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X-ray analysis of the structure of liquid Rb and Cs

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X-ray-transmission measurements have been performed and the diffraction patterns using Ag $K\alpha$ and Mo $K\alpha$ radiation have been determined for liquid rubidium at 40 and 90 °C and for liquid cesium at 65 and 100 °C, respectively. A new sample holder has been used. The structure factors $a(q)$ do not agree very well with measurements of neutron diffraction, but there is good agreement with the x-ray pattern of Huijben *et al.* in the case of Cs.

I. INTRODUCTION

One of the most important quantities of the liquid state is the structure factor $a(q)$ which is the Fourier transform of the correlation function $[g(r)-1]$. The structure factors can be obtained both from x-ray and neutron diffraction experiments. The structure factors $a(q)$ of alkali metals (Li, Na, K, Rb, Cs) were determined by Gingrich *et al.* in 1961 from neutron diffraction measurements.[1] Greenfield *et al.* (1971) repeated the measurement on liquid Na and K with x rays.[2] The agreement with Gingrich's data is satisfactory,[3] while the x-ray data on K of Thomas *et al.* (1938) disagree.[4] Gamertsfelder is the first who published x-ray data of liquid Li.[5] Huijben *et al.* recently (1976) published x-ray data on liquid Cs, which differ from Gingrich's data, because the maxima are shifted.[6] However, in the case of liquid gallium, there is no significant difference between the x-ray and neutron data.[7,8]

It is one aim of this paper to find out which data are reliable. This is important for the structure analysis. A second aim is to obtain x-ray diffraction data of liquid Rb, which are till now unknown. Hence, an attempt was made to use x-ray diffraction to determine the structure factors of liquid Rb and Cs. We have employed a transmission geometry which is different from the system used by Greenfield *et al.*[2] and by Huijben *et al.*[6] Mo radiation was taken to determine the structure factors of liquid Cs and Ag radiation was taken to determine both the structure factors of liquid Rb and Cs. The use of two wavelengths serves to prove the internal consistency of data on Cs. The experimental data were obtained and analyzed at different temperatures.

II. EXPERIMENTAL

Our x-ray diffraction pattern was taken using Mo$K\alpha$ and Ag$K\alpha$ radiations in a transmission geometry and the measurements were made using the Bragg-Brentano focusing, Philips horizontal goniometer (Fig. 1). The primary radiation emitted from the line focus (L) passed through the Soller slit (p) and $\frac{1}{2}°$ divergences slit (D). The scattered beam from the sample S was limited by a 0.2-mm receiving slit (R) and the K_β radiation was removed by a filter of 0.05-mm Pd or Zr foil (F). The scattering intensity arising from the continuous spectrum and the Compton radiation was mostly removed by a bent graphite monochromator (M). The resolution ($\Delta\lambda/\lambda$) is about 3×10^{-2}. The scattered intensity was measured by a scintillation counter (C).

The purity of the sample Rb and Cs is 99.98% which is given by Light Laboratories, Ltd., England. The elements for Rb and Cs are the most reactive metals. When these are contaminated with a trace of air or moisture, oxide and hydroxide are formed immediately. Therefore the sample was filled in a glass capillary (ϕ =0.57 mm with wall thickness of 0.007 mm) [Fig. 2(a)] under high vacuum ($< 10^{-6}$ Torr). After filling, the glass capillary was end fused and mounted in the heating unit which is described in details in Fig. 2(b). The absorption of Mo radia-

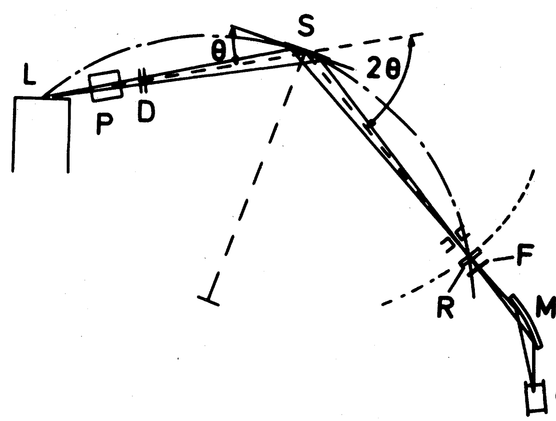

FIG. 1. Focusing system of the Philips horizontal goniometer.

