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Static structure factor and electron-electron correlations in Be. A comparison of experiment with electron-gas theory

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The inelastic scattering cross section of metallic Be has been determined from an x-ray scattering experiment. The conditions under which the electronic contribution (static structure factor) can be extracted from such an experiment are discussed together with the approximations which have to be introduced in order to distinguish between core and band contributions. Accordingly, the static structure factor and the exchange and correlation energy of conduction electrons in Be have been determined. These quantities agree within experimental accuracy ($\sim 5\%$) with current electron-gas theory. From the static structure factor the electron-electron pair-correlation function has been deduced and compared with corresponding calculations for jellium. To this purpose the unavoidable experimental limitations on data accuracy and the theoretical difficulties which are encountered when performing direct first-principles calculations are discussed.

I. INTRODUCTION

The accurate description of the collective behavior of a many-fermion system is a basic problem encountered in widely different physical fields like solid-state and nuclear-matter theory. In the case of electrons, the problem is further complicated by the long range of the Coulomb potential which prevents a straightforward application of perturbative approaches.

In particular, for what concerns conduction electrons in simple metals usually modeled as a free-electron gas, since the pioneering work of Wigner and Seitz[1,2] going beyond standard Hartree-Fock approximation, an accurate knowledge of the high-density behavior has been obtained[3–5] and approximate theories at metallic densities have been developed.[6–8] Also, considerable theoretical effort has been devoted to the dynamic and static structure factor of the electron gas. The static structure factor is particularly interesting since from it the two-body correlation function and from this the exchange and correlation energy of the system can be calculated.[4] Apart from its fundamental interest, the study of the uniform electron gas is important because it affords a qualitative description of real metallic systems which, because of the presence of ion cores, have a nonhomogeneous charge density. This circumstance affects the validity of some of the results (sum rules in particular) established for jellium and at the same time poses the problem of the interaction between core and conduction electrons.

Although the theory of the two-body correlation function has been developed to a reasonable degree of accuracy only in the jellium case,[4,9] connections between the two-body correlation function (static and dynamic) and single-particle properties[10–12] exist also in real systems. Moreover, if experimental information on jellium properties were available, very interesting checks on the correlation energy and the structure factor itself could be made. Obviously, no direct experimental information can be gained on the structure factor of jellium itself; nevertheless, closely related experiments have been performed on simple metals. Actually, while extensive experimental research has been performed on the dynamic structure factor of several real systems,[13] little is known about the static structure factor, which in principle can be obtained from the dynamic one by integrating over the energy losses due to electronic excitations. In an actual experiment, however, this procedure leads among others to normalization problems when comparing values obtained for different values of momentum transfer, so that a direct measurement is certainly preferable.

Recently, two independent measurements by means of x-ray scattering of the static structure factor of metallic beryllium have been reported,[14,15] resulting in significant differences for conduction electrons. This discrepancy, coupled to the fact that the experimental techniques and procedures for data reduction in the two measurements were basically different, casts significant doubts on the results of both experiments.

Because of the importance of having reliable experimental data on the correlation function in real many-body systems as explained above, we have performed a new measurement of the static structure factor of beryllium employing a different experimental setup and a more sophisticated data-reduction procedure. The comparison with available theoretical predictions has been performed without making any assumption relative to the relation between conduction electrons in real systems and in the jellium model.

In the following sections we shall first outline the basic theory that allows the connection between the x-ray scattering cross section and the static structure factor. Then we shall recall the available theoretical approaches to the calculation of the structure factor. Finally, the experimental procedures and results will be presented and discussed.

II. THEORETICAL BACKGROUND

Even though the response theory of electron systems to electromagnetic fields is a well-developed subject described in standard text books,[4,16] nonetheless, it is useful to consider in some detail the case of x-ray scattering and specify the conditions under which a simple relation obtains between the scattering cross section and the static structure factor. To this purpose in what follows we will use the van Hove formalism[17] and the procedure employed in Refs. 4, 16, and 18.

Consider a target system composed by N nuclei (occupying positions $\vec{R}_l$ which later on will be assumed to form a periodic lattice) and NZ electrons. Let us assume that the energy of the incoming x-ray beam is high with respect to all binding energies of the electrons but small with respect to electron rest energy m_0c^2 so that our system can be described by classical quantum mechanics with small first-order corrections due to relativistic effects.

Under these conditions the x-ray scattering cross section from the electrons is

$$\frac{d^2\sigma}{d\Omega\, d\epsilon} = r_0^2 \frac{K}{K_0} d_f \cos^2\theta \times \frac{1}{2\pi\hbar} \int dt\, d\vec{r}\, d\vec{r}\,' \langle \rho(\vec{r},0)\rho^\dagger(\vec{r}\,',t)\rangle \times \exp[i\vec{Q}\cdot(\vec{r}-\vec{r}\,')+i\omega t]\,, \tag{1}$$

where $\vec{K}_0$ and $\vec{K}$ are the wave vectors of incoming and outgoing photons, θ is the angle between the polarization vectors of the photons before and after the scattering process, $\rho(\vec{r},t)$ is the electron density operator in the Heisenberg representation, $\hbar\omega$ and $\hbar\vec{Q}$ are the exchanged energy and momentum, respectively, and d_f is $\hbar c(\partial K/\partial E_f)$, E_f being the total system energy,[16] i.e., the sum of the outgoing photon energy and the energy of the target system after the scattering event. Although d_f can be calculated exactly only in the case of a single free electron, one has that in a many-electron system $d_f(\text{free}) \le d_f \le 1$ and that d_f approaches $d_f(\text{free})$ for increasing $\hbar\vec{Q}$. Then, as described in the literature,[4,18] the x-ray cross section is simply related to the dynamic structure factor

$$S(\vec{Q},\omega) = \frac{1}{2\pi NZ} \int dt\, d\vec{r}\, d\vec{r}\,' \langle \rho(\vec{r},0)\rho^\dagger(\vec{r}\,',t)\rangle \times \exp[i\vec{Q}\cdot(\vec{r}-\vec{r}\,')+i\omega t]\,. \tag{2}$$

