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Structure factor and effective two-body potential for liquid gallium

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The structure factor of gallium has been measured by neutron scattering at temperatures 326 and 959 K and densities 0.0525 and 0.0490 at./Å^3 (6.08 and 5.674 g/cm^3). The domain of measured wave vectors ranges from 0.26 to 16.2 Å^{-1}. The precision of the experiments allowed us the determination of an effective pair potential between the gallium atoms at these two thermodynamic states.

I. INTRODUCTION

Neutron and x-ray diffraction experiments[1-5] in the temperature range 200–1300 K have shown that the structure factor of liquid gallium has a very small value at low wave vectors and that the main peak is dissymmetric. These features, common to other liquid metals (germanium, bismuth, etc.), are particularly pronounced in the case of gallium.

Although several studies were devoted to the theoretical interpretation of the structure factor of this liquid metal in terms of an effective pair interaction,[6,7] up to now no quantitative agreement could be obtained between the theoretical and experimental structure factors. However, this work gave evidence for the necessity of disposing of experimental values of the structure factor over a large domain of wave vectors. Indeed, wave vectors smaller than 2 Å^{-1} are essential for a correct estimate of the repulsive part of the effective interaction at short distance while large wave vectors are necessary to obtain a precise evaluation of the first peak of the pair correlation function between gallium atoms, or, equivalently, of the localization and number of atoms inside the nearest-neighbor shell of a given atom. Then, the limitations on the wave-vector spacing and range of the published neutron-diffraction results seemed to render the determination of an effective pair interaction in liquid gallium difficult. For these reasons, we performed new measurements using the spectrometer available at the Institut Laue–Langevin, Grenoble, which enables to cover the wave-vector range 0.2–16 Å^{-1} with an excellent precision. These new measurements allowed us, by use of an inversion procedure, to determine an effective pair interaction in gallium at ~300 and ~950 K independent of any theoretical assumption on the electron-ion interaction, screening effects, etc.

The paper is organized as follows. In Sec. II we describe the experimental measurements and the various corrections which have been applied to obtain the structure factor from the raw experimental data. In Sec. III an effective pair potential is calculated by inversion of the structure factor. The limitations of the inversion procedure which relies on the use of numerical simulations, are discussed in detail. Section IV includes comparison of the present measurements with previously published results at nearby thermodynamic states. The main results of this work are finally summarized in a brief conclusion.

II. EXPERIMENTS AND DATA CORRECTIONS

The neutron-diffraction experiments were performed on the D4B diffractometer at the Institut Laue–Langevin (Grenoble, France).[8] The sample, sealed under vacuum in a cylindrical quartz cell, was 99.9999% pure gallium. The cell had inner and outer diameters of 8.92 and 10.2 mm, respectively. The neutron beam was illuminating a 5-cm sample height as defined by B_4C slits placed a few centimeters before the sample and masking the sample top and bottom.

The temperature of the sample was regulated to ±0.3 K by a cylindrical foil vanadium furnace of thickness 0.1 mm and diameter 23 mm. The sample and the furnace were placed under vacuum in the standard D4B bell jar with thin aluminum windows.

The wavelength λ of the monochromatic neutron beam was 0.7041 Å which allowed us to reach a maximum k value of ~16 Å^{-1} [$k = 4\pi \sin(\theta)/\lambda$, 2θ diffraction angle]. The intensities were measured with two 64-cell, ^{3}He multidetectors. The first multidetector was placed at 1.50 m from the sample covering an angle of 6.4° (2θ) (64 increments of 0.1°), the second multidetector placed at 0.75 m from the sample was covering 12.8° (2θ) (64 increments of 0.2°). The efficiency of each multidetector cell was measured to an accuracy better than 0.1%. The two detectors were simultaneously counting the scattered neutrons during monitored periods of about 100 sec and displaced, respectively, in steps of 1.5° and 2° in order to cover the angular ranges 1.68° to 64.78° and 46.4° to

131.4°. The overlap between the two angular ranges was used to connect both sets of measurements.

The experiments were performed at temperatures 326 and 959 K. In order to correct the raw experimental data we recorded separately, at each temperature, the spectra for sample+container+furnace (N^{S+C+F}), container plus furnace (N^{C+F}) and furnace (N^{F}). In addition, the spectrum of a cadmium rod (having same dimensions as the sample) in the furnace ($N^{\mathrm{Cd}+F}$) was collected at room temperature. These spectra are reported in Figs. 1(a) and 1(b). Reproducibility of the data collection (which includes mechanical and chemical stability of the sample environment, temperature stability, and effective stability of the number of sample atoms in the beam as well as stability of the neutron data acquisition chain) was carefully checked by repeating several times (3 to 4) each spectrum. Reproducibility was always well within the statistical accuracy. A procedure for rejecting the few noisy detector cells was applied. In a first data treatment, the furnace spectrum was considered as the background for this experiment. At low angles this background contains the scattering due to air along the monochromatic beam and is modified by the presence of the sample. Appropriate corrections to reconstitute the background when the sample is present are made with the help of a pure absorber (cadmium) spectrum.

The container and sample self-absorption corrections were made as usual, following Paalman and Pings.[9] Alternatively, we have also made the sample, cell, and furnace corrections following a generalized Paalman and Pings procedure,[10(a)] with again an additional correction for sample transmission-dependent background. The two correction routes were carefully compared[10(b)] especially at the low angles. The agreement was quite satisfactory, the difference never exceeding twice the average statistical standard deviation on a data point. Moreover, we verified that plausible errors in the sample or container