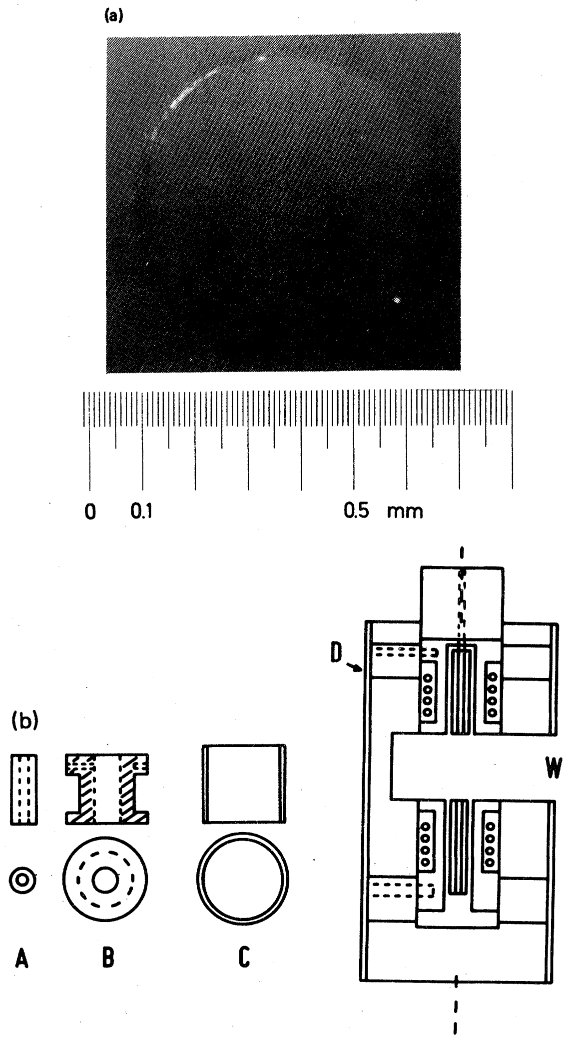

FIG. 2. (a) Microscopic picture of the glass capillary. (b) Sample holder and associated heating unit. *A*: Stainless-steel cylinder for fixing the glass capillary. *B*: Soapstone cylinder wrapped by nickel wire for heating. *C*,*D*: Stainless tube and brass tube, respectively. *W*: Window sealed with Mylar foil.

tion is too high for the Rb sample and the fluorescence is correspondingly very high. Therefore, only Mo radiation was used to measure Cs. The Ag radiation measurements were carried out both for Rb and Cs. The use of two different wavelengths is applied to check the internal consistency of the data for Cs. The temperature is monitored by means of a copper-Constantan thermocouple. For both the full and empty glass capillary, at each temperature, data were taken at $\Delta\theta = 0.125°$ interval from $\theta = 3°$ to 30°. Data were taken at constant time of 2000 sec. The statistical deviation of the measured intensity was below 1%. Before the x-ray diffraction pattern of liquid samples was taken, the alignment of the diffractometer was tested by means of scattering on the standard sample of LiF and Si. The deviations between the measured and the calculated scattering angles were smaller than 0.3%. The smallest q values ($q = 4\pi \sin\theta/\lambda$) of our measurements were 0.93 $Å^{-1}$ for Mo radiation and 1.17 $Å^{-1}$ for Ag radiation, respectively. The missing intensity values in these ranges were obtained by extrapolation to $q=0$. Of course, this is a crude approximation. But it has negligible influence on the determination of the structure from $g(r)$.