Neglecting the ω dependence of $(K/K_0)d_f$, one can integrate the cross section of Eq. (1) over the whole energy range,

$$\frac{d\sigma}{d\Omega} = \int \frac{d^2\sigma}{d\Omega\, d\epsilon} d\epsilon \simeq r_0^2 \frac{K}{K_0} d_f NZ \cos^2\theta \int d\omega\, S(\vec{Q},\omega)\,, \tag{3}$$

so that an x-ray scattering experiment gives information on the static structure factor,

$$S(\vec{Q}) = \int d\omega\, S(\vec{Q},\omega)\,. \tag{4}$$

At this point we note that in Eq. (3) there are no approximations other than those involved in assuming $(K/K_0)d_f$ to be energy independent, which is known to be true only when the electron binding energy is negligible with respect to incoming photon energy. However, when comparing theory and experiment d_f is usually approximated as K/K_0 which in the case of free electrons amounts to expanding d_f as a power series in $\hbar cK/m_0c^2$ and retaining only the first-order term. Then, as noted above, it is clear that because of the contrasting demands upon the incoming photon energy, a significant interpretation of an experiment will be possible only for low-Z elements and for a judicious choice of x-ray wavelength.

The general properties of the static structure factor are well known in the case of homogeneous electron systems. However, real many-electron systems are not homogeneous since the electronic number density $n(\vec{r}) = \langle \rho(\vec{r})\rangle$ is not constant throughout the Wigner-Seitz cell. As such it is useful to describe the general properties of $S(\vec{Q})$ as well as its possible theoretical derivations in the case of nonhomogeneous systems.

First, using Eqs. (2) and (4) we can write

$$S(\vec{Q}) = \frac{1}{NZ} \int d\vec{r}\, d\vec{r}\,' \langle \rho(\vec{r},0)\rho^\dagger(\vec{r}\,',0)\rangle \times \exp[i\vec{Q}\cdot(\vec{r}-\vec{r}\,')]\,, \tag{5}$$

so that $S(\vec{Q})$ is the Fourier transform of the probability of having an electron at the point $\vec{r}\,'$ when another electron is at the same time at point $\vec{r}$. When $|\vec{r}-\vec{r}\,'|$ is large no correlation between two electrons at $\vec{r}$ and $\vec{r}\,'$ exists. As such,

$$\lim_{|\vec{r}-\vec{r}\,'|\to\infty} \langle \rho(\vec{r})\rho^\dagger(\vec{r}\,')\rangle = \langle \rho(\vec{r})\rangle \langle \rho^\dagger(\vec{r}\,')\rangle = n(\vec{r})n(\vec{r}\,')\,. \tag{6}$$

Moreover, one has

$$S(\vec{Q}) = \frac{1}{NZ} \int d\vec{x}\, d\vec{r} \langle \rho(\vec{r})\rho^\dagger(\vec{r}+\vec{x})\rangle e^{-i\vec{Q}\cdot\vec{x}} = \frac{1}{NZ} \int d\vec{x}\, f(\vec{x}) e^{-i\vec{Q}\cdot\vec{x}}\,, \tag{7}$$

where

$$f(\vec{x}) = \int d\vec{r} \langle \rho(\vec{r})\rho^\dagger(\vec{r}+\vec{x})\rangle\,. \tag{8}$$

For large x, using Eq. (6), one has

$$\lim_{x\to\infty} f(\vec{x}) = \int d\vec{r}\, n(\vec{r})n(\vec{r}+\vec{x}) = p(\vec{x})\,. \tag{9}$$

The function $p(\vec{x})$ is known in the theory of structure determination by x-ray diffraction as Patterson's map. The above relations have a general validity, but as we are interested in the case of beryllium we shall consider the special case of a periodic lattice. In a crystalline system the electronic number density $n(\vec{r})$ has the lattice periodicity

$$n(\vec{r}+\vec{R}_l) = n(\vec{r})\,, \tag{10}$$

$\vec{R}_l$ being a translation vector of the lattice. Then, using the periodicity, it is easy to show that

$$\int p(\vec{x}) e^{-i\vec{Q}\cdot\vec{x}} d\vec{x} = N^2 \sum_{\vec{G}} \delta_{\vec{Q},\vec{G}} |F(\vec{Q})|^2\,, \tag{11}$$

where $\vec{G}$ is a reciprocal-lattice vector and $F(\vec{Q})$ is the usual structure factor of the unit cell:

$$F(\vec{Q})=\int_{\mathrm{WS}} n(\vec{r})e^{-i\vec{Q}\cdot\vec{r}}d\vec{r}\ , \tag{12}$$