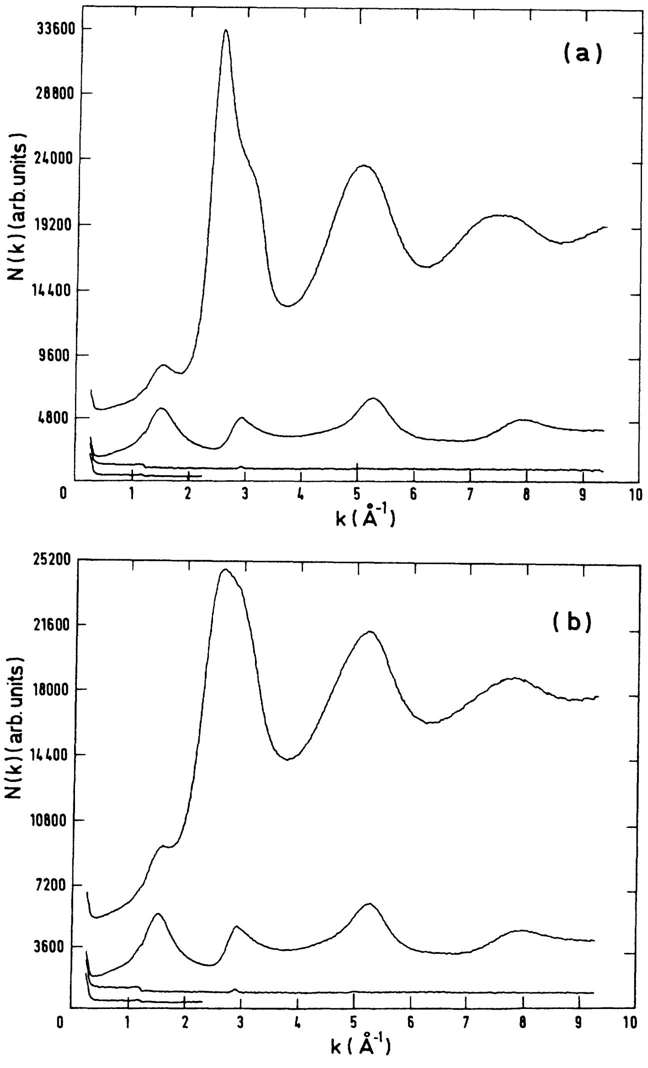

FIG. 1. (a) Experimental spectra at 326 K. From top to bottom N^{S+C+F},N^{C+F},N^{F} and $N^{\mathrm{Cd}+F}$ (arbitrary units). (b) Same as Fig. 1(a) but for 959 K.

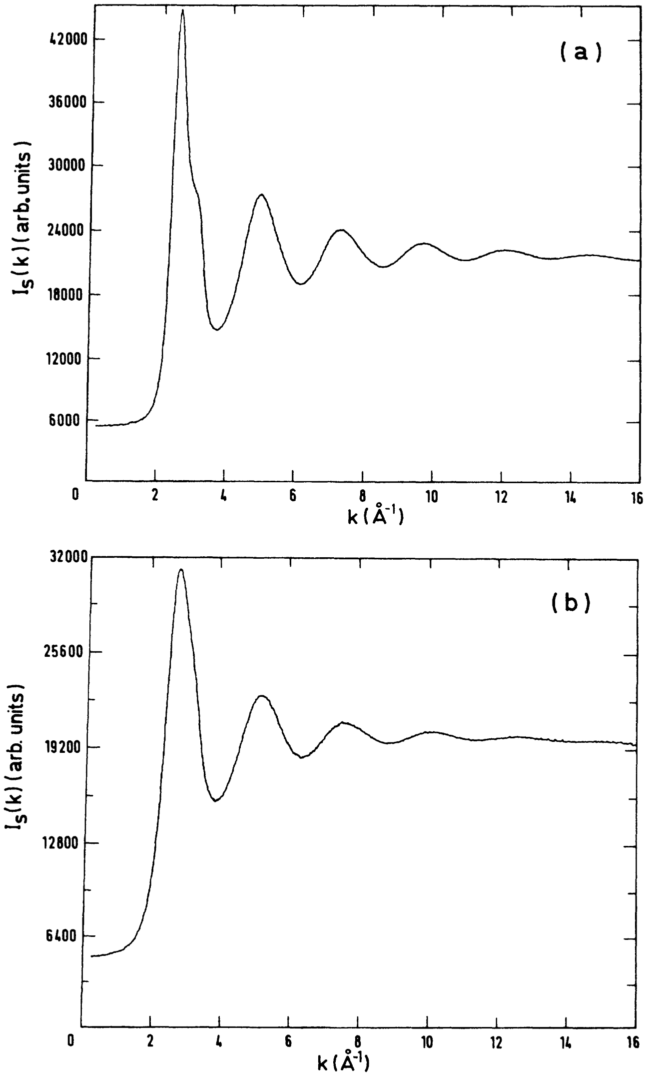

FIG. 2. (a) Experimental spectrum at 326 K corrected for background scattering and self-absorption (arbitrary units). (b) Same as Fig. 2(a) but for 959 K.

diameters or total scattering cross sections never exceeded twice the statistical error. The corrected intensities $I^S(2\theta)$ are given in Figs. 2(a) and 2(b).

Inelasticity (or Placzek) correction[11] has been evaluated following a method developed by Yarnell *et al.*,[12]

$$I(2\theta)=I^S(2\theta)-I^S(2\theta_M)\frac{A-4B\sin^2\theta}{1+A-4B\sin^2\theta_M}\ , \qquad (2.1)$$

where A and B are constants depending on the detector efficiency and the mass and temperature of the sample (cf. Table I); $2\theta_M$ is a value of the diffraction angle for which $I(2\theta)$ is expected to be equal to its asymptotic large wave-vector limit.

The inelasticity correction on the self-scattering term is well established for monatomic heavy elements, it is smoothly angular dependent; the ratio $[I^S(2\theta)-I(2\theta)]/I^S(2\theta_M)$ varies from about 0.008 at $2\theta=50°$ to 0.04 at $2\theta=120°$. Errors on the angular dependence of this correction are inferior to 0.001. However, we have fully neglected possible inelasticity correction on the coherent scattering part of the spectrum.

Two further corrections are required, those for multiple scattering (quasi-isotropic) and incoherent scattering (isotropic). The multiple-scattering correction can be estimated by the method of Blech and Averbach[13] and amounts to 16.4% of the average intensity level. On the contrary, the incoherent cross section σ_{inc} is not available with sufficient precision to estimate the latter correction.[14] In fact, most of the existing values for σ_{inc} (cf. Table II) except the one from Koester *et al.*[14] would lead to values of $S(k)$ incompatible at low k with the value of $S(0)$ deduced from compressibility measurements.

For this reason we did not attempt to determine the scattered intensity and $S(k)$ in an absolute manner using a vanadium standard for normalization. Instead, we used a self-normalization procedure in which the structure factor is determined from the relation,

$$S(k)=\frac{I(k)-X}{I(\infty)-X}\ . \qquad (2.2)$$

Here X denotes the (k-independent) correction from multiple and incoherent scattering.

The value of X is obtained by applying (2.2) for $k=0$, and identifying $S(0)$ with the isothermal compressibility of gallium[15] χ_T according to the relation

$$S(0)=\rho k_B T \chi_T \qquad (2.3)$$

(ρ density, k_B Boltzmann constant, T temperature).

In Eq. (2.2), $I(0)$ has been approximated by the extrapolation of $I(k)$ to zero k wave vector. Since the intensities are very weakly dependent on k at low k ($k<1$ Å^{-1}) and high k values, we estimate the error due to the self-normalization procedure to be about equal to the statistical error. The structure factor is given by Eq. (2.2). The results for 326 and 959 K are shown in Figs. 3(a) and 3(b) and tabulated in Ref. 16, Tables IIIa and IIIb.

TABLE I. Linear total absorption coefficients μ_T^c and μ_T^s for container and sample and parameters A and B of Eq. (2.1) for inelasticity correction.

