, several studies have

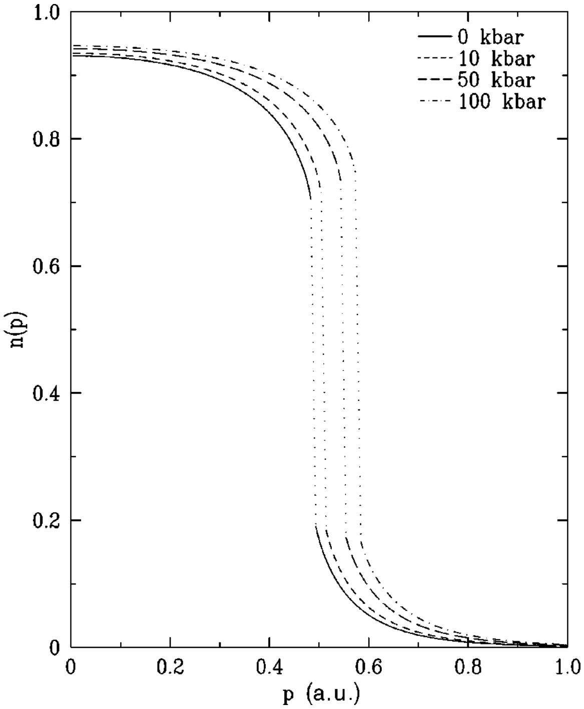

FIG. 1. Calculated momentum densities at various pressures based on a model by Daniel and Vosko (Ref. 9). The quasiparticle renormalization parameter Z_F is given by the jump at position of the discontinuity.

been done on a wide range of materials varying the sample environment (temperature, magnetic field), crystal direction or doping.[13] We will report Compton scattering studies on sodium under high pressure using hard x rays from a third generation synchrotron source using large volume cell with a boron gasket. To our knowledge, there has been only one earlier reported attempt to measure Compton scattering under high pressure.[14]

The experiment was carried out at beamline ID15 at the European Synchrotron Radiation Facility (ESRF). The radiation from an asymmetric wiggler source was monochromatized and horizontally focused using a cylindrically bent and asymmetrically cut Si(311) crystal in Bragg geometry. The size of the beam was restricted by heavy metal slits to 150 μm horizontally and the vertical slit size was varied from 80 to 350 μm depending on the pressure. The photon flux at 55.8 keV was about 10^{12} photons/s/mm^2. The scattered energy spectrum from the sample was measured using a Ge detector with 380 eV energy resolution at the elastic line. The scattering angle was 160°. The scattered radiation entering the detector was limited by a pair of slits so that the detected area was 0.5 mm(H) and 1 mm(V). Small beam and slit sizes together with a careful alignment made it possible to discriminate almost completely the scattering from the pressure cell. The details of the experimental setup are reported elsewhere.[15] The measured energy spectra were corrected for effects of the pressure cell and the self absorption of the sample and linear background. Finally, a conversion to momentum scale was performed using the relativistic cross section correction.[16]

TABLE I. Pressure dependence of various parameters for sodium.

P (kbar)	V/V_0	r_s	p_F	Z_F (Ref. 9)
0.001	1.0	3.93	0.488	0.48
0.68	0.99	3.92	0.490	0.48
5.4	0.93	3.83	0.501	0.49
10	0.88	3.77	0.510	0.49
24	0.80	3.64	0.527	0.51
33	0.76	3.58	0.536	0.52
42	0.73	3.54	0.543	0.52
100	0.60	3.32	0.578	0.55

The sample was 99.95% pure commercially available sodium delivered in a prescored glass ampoule. During the sample manipulation an extreme care was taken to avoid any kind of contamination or chemical reaction. The ampoule was broken within a safe gas environment inside a glove box and an adequate amount of sodium was used to fill a 2 mm diameter hole in the pressure cell gasket. The gasket was made of boron mixed with 15% of special epoxy containing light organic elements only. The 2 mm circular hole was covered by 0.2 mm thick tube made of boron nitride and the sample was closed inside the gasket with small caps made of same material. The gasket assembly was then closed within an airtight plastic bag and transferred to the beamline inside a safe gas environment. The plastic bag together with the gasket was placed on the large volume cell press and immediately pressure of 10 kbar was applied. Therefore, the safe gas environment was lost at the same moment as the sodium was exposed to high pressure which prevents any oxidation. The large pressure modifies the gasket so that it stays airtight even after releasing the pressure. This was confirmed after the experiment by opening and inspecting the gasket inside a glove box. The sodium filled the center of the gasket and still had shiny metal surface throughout.