where the integration is extended to the Wigner-Seitz cell. Because the long-range behavior of $f(\vec{x})$ is described by $p(\vec{x})$ it is clear that $f(\vec{x})-p(\vec{x})$ is a rather short-ranged function, so that its contribution to the scattering is diffuse in the whole reciprocal space. The function $f(\vec{x})-p(\vec{x})$ contains all the inelastic contributions to the scattering cross section. This can be easily shown by splitting $S(\vec{Q})$, as described by Eq. (5), in an elastic and inelastic part:

$$\begin{aligned} NZS(\vec{Q}) &= NZ[S_{el}(\vec{Q})+S_{in}(\vec{Q})] \\ &= \int d\vec{r}d\vec{r}'\langle 0|\rho(\vec{r})|0\rangle\langle 0|\rho^{\dagger}(\vec{r}')|0\rangle e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')} \\ &\quad + \sum_{n\neq 0}\int d\vec{r}d\vec{r}'\langle 0|\rho(\vec{r})|n\rangle\langle n|\rho^{\dagger}(\vec{r}')|0\rangle e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')} \\ &= N^2\sum_{\vec{G}}\delta_{\vec{Q},\vec{G}}|F(\vec{Q})|^2+\int d\vec{x}[f(\vec{x})-p(\vec{x})]e^{-i\vec{Q}\cdot\vec{x}}\ , \end{aligned} \tag{13}$$

where $|0\rangle$ indicates the ground state and $|n\rangle$ an excited state of the system. We have to remember that although $|n\rangle$ contains the contributions from both electrons and nuclei the two contributions can be separated because of the large energy difference between the spectra of electronic and nuclear excitations which allows only negligible coupling between the two. This coupling contributes to the nuclear motion as a phonon energy renormalization and perturbs the electronic spectrum in a region of the order of k_BT about the chemical potential. Therefore, we can consider $S_{in}(\vec{Q})$ as composed by two contributions $S_{\mathrm{TDS}}(\vec{Q})$ and $S_{ee}(\vec{Q})$, corresponding to nuclear motion [thermal diffuse scattering (TDS)] and to dynamic electron-electron correlations.

We have also to remember two simple sum rules. The first one is the so-called compressibility sum rule[19] which states that

$$\lim_{Q\to 0} S(\vec{Q})=nk_BT\kappa_T(\hat{Q})\ , \tag{14}$$

n and $\kappa_T(\hat{Q})$ being the average electron density and the isothermal compressibility, respectively. It is interesting to observe that the sum rule of Eq. (14) is completely exhausted by the TDS contribution, i.e.,

$$\lim_{Q\to 0} S_{ee}(\vec{Q})=0\ . \tag{15}$$

The other simple relation is

$$\lim_{Q\to\infty} S_{ee}=\lim_{Q\to\infty} S(\vec{Q})=1\ . \tag{16}$$

We observe that taking the Fourier transform of $S_{ee}(\vec{Q})-1$ it is possible to show[20] that

$$\begin{aligned} \frac{1}{(2\pi)^3}&\int [S_{ee}(\vec{Q})-1]e^{i\vec{Q}\cdot\vec{r}}d\vec{Q} \\ &= \int n(\vec{r}_1)n(\vec{r}-\vec{r}_1)g(\vec{r}_1,\vec{r}-\vec{r}_1)d\vec{r}_1\ , \end{aligned} \tag{17}$$

where $g(\vec{r}_1,\vec{r}-\vec{r}_1)$ is the probability density of finding two electrons $\vec{r}$ apart, the first being at $\vec{r}_1$. The function $g(\vec{r}_1,\vec{r}-\vec{r}_1)$ has a number of exact properties that have been extensively discussed by Rajagopal *et al.*,[20] so that a correct analysis of experimental data must take them into account.

No analytical theory is at present available in order to calculate explicitly $g(\vec{r}_1,\vec{r}_2)$; however, several approximate approaches have been applied rather successfully to the electron gas.[21,22] In the case of nonhomogeneous extended systems the only approach available, other than the Hartree-Fock approximation, is the slowly varying density (SVD) approximation. Using the same argument employed by Sham and Kohn[11] when studying the self-energy kernel, we can write

$$\begin{aligned} &g(\vec{r}_1,\vec{r}_2)\simeq g_h[\,|\vec{r}_1-\vec{r}_2|;n(\vec{r}_0)]\ , \\ &\vec{r}_0=\tfrac{1}{2}(\vec{r}_1+\vec{r}_2)\ , \end{aligned} \tag{18}$$

where $g_h(r;n)$ is the correlation function of the homogeneous electron gas with density n. Then Eq. (17) becomes

$$f(\vec{x})-p(\vec{x})=\int n(\vec{r})n(\vec{r}+\vec{x})\{g_h[x;n(\vec{r}+\vec{x}/2)]\}d\vec{r}\ . \tag{19}$$

Since Eq. (19) is based on the short-range character of $g_h(x)-1$ within the same approximation, we have

$$f(\vec{x})-p(\vec{x})\simeq 4\pi N\int_{\Omega_0}[n(r)]^2\{g_h[x;n(\vec{r})]-1\}r^2dr\ , \tag{20}$$

assuming a spherically symmetrical electron density within each atomic sphere Ω_0. From Eq. (20) it is easily seen that

$$ZS_{ee}(Q)\simeq 4\pi\int_{\Omega_0}n(r)S_h[Q;n(r)]r^2dr\ , \tag{21}$$

where $S_h(Q;n)$ refers to the homogeneous electron gas of density n.