T (K)	Density (atoms/Å^3)	μ_T^c (cm^{-1})	μ_T^s (cm^{-1})	A	B
326	0.0525	0.207	0.430	1.23×10^{-3}	0.0133
959	0.0490	0.207	0.402	3.62×10^{-3}	0.0142

TABLE II. Experimental values of coherent scattering length b, coherent scattering cross section σ_{coh}, and incoherent scattering cross section σ_{inc}.

b (10^{-12} cm)	σ_{coh} (barn)	σ_{inc} (barn)	$\sigma_{\mathrm{coh}}+\sigma_{\mathrm{inc}}$ (barn)	$\sigma_{\mathrm{inc}}/(\sigma_{\mathrm{coh}}+\sigma_{\mathrm{inc}})$	Ref.
0.725	6.61	0.09	6.7	0.0134	14(a)
0.729	6.678	0.392	7.07	0.0554	14(b)
0.7288	6.67	0.03	6.7	0.004 47	14(c)
0.72	6.51	0.99	7.5	0.133	14(d)
0.7288	6.675	0.47	7.145	0.0658	14(e)

From a spline fitting procedure we estimate that the average statistical error associated to each $S(k)$ data point [there are about 1000 experimental values in one $S(k)$] is equal to 0.002 (two standard deviations) for both temperatures. It is, of course, more difficult to assess the magnitude of the systematic errors. We have seen that

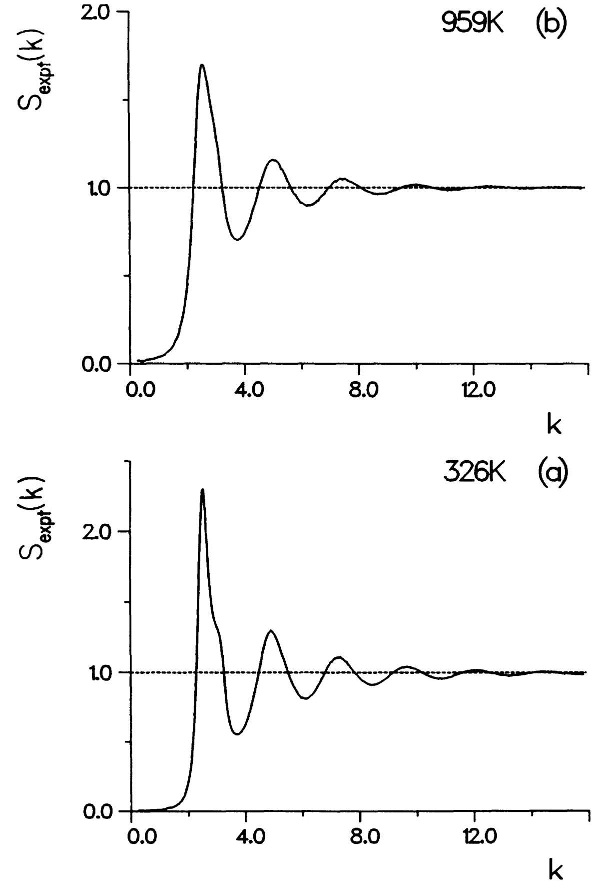

FIG. 3. (a) Structure factor $S_{\mathrm{expt}}(k)$ for liquid gallium at 326 K (density 0.0525 atoms/Å^3) measured in the range $k=0.26$–16 Å^{-1}. (b) Same as Fig. 3(a) but for 959 K (density 0.0490 atoms/Å^3).

each correction taken separately does not introduce errors greater than about twice the statistics. However, we have neglected possible cross terms (between container corrections and multiple scattering, or between multiple scattering and inelasticity, etc.) and we have assumed that to first approximation the results were independent of the order in which these corrections were performed. Several hypotheses were also introduced: the isotropicity of the multiple scattering, the neglect of coherent inelasticity corrections, and the neglect of neutron-electron interactions. Since self-normalization was introduced, all constant-level errors in the data have been eliminated.

Smoothly angular-dependent systematic errors are difficult to be traced and are probably the dominant ones. However, these errors will essentially produce oscillations at very low r values in the pair distribution function $g(r)$ and will be taken care of by the data analysis which forces $g(r)$ to be equal to zero at small r. We believe that for the present study the most severe problems would be those related to abrupt systematic errors over narrow angular ranges. Such an error has been found in the data around 0.8 Å^{-1} [see Fig. 2(a)] and comes from yet unmastered background correction problems. Since it is very localized it has been smoothed in the data treatment (cf. Sec. III).

III. THEORETICAL ANALYSIS

A. Determination of an effective two-body potential

The theoretical analysis of the experimental structure factors $S_{\text{expt}}(k)$ developed in this section is made within the framework of a simplified description of liquid metals considered as classical liquids of atoms interacting by an effective two-body potential. This potential takes into account the direct interaction between the ionized atoms of the metal and the screening effect of the conduction electrons. It can be calculated, in principle, by a quantum-mechanical theory of liquid metals but in practice its evaluation is difficult and necessitates numerous approximations.[17]

The effective potentials proposed in the literature depend on a dielectric function characteristic of the conduction electrons and on parameters introduced to describe in a simplified way the ion-electron interaction.[18] The appropriate choice of the dielectric function and the parameters is obtained from comparison of experimental properties, e.g., the structure factor, with those calculated by means of the effective potential.[7,19] This scheme for determining the effective potential $v_{\text{eff}}(r)$ by fitting the structure factor assumes that the analytical form of the theoretical potential is susceptible to approximate the real effective potential in a precise way and that the methods for calculating $S(k)$ from $v_{\text{eff}}(r)$ are reliable. These assumptions can lead to imprecisions on $v_{\text{eff}}(r)$ which were discussed in Ref. 20. In this work we attempt to determine $v_{\text{eff}}(r)$ by inversion of $S_{\text{expt}}(k)$. In order to do so we employ the method of Ref. 21, which we summarize briefly.

From the known $S_{\text{expt}}(k)$, the pair distribution function $g_{\text{expt}}(r)$ is calculated by Fourier transform (FT). The hypothesis of the existence of an effective potential allows us to write $g_{\text{expt}}(r)$ in the form[22]

$$g_{\text{expt}}(r)=\exp[-\beta v_{\text{eff}}(r)+h_{\text{expt}}(r)-c_{\text{expt}}(r)+B_{\text{expt}}(r)] , \tag{3.1}$$

where $h_{\text{expt}}(r)=g_{\text{expt}}(r)-1$. $c_{\text{expt}}(r)$, the direct correlation function, is given by

$$c_{\text{expt}}(r)=\frac{1}{(2\pi)^3\rho}\int[1-1/S_{\text{expt}}(k)]e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k} . \tag{3.2}$$

$B_{\text{expt}}(r)$ is the "bridge" function. The latter is not known. To obtain an estimate of $v_{\text{eff}}(r)$, one assumes that $B_{\text{expt}}(r)$ is approximately given by the bridge function $B_{\text{HS}}(r,\eta)$ of a hard-sphere system with packing fraction η, given by the Lado criterion[23]

$$\int[g_{\text{expt}}(r)-g_{\text{HS}}(r,\eta)]\frac{\partial B_{\text{HS}}(r,\eta)}{\partial\eta}d\mathbf{r}=0 . \tag{3.3}$$

With $B_{\text{expt}}(r)\sim B_{\text{HS}}(r,\eta)$, Eq. (3.1) is referred to as the modified hypernetted chain equation (MHNC) in analogy with the HNC equation in which the bridge function is neglected.