III. ANALYSIS OF THE X-RAY DIFFRACTION MEASUREMENTS

The experimentally determined x-ray intensities were corrected for the effects of absorption, polarization, and dispersion. The corrected intensities were normalized and then converted into structure factors $a(q)$.

A. Corrections for polarization, absorption, and empty glass capillary scattering

The measurements were carried out, one with the sample holder filled with the sample $[I_{sc}(\theta)]$ and one with the empty capillary $[I_c(\theta)]$. Both the intensities $I_{sc}(\theta)$ and $I_c(\theta)$ are reduced due to the absorption in the liquid sample and the glass capillary. The cylindrical absorption factor for scattering in the glass capillary and absorption in both sample and capillary A_c has been calculated.[9] In the present case the absorption due to the glass capillary [$\exp(-\mu l) \cong 1$, where μ and l are the linear absorption coefficient and the path length in the glass capillary, respectively] was found to be negligible (wall thickness of the glass capillary $= 0.0007$ cm). The cylindrical absorption factor for scattering and self-absorption in sample $A_s(\theta)$ is thus a function of μr, where μ is the linear absorption coefficient of the specimen and r is its radius. The absorption factors $A_s(\theta)$ and μ are taken from the international tables for x-ray crystallography.[10] The generally valid formula for the absorption correction in cylindrical samples, derived by Paalman *et al.*,[11] goes over into the simpler form

$$I_s = (I_{sc} - I_c A_c)/[A_s P(\theta)]$$

under the conditions of the present experiment. Here $P(\theta)$ is the polarization factor. The contribution of incoherent scattering to the intensity counted by the detector is less than 2% at all scattering angles of the present experiment. The correction of the Compton scattering has been therefore omitted.

TABLE I. Experimental values of $a(q)$ for Rb(Ag $K\alpha$) and Cs(Mo $K\alpha$).