As discussed in the Introduction the study of simple metals can be used for the purpose of obtaining information on the electron gas. Keeping this in mind, we can try to separate the conduction-electron and the core-electron contributions. Obviously this separation is an approximation, inasmuch as there is no clear-cut distinction between core and conduction electrons. Such a distinction has validity within the Hartree-Fock approximation since in this case the various single-particle orbitals retain physical meaning. Using this approach, we can write[18]

$$ZS_{ee}(\vec{Q})=Z_cS_{\mathrm{core}}(\vec{Q})+Z_bS_{\mathrm{band}}(\vec{Q})+S_{\mathrm{int}}(\vec{Q})\ , \qquad (22)$$

where $S_{\mathrm{core}}(\vec{Q})$, $S_{\mathrm{band}}(\vec{Q})$, and $S_{\mathrm{int}}(\vec{Q})$ are the contributions from core electrons, conduction electrons, and interference effects. In this connection a useful property of $S_{\mathrm{band}}(\vec{Q})$ which can be used to test the validity of the separation procedure is related to the behavior of $S_{\mathrm{band}}(\vec{Q})$ in the neighborhood of $Q=0$. One has[4,9] that

$$S_{\mathrm{band}}(\vec{Q})=\frac{\hbar}{2m}\frac{Q^2}{\omega_p}+O(Q^3)\ , \qquad (23)$$

where ω_p is the classical plasma frequency. Since the Hartree-Fock approximation is expected to be rather good for the high-density core electrons,[4,12] $S_{\mathrm{core}}(\vec{Q})$ can be easily calculated from the free-ion wave functions, while $S_{\mathrm{int}}(\vec{Q})$ can be determined using the approach described in Ref. 18, i.e., employing the Waller-Hartree treatment using orthogonalized plane waves (OPW) for the conduction-electron states. The use of this approach for $S_{\mathrm{int}}(\vec{Q})$ is justified by its simplicity and by the fact that $S_{\mathrm{int}}(\vec{Q})$ is $\lesssim 1\%$ of $S_{ee}(\vec{Q})$.

Observing that the conduction-electron density is almost constant in a simple metal, it is possible to deduce the two-body correlation function in real space $g(r)$ from the "experimental" $S_{\mathrm{band}}(Q)$, by means of Eq. (17):

$$g(r)=1+\frac{1}{2\pi^2 nr}\int_0^\infty [S_{\mathrm{band}}(Q)-1]\sin(Qr)Q\,dQ\ . \qquad (24)$$

In practice, however, one has that because of the form of Eq. (24) a very accurate knowledge of $S_{\mathrm{band}}(Q)$ in the high-Q region is necessary in order to deduce a reasonably accurate $g(r)$ for small r, that is for $rk_F \lesssim 1$. A striking example of this difficulty has been offered by Singh and Pathak[23] who have compared their $g(r)$'s, calculated for several values of r_s, with those obtained by Vashishta and Singwi.[24] Although the static structure factors were extremely similar in the two calculations, the resulting correlation functions were remarkably different in the region $rk_F \lesssim 1$, when the static structure factors started to show systematic differences of order 1% in the high-Q region. In this connection it is important to remark that no guidance in order to deduce the shape of $g(r)$ for small r can be gained from the assumption that $g(0)=0$, as this assumption has been shown to be false for charged Fermi liquids at metallic densities.[21] However, as mentioned above, it has been established that $g(r)$ has a number of properties which for an electron-gas result in a "model" formula depending on only two parameters[20] currently interpreted as a measure of the size of the correlation in the parallel and antiparallel spin case, respectively.[25] An attempt to deduce $g(r)$ from the experimental data by means of this formula will be presented in the discussion of results.

III. EXPERIMENT AND RESULTS

The Be single crystal was a 2.4-mm-thick slab with the extended face parallel to a (110) plane. The experiment was performed along two directions in reciprocal lattice such that no Bragg scattering would occur. The bulk of measurements was performed with the scattering vector in the hexagonal plane at an angle of ~7° to the [100] reciprocal-lattice vector. With the use of monochromatic Co$K\alpha$ and Ag$K\alpha$ radiation, data were obtained covering the Q region [$Q=4\pi(\sin\theta)/\lambda$] from 0.7 to 22 $\mathrm{\AA}^{-1}$. In order to have a good resolution while maintaining a sufficient intensity, a Soller slit about 7 mm wide and having 0.25° resolution was placed in front of a NaI scintillation detector whose change of efficiency due to Compton energy loss in the sample was found to be negligible at all angles. A check of the geometrical correction accounting for sample absorption and irradiated volume was performed by collecting data along the same direction with the crystal set in transmission and in reflection. A comparison of the two measurements allowed one also to select, for each crystal setting, the angular range for which the cross section of the scattered beam was definitely smaller than the Soller-slit width. This condition was not fulfilled only in a small region at very high angle in transmission and very low angle in reflection. Transmission measurements with Ag$K\alpha$ were also performed along a direction forming an angle of ~7° with the [001] reciprocal-lattice vector in order to detect the presence of measurable anisotropy in the static structure factor. In all cases an incident beam was used having a cross section of $\sim 1\times 8$ mm^2 at the sample surface and 0.3° divergence. Beam stability was checked after all runs. Small corrections due to this factor were performed on a few Co$K\alpha$ runs. Enough counts were accumulated to make statistical errors absolutely negligible with respect to other sources of uncertainty. The background was measured several times for each wavelength and type of scan. In order to allow for sample transparence, runs were made without the sample and with a lead foil having the same shape of the crystal. Standard formulas for geometrical effects in unsymmetrical transmission and reflection were used. In order to account for x-ray polarization, the polarization ratio of our pyrolitic graphite monochromator was measured for both radiations using a direct method similar to that described by Le Page *et al.*[26] The measured ratios were 1.000(2) and 0.914(4) for Ag$K\alpha$ and Co$K\alpha$, respectively. The data obtained in the hexagonal plane with Ag$K\alpha$ and corrected for geometry and polarization are shown in Fig. 1.