Thus an initial estimate $\varphi_0(r)$ of $\beta v_{\text{eff}}(r)$ is obtained from the relation

$$\varphi_0(r)=-\ln[g_{\text{expt}}(r)]+h_{\text{expt}}(r)-c_{\text{expt}}(r)+B_{\text{HS}}(r,\eta) . \tag{3.4}$$

By performing a numerical simulation on a system of atoms interacting by $\varphi_0(r)$ one determines the corresponding pair correlation function $g_0(r)$ and structure factor $S_0(k)$. From these two functions, a second estimate $\varphi_1(r)$ of $\beta v_{\text{eff}}(r)$ is calculated according to the formula

$$\varphi_i(r)=\varphi_{i-1}(r)+\ln[g_{i-1}(r)/g_{\text{expt}}(r)]+c_{i-1}(r)-h_{i-1}(r)-c_{\text{expt}}(r)+h_{\text{expt}}(r) , \tag{3.5}$$

written for the ith estimate of $\beta v_{\text{eff}}(r)$ obtained from numerical simulation with the interaction $\varphi_{i-1}(r)$. This iterative process converges and leads to the correct estimate of $\beta v_{\text{eff}}(r)$. This point has been demonstrated in Ref. 20 by inversion of $S(k)$ for model systems with known potentials.

To calculate $g_{\text{expt}}(r)$ by FT of $S_{\text{expt}}(k)$ [first step in the calculation of $\beta v_{\text{eff}}(r)$], the only use of the values of $S(k)$ effectively measured is not sufficient. Indeed, these values are limited to the range $0.26\le k\le 16$ Å^{-1} which is still too restricted to correctly estimating $g_{\text{expt}}(r)$ at small r. In the case of our experimental results, Figs. 4(a) and 4(b) show that, by FT, one obtains $g(r)$'s which oscillate around 0 for $r\le 2.3$ Å as a consequence of the limited domain of integration in k space. Thus, the functions $S_{\text{expt}}(k)$ need to be extrapolated at small and large k, in a way such that $g_{\text{expt}}(r)\sim 0$ for $r\le 2.3$ Å, corresponding to the domain of mutual exclusion of the atoms. These extrapolations and the calculations of $g_{\text{expt}}(r)$ have been performed by a procedure which is described in the Appendix and has been already used in Ref. 20. It appears in the process of the computation of $g_{\mathrm{expt}}(r)$, that $g_{\mathrm{expt}}(r)$ cannot be ~ 0 for $r < 2.3$ Å, only if $S_{\mathrm{expt}}(k)$ is modified in the domain of $1.8 < k < 3.2$ Å^{-1}. We call this modified $S_{\mathrm{expt}}(k)$, $S'_{\mathrm{expt}}(k)$. $S'_{\mathrm{expt}}(k)$ differs slightly from $S_{\mathrm{expt}}(k)$ in the range of the values of k corresponding to the position of the first peak in $S_{\mathrm{expt}}(k)$ (see Table IV in Ref. 16). For the two temperatures considered these differences are at most 0.035, i.e., of the order of 1.5% of the height of this peak. These modifications of $S_{\mathrm{expt}}(k)$ are unfortunately unavoidable if a physically acceptable $g_{\mathrm{expt}}(r)$ has to be obtained (in particular vanishing for $r < 2.3$ Å). They can be obviously due to the shortcomings of the procedure of computation of $g_{\mathrm{expt}}(r)$ [extrapolation of $S_{\mathrm{expt}}(k)$ at low and large k and iterative processes], but they can be also a consequence of systematic errors on $S_{\mathrm{expt}}(k)$ which would amount, for $k = 2$–3 Å^{-1}, to $\sim 1.5\%$, this giving an upper limit to the magnitude of the errors discussed in Sec. II.

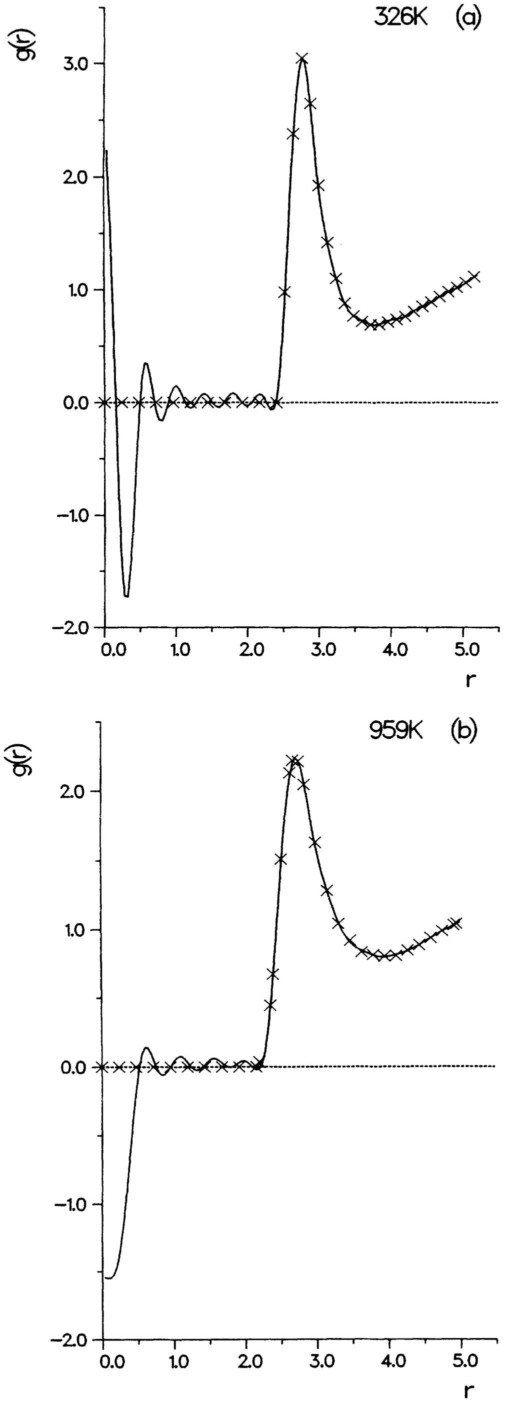

FIG. 4. (a) At 326 K, pair distribution function (solid line) computed by Fourier transform of $S_{\mathrm{expt}}(k)$ with integration limits 0.23 and 16 Å^{-1} and pair distribution function $g_{\mathrm{expt}}(r)$ (crosses) calculated by FT of $S'_{\mathrm{expt}}(k)$ with integration domain 0–64 Å^{-1} (see text). (b) Same as Fig. 4(a) but at 959 K.