The high pressures were applied by a mechanical ''Paris-Edinburgh'' press with hard metal anvils.[17] The special geometrical design guaranteed a uniform hydrostatic pressure over the full sample volume. An approximate pressure calibration was based on the pressure reading of the press fluid. A more precise calibration was done by measuring at each pressure the full diffraction image using an image intensifier and calculating the boron nitride lattice constant,[18] volume, and the corresponding pressure. An interesting detail of the sodium behavior was that instead of giving powder diffraction rings it produced single crystal Laue spots as a result of partial crystallization introduced by high pressure.

Since the pressure induced changes in the Compton profiles are relatively small, extra care has to be taken to verify the experimental system stability. Therefore, the acquired energy spectra were saved every 20 minutes while the total measurement time per pressure point was about 20 h. Consequently, for each pressure the individual spectra were verified to be identical within the statistical accuracy before addition thus excluding possible drifts in the gain or resolution function. The total number of counts within Compton profile was typically 2×10^7 counts and the statistics at the Compton peak was 0.2% for a 15 eV energy bin. The data were collected at six different pressures: 0.68, 5.4, 10, 23, 33, and 42 kbar. During the experiment the pressure was ramped up

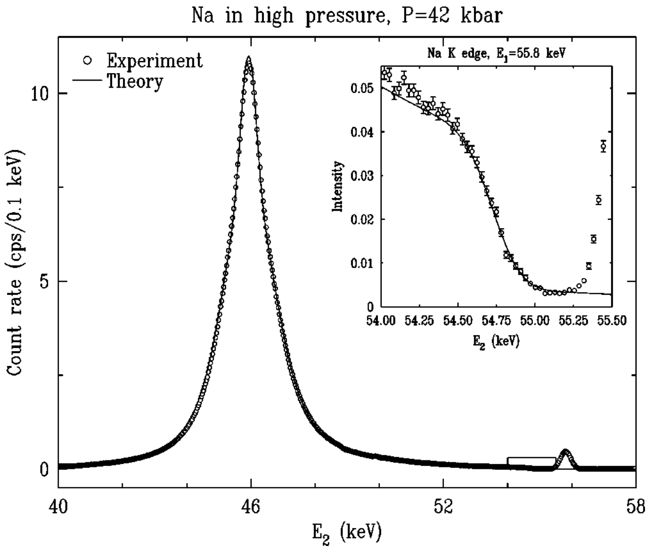

FIG. 2. The measured inelastic scattering spectrum from sodium at 42 kbar together with theoretical calculation discussed in the text. The onset shows the *K*-edge region.

from 10 to 42 kbar and then reduced to 5.4 and finally the high pressure press was totally released, which after calibration turned out to correspond to 0.68 kbar due to the residual internal pressure stress inside the gasket. Figure 2 shows the inelastic scattering spectrum at 42 kbar together with the theory convoluted with the experimental momentum resolution of 0.55 a.u. In the theoretical calculation the valence contribution and the correlation effects are included according to Daniel and Vosko[9] taking account the change of r_s induced by the pressure change. For the core electrons free atom Hartree-Fock profiles are used but they are cut off to incorporate the energy conservation requirements. As one can see, the general agreement with the experimental data is very good. Especially, the cut-off due to the sodium *K* edge is clearly visible which verifies the sample purity and insignificant scattering contribution from the pressure cell. The discrimination of the cell contribution is of uppermost importance for the Compton scattering studies because it is located exactly at the same position than the actual profile under study.