Multiple scattering was allowed for by introducing a polarization-dependent angular factor in the usual quasi-isotropic approximation developed for neutrons.[27] This factor could be calculated exactly in the case of an infinitely thin slab, which, considering the shape of our crystal, was considered a reasonable approximation. The multiple scattering coefficient derived for neutrons and appropriate to our sample thickness and geometry was then multiplied by this factor. Multiple scattering correction ranged for Ag$K\alpha$ from 8% to 12% and for Co$K\alpha$ from 2% to 3%.

The one-phonon component of TDS along the chosen experimental directions was calculated in the usual harmonic approximation from the dynamical matrix derived by De Wames *et al.*[28] for Be from experimental data and

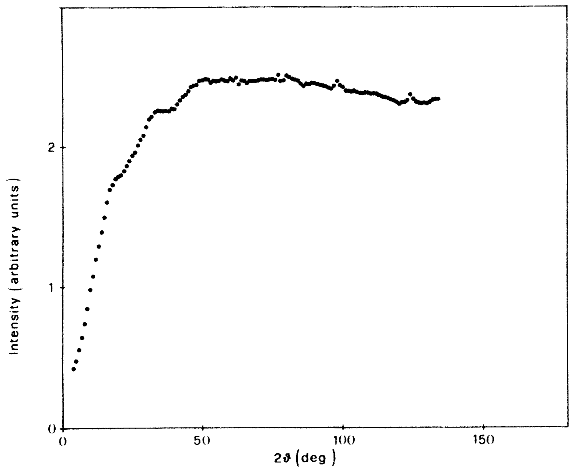

FIG. 1. Incoherent intensity scattered in transmission along the ⟨100⟩ direction from a Be single crystal is shown in arbitrary units. The data have been corrected for absorption, irradiated volume, and polarization.

using for the atomic form factor the values published by Benesch and Smith.[29] The higher-order components of TDS were obtained from the static approximation[19] which, because of the quasielastic nature of TDS, is particularly appropriate in the case of x rays. The total TDS contribution was, on average, 6% of the measured cross section with a peak value about twice as large in the regions of minimum distance from reciprocal-lattice points. The total inelastic cross section measured with Ag radiation was then normalized in the region of $Q \sim 20$ Å^{-1} to the sum of the incoherent atomic cross section (given in Ref. 29) multiplied by the factor $d_f K/K_0$ appearing in Eq. (1) and the calculated total TDS contribution. Upon subtraction of the TDS component and division by the factor $d_f K/K_0$, the normalized static structure factor for electron correlations (ZS_{ee}) was obtained for each direction. The results for the direction in the hexagonal plane obtained combining Co and Ag results are shown in Fig. 2 and listed in Table I. On the basis of the uncertainties in the corrections performed on the raw data, the resulting structure factors were estimated to be accurate to within a few percent.

In order to evidence the presence of anisotropy an agreement factor R for the structure factors measured along different directions was calculated:

$$R = \frac{1}{N} \sum_i \frac{|S_1(i) - S_2(i)|}{[S_1(i) S_2(i)]^{1/2}} .$$

[N indicates the number of points on the Q scale, and $S_1(i)$ and $S_2(i)$ the values of the structure factors in the two directions at the ith value of Q.] The value obtained for R (0.03) turned out to be of the order of the estimated uncertainties in each structure factor determination.

IV. DISCUSSION

Examination of Fig. 2 shows, particularly in the low-Q region, some dips and bumps in the present measurement which arise from structure in the TDS correction not exactly matched by the corresponding raw data. These irregularities give an idea of the maximum error introduced by the TDS correction. Similar features are of course present also in the data taken along the vertical axis of the crystal and are responsible for a large fraction of the difference between the two measurements. One can conclude that within experimental accuracy, no anisotropy in the structure factor has been detected and that the estimated error of $\sim 0.1e$ arising from systematic factors is reasonable. Shown in Fig. 2 are other curves obtained