These uncertainties on $S_{\mathrm{expt}}(k)$ induce an error on $g_{\mathrm{expt}}(r)$ which on the basis of a comparison between the Fourier transform of the raw $S_{\mathrm{expt}}(k)$ and $S'_{\mathrm{expt}}(k)$ can be estimated to be about ~ 0.5–1% for $r > 2.3$ Å [cf. Figs. 4(a) and 4(b)].

For the two temperatures of our measurements, $g_{\mathrm{expt}}(r)$ and $c_{\mathrm{expt}}(r)$ being known, Eq. (3.4) gives $\varphi_0(r)$. The error induced on $\varphi_0(r)$ resulting from the error on $g_{\mathrm{expt}}(r)$ can be estimated from the data presented in Sec. II of Ref. 20. In this article, for a model system of atoms interacting by a Lennard-Jones potential, the potentials $\varphi_0(r)$ computed from several $g(r)$'s obtained by numerical simulations were compared. For instance, a variation of ± 0.02 on $\varphi_0(r)$ was obtained from two $g(r)$'s calculated for the same thermodynamic state by two independent molecular-dynamics simulations of 16 800 integration steps and having a statistical error of $\sim 0.3\%$. From these previous results, an error of $\sim \pm 0.04$–0.07 can be expected on $\varphi_0(r)$ as a consequence of an error of 0.5–1% on $g_{\mathrm{expt}}(r)$. The potential $\varphi_0(r)$ is used to perform a simulation of a system of 1024 atoms by the Monte Carlo method. The simulations are done at densities 0.0525 and 0.0490 atoms/Å^3 corresponding to the experimental densities. The sides of the cubic simulation volumes (with periodic boundary conditions) are 26.9 and 27.5 Å, respectively.

The dimensions of these volumes lead to limit the range of the potential $\varphi_0(r)$ to $r_c = 11.6$ Å. Thus one has $\varphi_0(r) = 0$ for $r > r_c$ in the simulations. With this choice of cutoff of the potential, only the first oscillation is taken into account. For $r > r_c$, $|\varphi_0(r)|$ is smaller than 0.06 for 326 K and smaller than 0.02 for 959 K, which justifies the choice of the value used for r_c. This value is kept fixed for all simulations made with the potentials $\varphi_i(r)$, since $\varphi_i(r)$ cannot be known beyond the range of $\varphi_{i-1}(r)$ [cf. Eq. (3.5)].

The distribution functions $g_i(r)$ are also calculated for $r < r_c$. The direct correlation functions $c_i(r)$ and $S_i(k)$ are obtained from $g_i(r)$, extended for $r > r_c$ by means of the method exposed and tested in Ref. 20. This method amounts to solve the Ornstein-Zernike (OZ) equation,[22] relating $g(r)$ and $c(r)$ with the conditions

$$g(r) = g_i(r), \quad r < r_c \tag{3.6}$$

and $c(r)$ given by the HNC closure

$$c(r) = e^{-\varphi(r)+\gamma(r)} - 1 - \gamma(r), \quad r > r_c \tag{3.7}$$

where

$$\gamma(r)=g(r)-1-c(r)\ . \tag{3.8}$$

In our case, Eq. (3.8) reduces to

$$c(r)=e^{\gamma(r)}-1-\gamma(r)\ , \tag{3.9}$$

since

$$\varphi_i(r)=0 \quad \text{for } r>r_c\ .$$

In each simulation run 2.4×10^6 configurations where generated by the Monte Carlo method. The statistical error on $g_i(r)$ is of the order of 0.5–1 % and induces on $\varphi_i(r)$ an uncertainty of $\sim\pm0.06$ (cf. discussion above). Tables IV–VI in Ref. 16 present the structure factors $S_i(k)$, and the functions $g_i(r)$ and $\varphi_i(r)$ for 326 and 959 K, respectively. It is worthwhile to notice that $g_{\rm expt}(r)$ being compatible with $S'_{\rm expt}(k)$, it is expected that $S_i(k)$ converges to $S'_{\rm expt}(k)$ and not to $S_{\rm expt}(k)$.

B. Results

At 959 K five simulations have been performed starting with the potential $\varphi_0^h(r)$ (henceforth the superscript h will denote the high-temperature and l the low-temperature result). Table V in Ref. 16 shows that $g_0^h(r)$ is already an excellent approximation for $g_{\rm expt}^h(r)$. The most significant difference occurs in the amplitude of the oscillations beyond the first peak; in particular, the height of the second peak is overestimated. The subsequent iterations correct this defect of $g_0^h(r)$; after three or four iterations the differences between $g_i^h(r)$ and $g_{\rm expt}^h(r)$ become of the order of the uncertainties on $g_{\rm expt}^h(r)$ so that the iteration process has to be stopped after five iterations.

The functions $S_i^h(k)$ (cf. Table IV in Ref. 16) are also in good agreement with $S_{\rm expt}^h(k)$, the main differences concern the values of $S_i^h(0)$ and of the first peak of $S_i^h(k)$. In spite of the excellent agreement between $S_5^h(k)$ and $S_{\rm expt}^h(k)$ in the range $0.26\le k\le1.5$ Å^{-1}, $S_5^h(0)=0.027$ is considerably higher than $S'^h_{\rm expt}(0)=0.015$, and the height of the main peak of $S_5^h(k)$ exceeds that of $S'_{\rm expt}(k)$ by 0.01. The potentials $\varphi_i^h(r)$ converge to a potential which is oscillating with a small amplitude for $r>4$ Å and is strongly repulsive for $r<4$ Å.

At 326 K, $\varphi_0^l(r)$ gives by numerical simulation $g_0^l(r)$ very close to $g_{\rm expt}^l(r)$. After five iterations the functions $g_i^l(r)$ oscillate around $g_{\rm expt}^l(r)$ within the estimated errors and the convergence of the process cannot be improved by the further iterations. The functions $S_i^l(k)$ for $i\ge5$ are in excellent agreement with $S'^l_{\rm expt}(k)$ for $0.2<k<1.2$ Å^{-1}; as for the high temperature case the $k=0$ value of $S_9^l(k)$ (0.0058) exceeds that of $S'^l_{\rm expt}(0)$ (0.0050). The heights of the main peaks of $S_5^l(k)$ to $S_9^l(k)$ oscillate around a mean value 2.38 slightly higher than the height of the main peak in $S'^l_{\rm expt}(k)\sim2.36$ (cf. Table IV in Ref. 16 and Fig. 3). The position of the peak of $S_i^l(k)$ is shifted by 0.08 Å^{-1} to lower k values as compared to that of $S'^l_{\rm expt}(k)$. For $i\ge5$, the variations of $\varphi_i^l(r)$ are small, of the order of 1% for $r<6.5$ Å, there is a progressive enhancement of the positive part of the potential for $6.5<r<10$ Å, $\varphi_i^l(r)$ remains unchanged for $r>10$ Å. All these changes of $\varphi_i^l(r)$ result from those on $g_{i-1}^l(r)$: they are of little significance since for $i\ge5$, $g_i^l(r)$ coincides with $g_{\rm expt}^l(r)$ within the error bars estimated for this function.