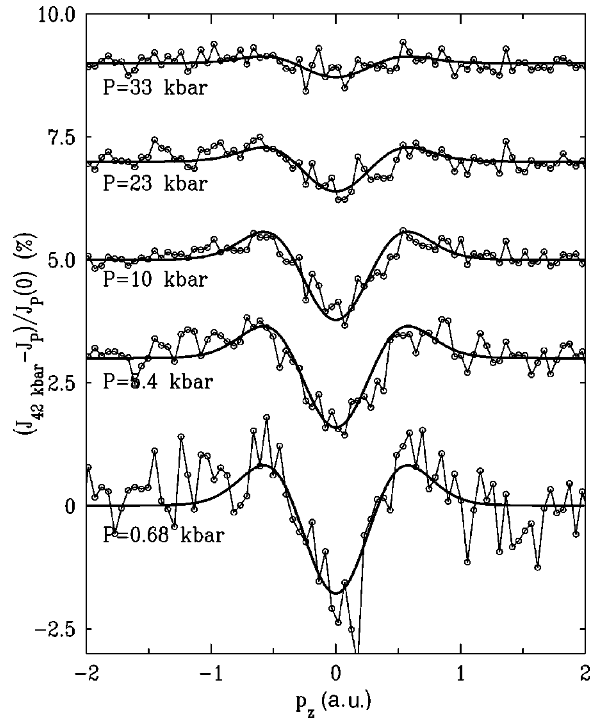

FIG. 3. The difference between Compton profiles at various pressures compared with the RPA theory including correlation effects (thick solid line).

Figure 3 shows the differences of Compton profiles under various pressures together with a RPA calculation discussed before.[9] When taking the differences a small (few percent) boron nitride contribution was subtracted to make the difference approach zero above 1.5 a.u. where no pressure change in the profile is expected. The boron nitride Compton profile was measured under the same experimental condition by slightly moving the sample cell so that the incident beam was hitting the boron nitride tube only. From the figure one can observe that the momentum density becomes broader. Also, due to the lattice constant change the Fermi momentum becomes larger. While the electrons are forced closer to each other the kinetic energy dominates ($\propto 1/r_s^2$) and the role of electron-electron correlation becomes less important ($\propto 1/r_s$). This can be seen in Figure 1 where the renormalization constant Z_F is increasing as a function of pressure. It should be noticed that the peak value of absolute Compton profile $J(0)$ within RPA can be significantly lower than value obtained for a noninteracting electron gas.[19] However, their relative pressure dependencies are similar and cannot be clearly distinguished with the present statistical accuracy.

We have also extracted the experimental Fermi momentum as a function of pressure based on the peak position of the second derivatives of the Compton profiles. This is generally known to correspond closely to the Fermi momentum where the Compton profile has a discontinuity.[20] However, the high momentum tail induced by the electron-electron correlation effects will shift the observed peak position. Therefore even relatively modest momentum resolution can be used to obtain quantitative information on the correlation effects. Since the second derivative is slightly asymmetric this method of determining the Fermi break depends also on the resolution function and great concern should be taken to model this properly. In our case the experimentally determined pressure dependence of Fermi momentum well obeys our RPA calculation but the statistical accuracy is not quite adequate to make detailed comparison between various theories with different Z_F.

As a summary, we have successfully performed Compton scattering measurements of a free electron system (sodium) under various pressures to study the electron-electron correlation effects. The general behavior of the free electron gas is in good agreement with a RPA theory.

The results clearly demonstrate the great potential of Compton scattering (even with low momentum resolution) to study the ground state electronic properties. With 1–2 orders of magnitude increase of photon flux which is obtainable with focusing optics such an experiment can be performed with almost one order of magnitude better momentum resolution. This would significantly help to separate the lattice and correlation effects.[21] Furthermore, with better focusing optics at high x ray energies the diamond anvil cell with a considerably extended pressure range offers a promising method to study, for example, phase transitions at extreme pressures via Compton scattering. Particularly, the Compton scattering will offer a unique tool to study the changes in the structure of Fermi surfaces related to electronic topological transitions. We want to emphasize that major complementary techniques (photoemission, positron spectroscopy, de Haas–van Alphen method) are extremely difficult, if not impossible, under high pressure. Moreover, the magnetic Compton scattering utilizing the circular polarization and sensitive to the spin density can be applied to study of pressure induced magnetic phase transitions.

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