2Θ	q	$a(q)$ (Rb) 40 °C	$a(q)$ (Rb) 90 °C	q	$a(q)$ (Cs) 65 °C	$a(q)$ (Cs) 100 °C
0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.250	0.049	0.000	0.000	0.039	0.000	0.000
0.500	0.098	0.000	0.000	0.077	0.000	0.000
0.750	0.147	0.000	0.000	0.116	0.000	0.000
1.000	0.196	0.000	0.000	0.154	0.000	0.000
1.250	0.245	0.000	0.000	0.193	0.002	0.004
1.500	0.294	0.000	0.000	0.232	0.013	0.014
1.750	0.343	0.000	0.001	0.270	0.022	0.017
2.000	0.392	0.002	0.002	0.309	0.038	0.021
2.250	0.441	0.004	0.004	0.348	0.038	0.028
2.500	0.490	0.006	0.007	0.386	0.038	0.031
2.750	0.538	0.009	0.010	0.425	0.038	0.033
3.000	0.587	0.013	0.014	0.463	0.038	0.038
3.250	0.636	0.017	0.018	0.502	0.038	0.038
3.500	0.685	0.021	0.023	0.541	0.038	0.038
3.750	0.734	0.026	0.028	0.579	0.038	0.038
4.000	0.783	0.032	0.034	0.618	0.038	0.038
4.250	0.832	0.038	0.041	0.656	0.040	0.038
4.500	0.881	0.045	0.062	0.695	0.042	0.038
4.750	0.930	0.070	0.077	0.733	0.050	0.038
5.000	0.979	0.121	0.097	0.772	0.053	0.038
5.250	1.028	0.190	0.128	0.811	0.063	0.043
5.500	1.077	0.290	0.166	0.849	0.072	0.048
5.750	1.126	0.380	0.249	0.888	0.082	0.077
6.000	1.174	0.487	0.388	0.926	0.099	0.088
6.250	1.223	0.683	0.635	0.965	0.156	0.124
6.500	1.272	0.888	0.708	1.003	0.211	0.145
6.750	1.321	1.221	1.021	1.042	0.280	0.183
7.000	1.370	1.666	1.469	1.081	0.346	0.220
7.250	1.419	2.111	1.936	1.119	0.463	0.330
7.500	1.468	2.478	2.287	1.158	0.589	0.490
7.750	1.516	2.618	2.341	1.196	0.824	0.753
8.000	1.565	2.418	2.195	1.235	1.149	1.053
8.250	1.614	2.050	1.808	1.273	1.550	1.408
8.500	1.663	1.693	1.480	1.312	2.053	1.867
8.750	1.712	1.406	1.223	1.350	2.545	2.266
9.000	1.761	1.202	1.145	1.389	2.854	2.502
9.250	1.809	1.116	1.084	1.427	2.851	2.482
9.500	1.858	1.046	1.044	1.466	2.534	2.260
9.750	1.907	0.933	0.937	1.504	2.118	1.925
10.000	1.956	0.832	0.842	1.543	1.787	1.668
10.250	2.005	0.748	0.763	1.581	1.495	1.389
10.500	2.053	0.684	0.703	1.620	1.251	1.206
10.750	2.102	0.642	0.662	1.658	1.099	1.082
11.000	2.151	0.622	0.643	1.696	1.021	0.993
11.250	2.200	0.623	0.643	1.735	0.907	0.880
11.500	2.248	0.644	0.662	1.773	0.819	0.817
11.750	2.297	0.682	0.697	1.812	0.780	0.792
12.000	2.346	0.733	0.746	1.850	0.746	0.775
12.250	2.394	0.795	0.803	1.888	0.717	0.760
12.500	2.443	0.862	0.867	1.927	0.667	0.713
12.750	2.492	0.932	0.932	1.965	0.634	0.679
13.000	2.540	0.999	0.996	2.004	0.617	0.660
13.250	2.589	1.060	1.055	2.042	0.616	0.655
13.500	2.638	1.114	1.106	2.080	0.629	0.663
13.750	2.686	1.156	1.147	2.119	0.656	0.684
14.000	2.735	1.187	1.177	2.157	0.695	0.715
14.250	2.783	1.206	1.195	2.195	0.742	0.755
14.500	2.832	1.211	1.202	2.234	0.797	0.801
14.750	2.880	1.206	1.197	2.272	0.855	0.852
15.000	2.292	1.189	1.182	2.310	0.916	0.905
15.250	2.978	1.164	1.159	2.348	0.975	0.957
15.500	3.026	1.133	1.130	2.387	1.031	1.008
15.750	3.075	1.098	1.096	2.425	1.082	1.054
16.000	3.123	1.060	1.060	2.463	1.127	1.096
16.250	3.172	1.023	1.025	2.501	1.163	1.130
16.500	3.220	0.988	0.991	2.540	1.190	1.157
16.750	3.268	0.957	0.961	2.578	1.208	1.176
17.000	3.317	0.932	0.936	2.616	1.216	1.187
17.250	3.365	0.912	0.916	2.654	1.216	1.190
17.500	3.414	0.900	0.903	2.692	1.206	1.185
17.750	3.462	0.893	0.897	2.731	1.190	1.173
18.000	3.510	0.893	0.896	2.769	1.167	1.156
18.250	3.559	0.899	0.901	2.807	1.139	1.134
18.500	3.607	0.909	0.910	2.845	1.108	1.108
18.750	3.655	0.923	0.924	2.883	1.074	1.080
19.000	3.704	0.939	0.939	2.921	1.041	1.051
19.250	3.752	0.957	0.957	2.959	1.008	1.022
19.500	3.800	0.975	0.974	2.997	0.977	0.995
19.750	3.848	0.991	0.991	3.035	0.950	0.970
20.000	3.897	1.007	1.006	3.073	0.926	0.949
20.250	3.945	1.019	1.019	3.111	0.908	0.931
20.500	3.993	1.030	1.030	3.149	0.894	0.917
20.750	4.041	1.037	1.037	3.187	0.886	0.908
21.000	4.089	1.041	1.042	3.225	0.884	0.903
21.250	4.138	1.043	1.044	3.263	0.886	0.902
21.500	4.186	1.042	1.043	3.301	0.892	0.905
21.750	4.234	1.039	1.040	3.339	0.903	0.912
22.000	4.282	1.035	1.036	3.377	0.916	0.922
22.250	4.330	1.030	1.031	3.415	0.932	0.934
22.500	4.378	1.024	1.025	3.453	0.950	0.948
22.750	4.426	1.018	1.018	3.491	0.968	0.962
23.000	4.474	1.013	1.012	3.529	0.985	0.977
23.250	4.522	1.008	1.007	3.566	1.002	0.991
23.500	4.570	1.004	1.002	3.604	1.017	1.005
23.750	4.618	1.001	0.999	3.642	1.031	1.017
24.000	4.666	0.998	0.996	3.680	1.041	1.027
24.250	4.713	0.997	0.994	3.718	1.049	1.035
24.500	4.761	0.995	0.993	3.755	1.055	1.041
24.750	4.809	0.995	0.992	3.793	1.057	1.044
25.000	4.857	0.994	0.992	3.831	1.057	1.045
25.250	4.905	0.994	0.992	3.868	1.054	1.044
25.500	4.952	0.993	0.992	3.906	1.049	1.042
25.750	5.000	0.993	0.992	3.944	1.042	1.038
26.000	5.048	0.992	0.992	3.981	1.035	1.032
26.250	5.096	0.991	0.992	4.019	1.026	1.026
26.500	5.143	0.990	0.992	4.057	1.017	1.019
26.750	5.191	0.989	0.991	4.094	1.008	1.012
27.000	5.239	0.987	0.991	4.132	1.000	1.005
27.250	5.286	0.986	0.990	4.169	0.992	0.999
27.500	5.334	0.986	0.989	4.207	0.986	0.994
27.750	5.381	0.986	0.989	4.244	0.981	0.989
28.000	5.429	0.986	0.989	4.282	0.977	0.986
28.250	5.476	0.987	0.990	4.319	0.975	0.983
28.500	5.524	0.989	0.991	4.357	0.974	0.982
28.750	5.571	0.991	0.993	4.394	0.975	0.982
29.000	5.619	0.994	0.995	4.432	0.977	0.982
29.250	5.666	0.998	0.997	4.469	0.979	0.984