At both temperatures excellent agreement between $g_i(r)$ and $g_{\rm expt}(r)$ was yielded for $r<r_c$. The convergence on $\varphi_i(r)$ was reached within the statistical errors estimated to be $\sim\pm0.04$–0.07 on the basis of a statistical uncertainty of 0.5–1 % on the $g_i(r)$ computed by simulation. This agreement was obtained with a potential $\varphi_i(r)$ equal to zero for $r>r_c$. This constraint must be taken into account in a complete interpretation of the results of our inversion procedure, in particular with regard to the differences which exist between $S_i(k)$ and $S'_{\rm expt}(k)$.

C. Discussion of the results

In order to estimate the influence of the cutoff in $\varphi_i(r)$ on our simulations results, we applied the MHNC approximation to a model system in which the atoms interact by a potential $v_a(r)$ with known analytical form. This approximation is sufficient to get an order of magnitude estimate of the variations induced on $g(r)$ and $S(k)$ by the cutoff of the potential.

The potential that we have chosen uses the empty core model of Ashcroft[18] for the ion-electron interaction and the local-density approximation for the dielectric function $\epsilon(k)$ of the conduction electrons. The latter corresponds thus to a local field[24] of the form $G(k)=b_0k^2/k_F^2$ where k_F is the Fermi moment of the electrons. In the expression of $\epsilon(k)$ the electron-sphere radius r_s and hence k_f, is considered as a parameter. By adjusting the set of parameters in $v_a(r)$ and using the MHNC approximation for calculating the structure factor, Aers *et al.*[25] succeeded in obtaining a representation of the experimental structure factor of germanium at $T=1253$ K and $\rho=0.0461$ atoms/Å^3. In particular, the potential $v_a(r)$ reproduces the shoulder which exists on the right side of the main peak of $S(k)$ at this temperature and thus seems well adapted for an analysis of $S_{\rm expt}(k)$ of gallium which shows the same characteristic.

The potential $v_a(r)$ is a function of four parameters: r_s, the radius R_0 and the depth A_0 of the empty core potential, and the constant b_0 of the local field. In the MHNC approximation the packing fraction η entering in the hard-sphere bridge function $B_{\rm HS}(r,\eta)$ is also an adjustable parameter. Using $v_a(r)$, only a qualitatively representation of $S_{\rm expt}(k)$ was possible for gallium. The best fit was obtained at 959 K and $\rho=0.049$ atoms/Å^3 for $r_s=1.1625$ Å, $R_0=0.4156$ Å, $A_0=0.1$ Å$^{-1}/e^2Z$, $b_0=0.210$, $\eta=0.3547$, and at 326 K $\rho=0.0525$ atoms/Å^3 for $r_s=1.575$ Å, $R_0=0.4329$ Å, $A_0=0$, $b_0=0.195$, and $\eta=0.4042$ (e electron charge, Z valence of gallium equal to 3).

When the OZ equation is solved with the MHNC closure and potential cutoffs at 40 or 11.6 Å, the only values of $S(k)$ which are modified are those in the vicinity of the main peak. The variations are of the order of 1–2 %. At 326 K the maximum of $S(k)$ is 2.40 with a cutoff of 40 Å and 2.44 with a cutoff of 11.6 Å and its position is shifted towards small k by 0.02 Å^{-1}, while at 959 K the values of the maximum are 1.80 and 1.81, respectively, and the shift of the peak position is negligible (~ 0.01 Å^{-1}).

In the extension procedure of $g_i(r), S_i(k)$ is obtained from the solution of the OZ equation with $\varphi_i(r)=0$ for $r>r_c$ and the conditions (3.6) and (3.9) as closure relations. As for the MHNC equation the cutoff is taken into account by Eq. (3.9) and its effect on $S_i(k)$ can only be similar.

Then, the difference between the height and the position of the main peak between $S'_{\rm expt}(k)$ and $S_i(k)$ $(i>3)$ can be interpreted as essentially due to the cutoff introduced in the numerical simulations. Both in the case of the calculation of $S(k)$ with a cutoff for the potential $v_a(r)$ and in the case of the computation of $S_i(k)$, the variation of the height of the main peak is 0.02–0.04 and the shift of the position of this peak is towards low k. At 329 K, the shift (~ 0.08 Å^{-1}) is more pronounced than the shift resulting of the cutoff of $v_a(r)$. But this seems a consequence of an amplitude of the oscillation in $v_i(r)$ larger than in $v_a(r)$ for $r>4$ Å; indeed the shift is larger at 329 K than 959 K temperature where the effect of the long-range part of the potential becomes weak.

As the effect of the cutoff on $S(k)$ is very localized near the main peak, the effect on $g(r)$ is distributed on a large domain of r. For a given value of r between 2.3 and 11.6 Å, it is smaller than 0.001 as it is established in solving the OZ equation with the MHNC closure for the potential $v_a(r)$.

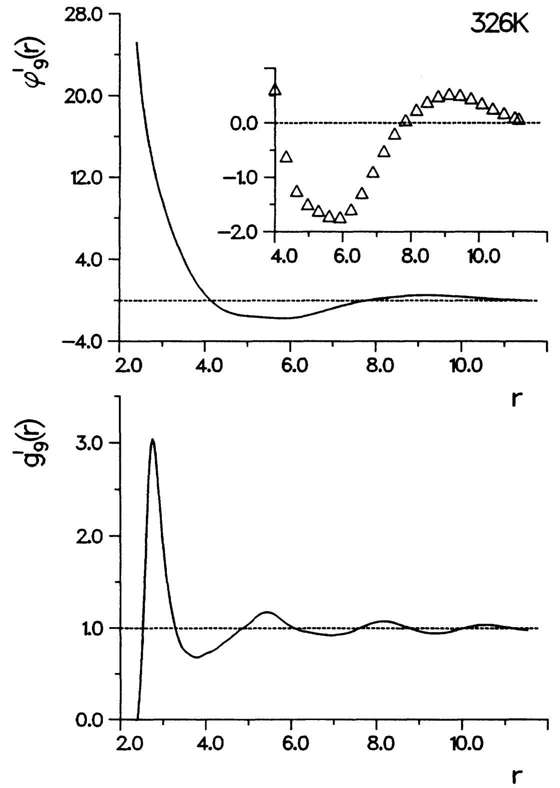

FIG. 5. Pair distribution function $g_9^l(r)$ and interaction $\varphi_9^l(r)$ at 326 K. The insert gives the long range part of $\varphi_9^l(r)$ [statistical error on $\varphi_9^l(r)$ is $\sim \pm 0.04$–0.07].