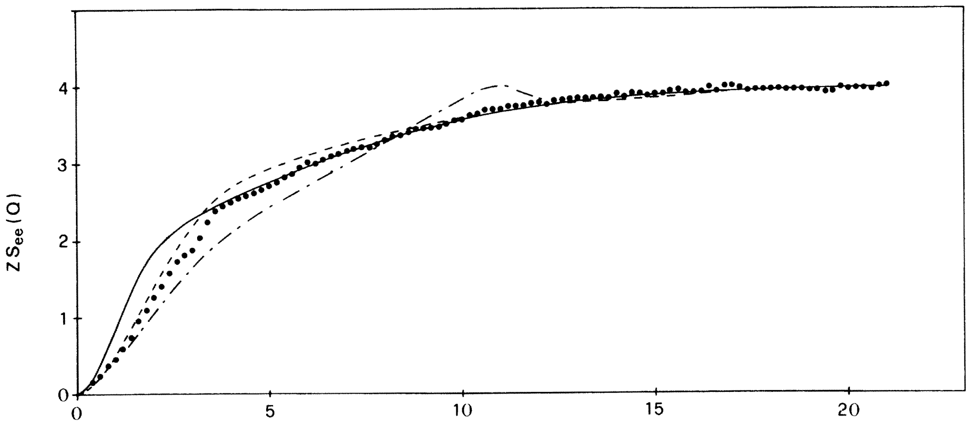

FIG. 2. Normalized static structure factor for electrons (ZS_{ee}) along the ⟨100⟩ direction of a Be single crystal (closed circles). Also shown is the free-atom calculation of Ref. 29 (solid line), the result of a SVD calculation as explained in the text (dashed line), and the measured structure factor of Ref. 15 (dashed-dotted line).

TABLE I. Experimental static structure factor for electrons (ZS_{ee}).

Q	S_{ee}	Q	S_{ee}
0.4	0.16	11.0	3.70
0.6	0.23	11.2	3.76
0.8	0.37	11.4	3.76
1.0	0.45	11.6	3.75
1.2	0.59	11.8	3.78
1.4	0.75	12.0	3.80
1.6	0.94	12.2	3.77
1.8	1.08	12.4	3.82
2.0	1.27	12.6	3.83
2.2	1.42	12.8	3.84
2.4	1.58	13.0	3.85
2.6	1.72	13.2	3.84
2.8	1.82	13.4	3.84
3.0	1.89	13.6	3.85
3.2	2.05	13.8	3.83
3.4	2.25	14.0	3.92
3.6	2.40	14.2	3.87
3.8	2.47	14.4	3.92
4.0	2.49	14.6	3.90
4.2	2.53	14.8	3.89
4.4	2.58	15.0	3.90
4.6	2.62	15.2	3.92
4.8	2.67	15.4	3.95
5.0	2.69	15.6	3.95
5.2	2.77	15.8	3.93
5.4	2.83	16.0	3.92
5.6	2.87	16.2	3.93
5.8	2.96	16.4	3.98
6.0	3.02	16.6	3.94
6.2	3.02	16.8	4.02
6.4	3.07	17.0	4.02
6.6	3.10	17.2	3.97
6.8	3.13	17.4	3.92
7.0	3.18	17.6	3.94
7.2	3.20	17.8	3.95
7.4	3.22	18.0	3.95
7.6	3.20	18.2	3.97
7.8	3.26	18.4	3.95
8.0	3.30	18.6	3.96
8.2	3.35	18.8	3.94
8.4	3.37	19.0	3.91
8.6	3.42	19.2	3.93
8.8	3.45	19.4	3.90
9.0	3.46	19.6	3.91
9.2	3.46	19.8	3.98
9.4	3.45	20.0	3.96
9.6	3.50	20.2	3.97
9.8	3.55	20.4	3.96
10.0	3.54	20.6	3.95
10.2	3.63	20.8	3.96
10.4	3.66	21.0	4.00
10.6	3.70	21.2	4.02
10.8	3.72	21.4	4.09

from experiment and calculations. Relative to the free-atom calculation of Ref. 29 present experiment shows extremely good agreement for $Q \gtrsim 4$ Å^{-1}. This result is not unexpected since beyond this value all deviations from the asymptotic value of $S(Q)$ arise essentially from core electrons which, in a recent calculation by Dovesi *et al.*[30] have been shown to exhibit small charge-density differences of 1% between solid and free atom. The simplistic procedure of data reduction adopted in the polycrystal experiment is reflected in the differences with the present, more accurate study. In addition, in a polycrystal experiment, the subtraction of Bragg scattering may lead to serious errors particularly in those regions where Bragg peaks are not well resolved. We believe that the bump in the polycrystal experiment at $Q \sim 10$ Å^{-1} might be due to this cause. Last, we remark that the area under the two experimental structure factor curves is nearly the same. This coincidence, probably accidental, has a direct bearing upon electron-gas correlation energy as detailed below. Also shown in Fig. 2 is the structure factor calculated in the SVD approximation from the charge density obtained by Moruzzi *et al.*[31] for fcc beryllium from a first-principles calculation. Considering the importance of the SVD approach for determining one-electron potentials in band calculations, its capability to reproduce present results to a good approximation is certainly remarkable.

It has already been pointed out[32] that in the formalism of Kohn and Sham,[10] using the virial theorem, it is possible to write the ground-state energy of an electron system in terms of measurable x-ray quantities. It is also possible to avoid the approximations introduced by Weiss and Mazzone[33] and account exactly for the exchange and correlation energy of the system by means of $S(Q)$.[34] Performing such calculations on Be one has that the contribution to the total energy (~ 400 eV/atom) computed from $S(Q)$ is ~ 90 eV/atom and that the exchange and correlation contribution to cohesive energy is 3.8 eV/atom. The nucleus-electron and electron-electron terms, calculated from the experimental structure factors of Larsen,[35] contribute to the cohesive energy another 0.7 eV/atom. These values should be compared with the experimental (~ 3.3 eV/atom) cohesive energy. Considering that present (4.5 eV/atom) cohesive energy is obtained from the difference of free-atom[29] and solid total energies, one has that experimental scattering cross sections for Be have to be regarded as very accurate, at least at the present state of the art. Moreover, since a large fraction of the cohesive energy arises from exchange and correlation effects in conduction electrons, accurate $S(Q)$ curves are necessary to this purpose, at least for low-Z elements.