TABLE I. (*Continued*).

29.500	5.713	1.001	1.000	4.506	0.983	0.986
29.750	5.761	1.005	1.004	4.544	0.987	0.989
30.000	5.808	1.009	1.007	4.581	0.992	0.992
30.250	5.855	1.013	1.010	4.618	0.996	0.996

B. Normalization

The corrected intensity $I_s(\theta)$ has to be normalized. The normalization factor N was calculated according to the procedure published by Hosemann *et al.*[12] After multiplication of the corrected intensity $I_s(\theta)$ with the factor N,

$$I_n = N I_s(\theta),$$

the structure factor $a(q)$ of the specimen is then given by

$$a(q) = [I_n(q)]/f^2(q) .$$

The atomic scattering factors were calculated from a formula proposed by Cromer and Mann[13] based on relativistic Hartree-Fock atomic wave functions. We have adopted the correction factor for anomalous dispersion calculated by Cromer and Liberman.[14]

C. Correlation function $g(r)$ of Rb and Cs

The experimental structure factors of a liquid are related to the correlation function $g(r)$ by the equation

$$4\pi r^2 g(r)\rho_0 = 4\pi r^2 \rho_0 + \frac{2r}{\pi}\int qi(q)\sin(qr)dq ,$$

where $g(r)$ is the correlation function, ρ_0 is the average macroscopic density of the liquid, and $i(q) = a(q) - 1$. The related quantity $g(r)\rho_0$ gives the probability of finding an atom at a distance r from a reference atom in the liquid. The ripples of the correlation functions which were produced by the termination error are removed using a procedure published by Zei *et al.*[8]