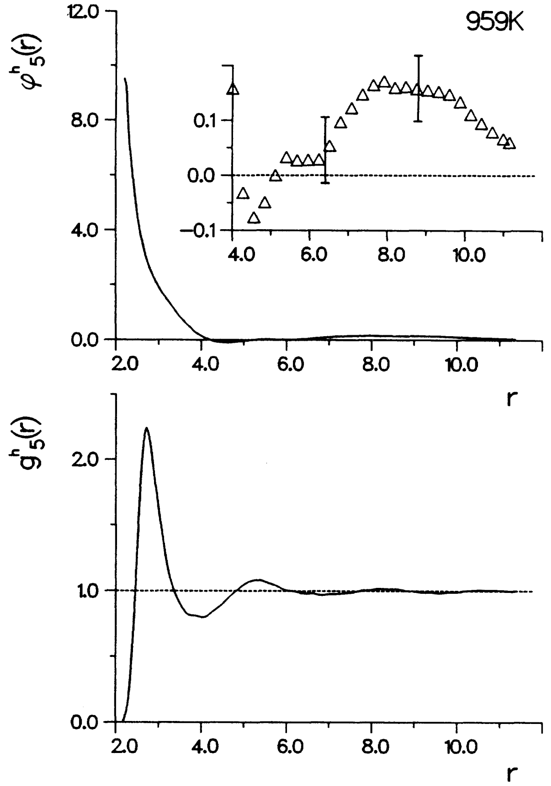

FIG. 6. Same as Fig. 5 but for $g_5^h(r)$ and $\varphi_5^h(r)$ at 959 K. The error bars indicate the typical statistical uncertainty on $\varphi_5^h(r)$.

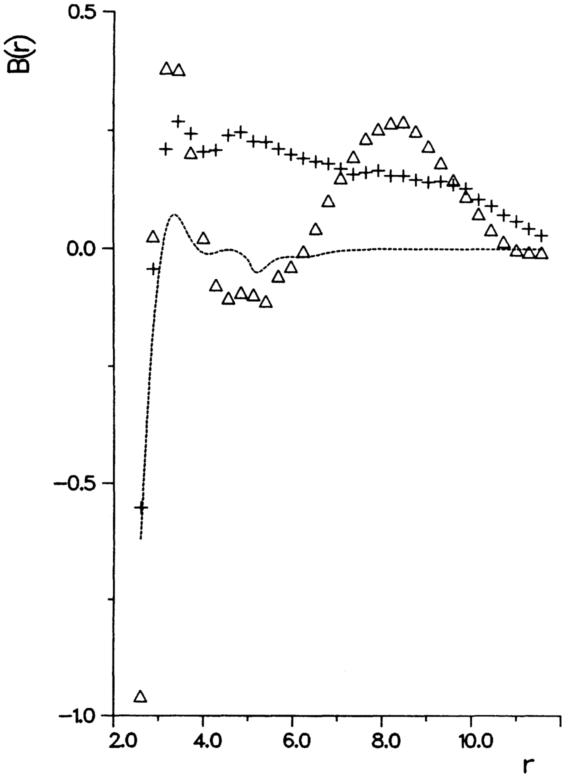

FIG. 7. Comparison between the bridge functions of a hard-sphere system at $\eta=0.41$ (dashed line) (Ref. 25) and those calculated for liquid gallium using the effective two-body potentials $\varphi_9^l(r)$ and $\varphi_5^h(r)$ (triangles, 326 K; crosses, 959 K).

At $k=0$, the values of $S_9^l(0)$ and $S_5^h(0)$ are 0.0058 and 0.022 to be compared with the values obtained from the compressibility 0.0050 and 0.015. To be significant such a comparison must take into account the experimental errors on $S_{\text{expt}}(k)$ for $k \leq 0.4$ Å^{-1}. In absolute value these are $\sim 5\times10^{-4}$ (326 K) and $\sim 3\times10^{-3}$ (959 K) (cf. Table III in Ref. 16). On the basis of the sole neutron scattering measurements, the estimated values of $S_{\text{expt}}(0)$ have a similar error and are compatible with the values of $S_9^l(0)$ and $S_5^h(0)$ obtained from the inversion procedure.

From the preceding discussion and the results presented in Tables IV–VI in Ref. 16 one can conclude that the potentials $\varphi_9^l(r)$ and $\varphi_5^h(r)$ permit, by simulation, to obtain a faithful representation of $g_{\text{expt}}(r)$ and $S_{\text{expt}}(k)$ provided the effects induced by the potential cutoff on the main peaks in $S_9^l(k)$,$S_5^h(k)$ and the asymptotic region of $g_9^l(r)$ and $g_5^h(r)$ are taken into account.

As seen from Figs. 5 and 6, the potentials obtained for the two temperatures are qualitatively similar. They are positive up to $r \sim 4$ Å and oscillatory beyond this distance. The period of the oscillations is about 8 Å and differs from the theoretical estimate πk_F^{-1} by a factor of 2 or 3. When $\varphi_i(r)$ is compared with $g_i(r)$ we remark that the first-nearest-neighbor shell is located inside the repulsive part of the potential and not at the minimum. From a quantitative point of view the comparison between $\varphi_9^l(r)$ and $\varphi_5^h(r)$ (cf. Table VI in Ref. 16) shows that the potentials depend strongly on the thermodynamic state. In particular the temperature dependence is not contained only in the trivial factor $(k_BT)^{-1}$. The ratio $\varphi_9^l(r)/\varphi_5^h(r)$ has a value of the order 4–5, very different from its *a priori* expected value ($T^h/T^l=\frac{956}{326}=2.94$) for $r<4$ Å for $r>4$ Å some values of the ratio can be very large, but these large values are due to a dephasing of the oscillations or to the statistical error (evaluated to be $\sim \pm 0.04$–0.07, cf. discussion above). In the theory of the effective potentials for liquid metals,[2] the potential depends on the density through k_F, for instance in the long-range part of the potential the period of the oscillations is πk_F^{-1} as mentioned above. In our measurement the density varies by 10%, the corresponding variation of k_F ($\sim 10\%$) seems too weak in order to explain the deviation of the ratio $\varphi_9^l(r)/\varphi_5^h(r)$ from its expected value 2.94 by 30–50 % for $r<4$ Å. A dependence on temperature of the potential $v_{\text{eff}}(r)$ thus cannot be ruled out.