As explained in the theoretical introduction it is possible to separate the structure factor in core and conduction-electron contributions plus a small interference term. The core contribution has been obtained from the configuration-interaction calculations of Thakkar and Smith[36] exploiting the close similarity of crystal and free-atom core electrons, while the interference term, which is less than 1% of the conduction-electron structure factor, has been obtained using orthogonalized plane wave (OPW) functions for the conduction-electron states and Herman and Skillman[37] wave functions for core electrons. The $S_{\text{band}}(Q)$ obtained with this procedure is shown in Fig. 3. The asymptotic value is reached for $Q \sim 2k_F$ in agreement, within the errors, with all electron-gas theories. For smaller values of Q the experimental curve deviates from Hartree-Fock approximation, also shown in Fig. 3, and is in close agreement, except perhaps at very small values of Q, with the Singh and Pathak[23] curve which is representa-

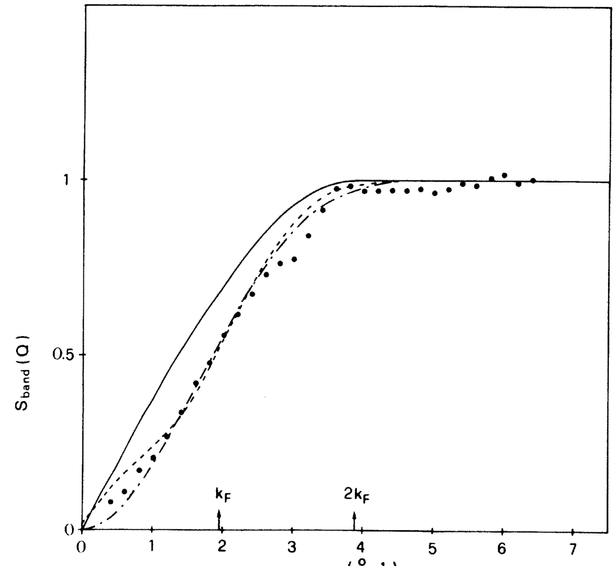

FIG. 3. Experimental band-electron static structure factor for Be (closed circles). Also shown are Hartree-Fock (solid line) and Singh and Pathak (dashed-dotted line) calculations for electron gas. The dashed line refers to a "model" $S_{band}(Q)$ obtained from Rajagopal pair-correlation function (see text).

tive of modern electron-gas theory.

Assuming that present $S_{band}(Q)$ is sufficiently representative of the jellium structure factor, the calculation of the jellium correlation energy, proportional to the integral of $S_{band}(Q)-1$, can be performed along the same lines followed in Ref. 15 for the results of the polycrystal experiment. Since the integral of $S_{band}(Q)-1$ is practically the same in the two experiments, the numerical values obtained from the polycrystal apply also to the present case. The main result is that the correlation energy deduced from a combination of the exact high-density treatment[3] and present experiment is, at metallic densities, only a few tenths of an eV higher than that calculated from the interpolation formula of Hedin and Lundqvist.[38]

As mentioned in the theoretical introduction Rajagopal *et al.*[23] have developed a "model" for the electron-gas pair-correlation function which obeys a number of constraints arising from the solution of the many-electron Schrödinger equation when a pair of electrons is allowed to come close while keeping the others fixed. In order to fix the value of the two parameters appearing in the model pair-correlation function we have chosen to calculate from this function a model $S(Q)$ and select the values of the parameters which give the best agreement between experimental and model $S(Q)$ curves. Because of the nature of the constraints the resulting model $S(Q)$ is not expected to be very accurate at low-Q values corresponding to large electron-electron separation. Comparison with the Singh and Pathak[23] curve reported in Fig. 3 shows that this is indeed the case and that, for $Q \gtrsim 1$ Å^{-1}, the model $S(Q)$ is very accurate and coinciding with experiment within estimated errors.

Starting from $S_{band}(Q)$ a well-known inversion procedure allows the calculation of an experimental pair-correlation function which can be compared with the same function calculated for the homogeneous electron gas. Two pair-correlation functions obtained from $S_{band}(Q)$ are shown in Fig. 4 together with the Hartree-Fock curve and a calculation by Zabolitzky[21] which has been obtained directly from a Bijl-Dingle-Jastrow function and therefore is not affected by the errors arising from an inversion of $S(Q)$ as confirmed by the fact that Zabolitzky's curve is practically indistinguishable from the pair-correlation function obtained directly from a Monte Carlo calculation.[22] In order to avoid numerical difficulties in the inversion of $S_{band}(Q)$, a polynomial fit has been used for the experimental data up to 4 Å^{-1}, while from that point on, $S_{band}(Q)$ was considered to have reached its asymptotic value since no physical meaning can be attached to fluc-