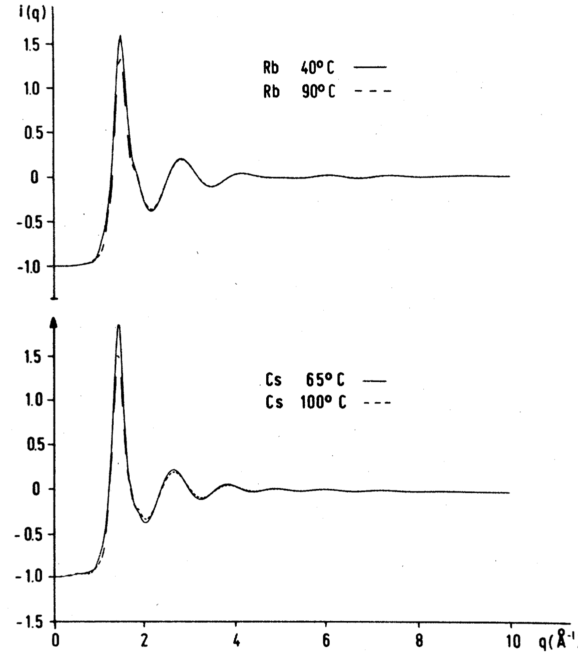

FIG. 3. Smoothed structure factors $[a(q) - 1]$ of Rb and Cs.

IV. RESULT AND DISCUSSION

Figure 3 shows the observed experimental structure factors $[a(q) - 1]$ of liquid Rb and liquid Cs as functions of q at temperatures 40, 90 °C, and 65, 100 °C, respectively. With rising temperature, the heights of the peaks decrease while

TABLE II. The positions and amplitudes of the first maximum of $i(q)$ for the present results on liquid Rb and Cs in comparison with the data of other authors.

Authors		Position of 1st maximum (Å^{-1})		Value of 1st maximum		Temperature (°C)	
		Rb	Cs	Rb	Cs	Rb	Cs
Zei	Ag $K\alpha$	1.50	1.40	1.62	1.45	40	40
	Mo $K\alpha$		1.40		1.85		65
Huijben *et al.* (Ref. 6)	Mo $K\alpha$		1.40		1.70		65
Gingrich *et al.* (Ref. 1)	n^{*} [a]	1.53	1.47	2.0	1.34	40	30
Copley *et al.* (Ref. 21)	n	1.54		2.3		40	
Page *et al.* (Ref. 22)	n	1.54		1.8		40	
Suzuki *et al.* (Ref. 23)	n	1.52		1.45		55	
Wingfield *et al.* (Ref. 24)	n	1.57		1.71		45	

[a] n^{*} neutron diffraction.

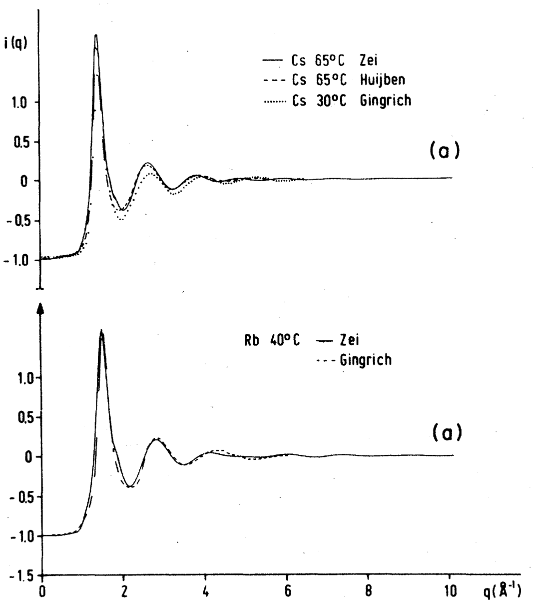

FIG. 4. Smoothed structure factors $[a(q)-1]$ of Rb and Cs compared with results from Huijben *et al.* and Gingrich *et al.*