Figure 7 shows the bridge function extracted from Eq. (3.1). At short distances $r \leq 3$ Å, they are qualitatively[26] similar to $B_{\text{HS}}(r,\eta)$ at $\eta \sim 0.4$. Beyond this distance, they decrease slowly in an oscillatory way at 326 K and monotonously at 959 K. In this region of r values, they cannot be represented by the hard-sphere bridge function $B_{\text{HS}}(r,\eta)$ which is essentially zero for $r>4$ Å. The importance of the bridge function for $r>3$ Å explains the impossibility of reproducing quantitatively $S_{\text{expt}}(k)$ by the MHNC equation and the effective potential $V_a(r)$.

IV. COMPARISON WITH PREVIOUS EXPERIMENTS

The two experiments realized with the D4B diffractometer at Institut Laue–Langevin enabled the structure factor of gallium to be measured over a wide range of wave vectors (0.26–16 Å^{-1}) with a high degree of precision. These measurements provide new information on the behavior of $S(k)$ for $k<2$ Å^{-1} at ordinary temperature and for the whole wave-vector range at high temperature. By comparison of the present results with those of gallium tabulated in Ref. 2 obtained by x-ray diffraction at temperatures 323, 473, 823, and 1073 K, the following discrepancies can be noted.

At 326 K, our measurements of $S(k)$ are systematically lower for $k \leq 2$ Å^{-1} than the values given in the tabulation at 323 K, in particular they are lower by a factor of 2–3 for $k \sim 1$ Å^{-1}. For $k>2$ Å^{-1} the agreement is good; however, in our measurements $S(k)$ is slightly more structured, the amplitude of the first peak and the subsequent oscillations being increased by $\sim$ 1–2 %.

Our measurement at low temperature seems to be compatible with that of Narten,[1] taking into account the temperature difference (~ 3 K), with that of Takeda *et al.*[5] (as far as one can judge from their Fig. 1) and also with the results of the Ref. 4.

At 959 K our results are incompatible with those given in Ref. 2. In the domain $k<2$ Å^{-1} they are lower than those tabulated at 823 K and for $k>2$ Å^{-1} the height of the first peak in our measurement is 5% smaller than that quoted for 1073 K. Similar differences occur for the amplitude of the oscillations beyond the first peak ($k>3$ Å^{-1}). Part of these discrepancies is likely to be due to ion-electron correlation present in the x-ray experiment.[5] Our experiment provides thus a new estimate of $S(k)$ for gallium at high temperature.

V. CONCLUSION

The inversion procedure for $S_{\text{expt}}(k)$ establishes that the effective potential is positive and repulsive in the domain of distances corresponding to the first-nearest-neighbor shell. This result is in agreement with the small value of $S(0)$ and the compressibility of gallium. The period of the oscillations of the potential beyond the repulsive part at short distances does not agree with the simplest theoretical prediction (πk_F^{-1}). The effective potential depends appreciably on the thermodynamic state.

The inversion method of Masserini and Reatto[21] which involves no adjustable parameter and no assumption on the theoretical form of the effective pair potential turns out to be quite adequate to take account of $S_{\text{expt}}(k)$ and $g_{\text{expt}}(r)$ of liquid metals provided precise measurements of $S_{\text{expt}}(k)$ are available over a large range of k wave vectors.

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APPENDIX: COMPUTATION OF $g_{\mathrm{expt}}(r)$.

At small k, $S_{\mathrm{expt}}(k)$ has been represented by the polynomial

$$S(k)=[S(0)(k_m-k)+kS(k_m)]/k_m +a(k-k_m)k^2 \quad (k\le k_m)\ , \tag{A1}$$

with $k_m=1.3$ Å^{-1}. Here $S(0)$ corresponds to the value derived from the compressibility of gallium at 326 and 959 K and $S(k_m)$ denotes the value of $S_{\mathrm{expt}}(k)$ at $k=k_m$. The free parameter a has been determined from a mean-square fit of $S_{\mathrm{expt}}(k)$ in the domain $0.26\le k\le 1.3$ Å^{-1}. The smoothing of $S_{\mathrm{expt}}(k)$ is necessary because of the relative errors in $S_{\mathrm{expt}}(k)$ at small k. For $k<k_m$, $S_{\mathrm{expt}}(k)$ is smaller than 0.027 at 326 K and smaller than 0.07 at 959 K so that in this domain of k an absolute error of 0.002 corresponds to a relative error of ~10–20%. These errors are tolerable for a calculation of $g_{\mathrm{expt}}(r)$ but not for $c_{\mathrm{expt}}(r)$, FT of $1-1/S_{\mathrm{expt}}(k)$.

A first estimate of $g_{\mathrm{expt}}(r)$, namely, $g_a(r)$, is obtained by FT of $S_{\mathrm{expt}}(k)$ extrapolated and smoothed for $k<k_m$. This estimate is modified by requiring $g_a(r)=0$ for $r<2.3$ Å. The modified function $g_a'(r)$ gives, by FT, $S_a(k)$ calculated for $k<64$ Å^{-1}. The values of $S_a(k)$ for $k>16$ Å^{-1} are used to extend $S_{\mathrm{expt}}(k)$ beyond the known experimental values, giving a function $S^0_{\mathrm{expt}}(k)$, with values between 0 and 64 Å^{-1}. The FT of $S^0_{\mathrm{expt}}(k)$ does not give a distribution function $g_b(r)$ which vanishes for $r\le 2.3$ Å. When the oscillations in this domain are discarded by imposing $g_b(r)=0$ for $r<2.3$ Å, then the FT of $g_b(r)$ is not compatible with $S_{\mathrm{expt}}(k)$ at small k. This inconsistency is progressively suppressed by effectuating recursively the following operations: from $S_b(k)$ identical to $S_{\mathrm{expt}}(k)$ for $k\le 1.8$ Å^{-1} one obtains, by FT, $g_c(r)$; after imposing $g_c(r)=0$ for $r<2.3$ Å, one calculates $S_c(k)$ and a modified function by imposing $S_c(k)=S_{\mathrm{expt}}(k)$ for $k<1.8$ Å^{-1} from which by FT one gets $g_d(r)$, etc. The function $S'_{\mathrm{expt}}(k)$ which results from this iterative process is equal to $S_{\mathrm{expt}}(k)$ for $k<1.8$ Å^{-1} and gives, by FT, a function $g(r)$ which satisfies $|g(r)|\le 0.001$ for $r<2.3$ Å.

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[16] See AIP document no. PAPS PLRAA-39-6310-05 for 5 pages of Tables III–VI showing structure factors, pair distribution functions, and effective two-body interactions. Order by PAPS number and journal reference from the American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The prepaid price is $1.50 for a microfiche, or $5.00 for a photocopy. Airmail additional.

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