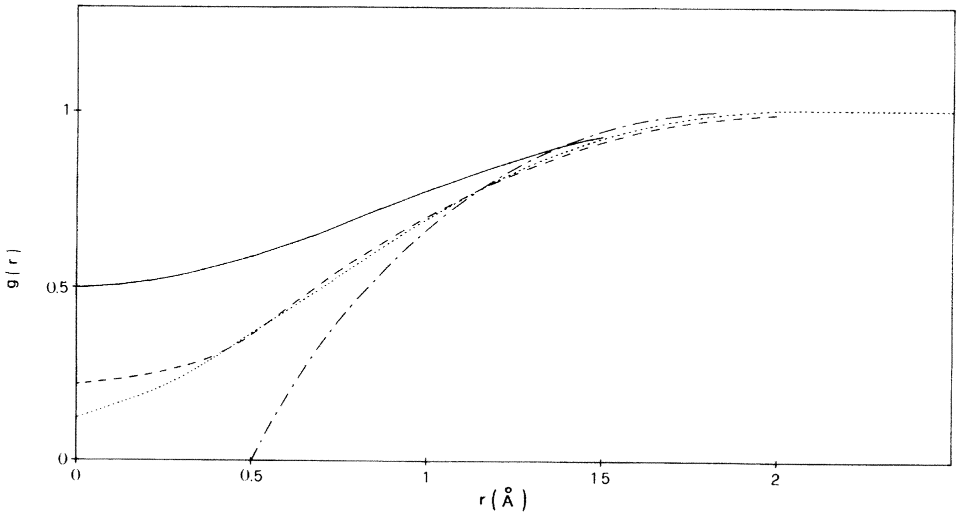

FIG. 4. Experimental $g(r)$ for conduction electron from a polynomial fit to $S_{band}(Q)$ (dashed-dotted line) together with Hartree-Fock (solid line), Zabolitzky (dashed line), and experimental Rajagopal-type $g(r)$'s (dotted line).

tuations at large-Q values. Of course, this procedure amounts to losing most of the information relative to $r \leq r_m \sim 2\pi/4$ Å. It is interesting to note that for $r \gtrsim r_m$ the experimental $g(r)$ is in good agreement with Zabolitzky's curve which in most of this region is also very similar to the Hartree-Fock approximation. Actually the experimental $g(r)$ is such that with the exception of the region around $r \sim 1$ Å, where it favors Zabolitzky's calculation, it nearly coincides with both curves. In other words we have that in the region where the experimental $g(r)$ is significant it shows the only behavior compatible with theoretical calculations. In view of the fact that this result has been obtained from experimental data without any assumption, we have that all physical information which can be extracted from that part of S_{band} which differs appreciably from its asymptotic value are inherently sound. This statement is in line with the fact that ground-state energy calculations based on the integral of $S(Q)-1$ have turned out to be very accurate. In order to have an experimental $g(r)$ accurate for all r's, an experiment has to be performed capable of measuring $S_{\text{band}}(Q)$ up to very-high-Q values to an accuracy better than, say, 1%. In view of the problems posed by the data-reduction procedure and the necessity of extracting $S_{\text{band}}(Q)$ from the total $S_{ee}(Q)$, to perform such an experiment seems, at the moment, a very difficult task. This problem may be circumvented by combining experimental and theoretical results. To this purpose we have used Rajagopal's[20] theory for $g(r)$, having fixed the value of the two free parameters with the help of present $S_{\text{band}}(Q)$, as explained above. The resulting pair-correlation function is shown in Fig. 4. We believe that, at the present experimental state of the art, this is probably the best procedure to obtain an accurate experimental $g(r)$ without any *ad hoc* assumptions. It is remarkable that this pair-correlation function is in very good agreement with Zabolitzky's calculation except at very-small-r values. In this region, however, Zabolitzky's curve does not satisfy the condition derived by Rajagopal *et al.*[20] stating that, for electrons having opposite spins, in the limit of r going to zero, $g(r)=g'(r)$, in atomic units. In summary, one has that the agreement between present experimental results for conduction electrons in Be and the corresponding theoretical predictions for uniform electron gas is very good.

The present pair-correlation function, on the other hand, is in sharp contrast with that derived for Be by Eisenberger *et al.*[14] from a conceptually similar experiment. Indeed, in the $g(r)$ of Ref. 14 a well-developed peak at $r \sim 0.3$ Å appears. In order to understand the nature of this peak we have inverted $S_{\text{band}}(Q)$ reported in Ref. 14 without extending analytically the data to $Q \rightarrow \infty$ but setting $S_{\text{band}}(Q)=1$ for $Q \geq 8$ Å^{-1}, as shown by the experiment. With this procedure we have been unable to obtain from the data of Ref. 14 a pair-correlation function having a peak at small r. It appears therefore that since the structure factor employed for the inversion by Eisenberger *et al.* was allowed "to approach unity with the asymptotic random-phase approximation (RPA) form such that $g(0)$ was equal to zero" the peak appearing in Ref. 14 is a result of this assumption. This conclusion is in line with current practice in liquid-structure determination where it is recommended to go beyond Q values of the order of 10 Å^{-1} if structures in direct space with size 1–3 Å have to be determined.[39] The extreme sensitivity of the small-r part of the pair-correlation function to changes in the structure factor is also clearly illustrated by Kaplow *et al.*[40] in a study of the influence on $g(r)$ of small systematic errors in the high-Q part of $S(Q)$.

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