their widths are slightly increasing. In Table I, we present our results for $a(q)$ for Rb at $T=40$, 90 °C and for Cs at 65, 100 °C. We compare our data with the x-ray data obtained by Huijben *et al.*[6] and the neutron data from Gingrich *et al.*[1] in Fig. 4. In the case of Cs [Fig. 4(a)], our data (Mo radiation) are in good agreement with the data from Huijben *et al.*, and show the same phase shift with respect to the neutron data. Only the value of the first maximum of Cs with Mo$K\alpha$ radiation is a slightly larger (1.85 instead of 1.70, Table II). Such a nice agreement does not exist with the neutron measurements. In Fig. 4(b) we compare our data (Rb) with the neutron data from Gingrich *et al.* It can be seen that both values of the maxima and their positions are different. Although there exist more recent experimental investigations for

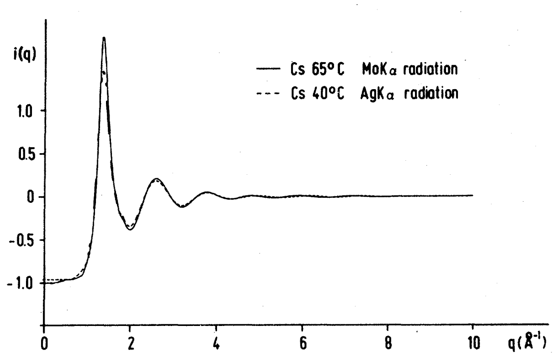

FIG. 5. Comparison of the structure factor of Cs obtained from Mo $K\alpha$ and Ag $K\alpha$ radiations.

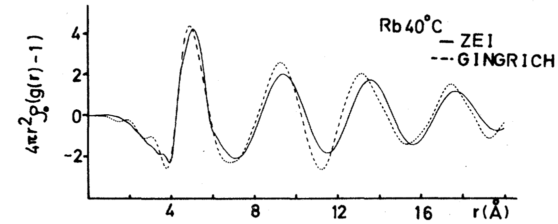

FIG. 6. Experimental correlation function $[4\pi r^2\rho_0(g(r)-1)]$ in comparison with results from Gingrich *et al.*

Rb, we have selected the data of Gingrich *et al.* because these are mostly used to compare with theoretical calculated structure factors.[15-20] A comparison with other recent experiments is given in Table II. The values listed there are taken from the curves in the respective publications, which is good enough for qualitative but not for quantitative comparison. It is remarkable that the first maximum is markedly shifted to higher q values in all neutron data, compared with our result. An explanation of this discrepancy is un-

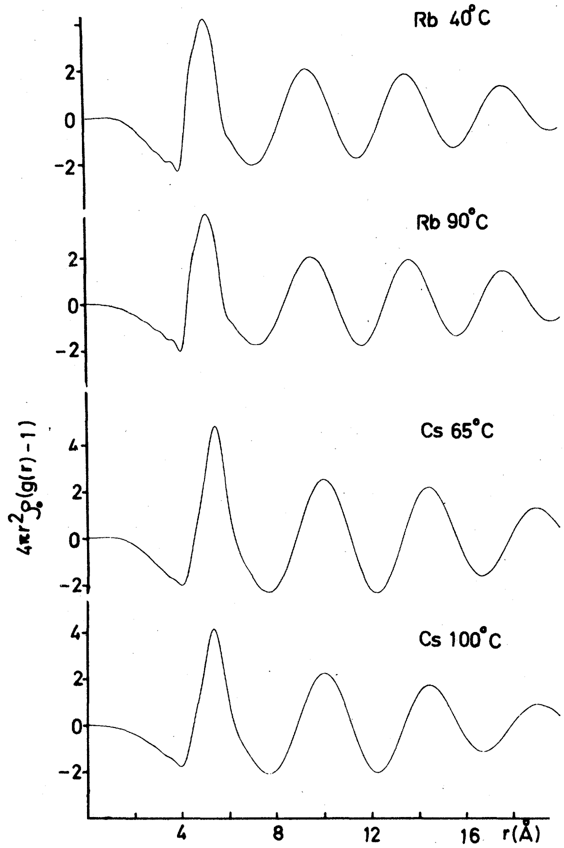

FIG. 7. Experimental correlation functions $[4\pi r^2\rho_0(g(r)-1)]$ at different temperatures.

known to us. The third column of Table II shows that also the peak heights of the first maximum are quite different. Our Cs first maximum (Fig. 5) obtained from Ag$K\alpha$ radiation is also somewhat smaller than for Mo$K\alpha$ radiation. This can be explained by the large counting rate of the Ag radiation, which leads to a counting loss. Therefore we suspect that the sizable differences between the results of the other authors could also be due to the electronic counting systems.

Figure 6 shows the comparison of our correlation function $g(r)$ with that of Gingrich *et al.* The position of the maxima of $g(r)$ from Gingrich's data shifts to smaller r values, as is to be expected, since the function $g(r)$ is the Fourier transform of the structure factor. A comparison of the correlation functions at different temperatures is shown in Fig. 7. The damping of $g(r)$ increases with increasing temperature. This is plausible, since the magnitude of the distance fluctuations increases. This effect is stronger in the case of Cs than in the case of Rb. This may be due to a larger atomic diameter and a soft repulsive core in the pair potential of Cs.[25] In both cases (Rb and Cs) the positions of the maxima and minima remain unchanged. An attempt to analyze the structure of these liquids will be published elsewhere.

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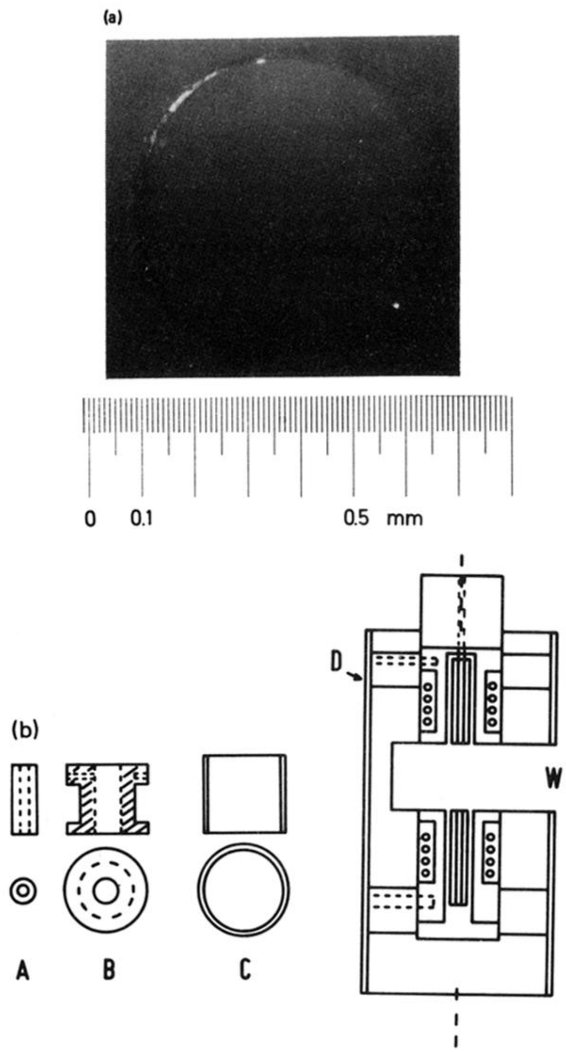

FIG. 2. (a) Microscopic picture of the glass capillary. (b) Sample holder and associated heating unit. *A*: Stainless-steel cylinder for fixing the glass capillary. *B*: Soapstone cylinder wrapped by nickel wire for heating. *C*,*D*: Stainless tube and brass tube, respectively. *W*: Window sealed with Mylar foil.