

Evidence for a paracrystalline bcc lattice in molten alkali metals

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(Received 15 May 1978)

It is proved that the structure of molten Li, Na, and K is given by a convolution polynomial with bcc microparacrystalline domains with a mean interatomic distance r_0 larger than in the solid state at the melting point and paracrystalline distance fluctuations g_{ik} of (12–16)%. An fcc lattice can be excluded. Within the errors of experiments body-centered-tetragonal lattices are also possible, but the ratio c/a must lie between 0.9 and 1.1. From the density and r_0 values it can be concluded that about (2–5)% of the atoms lie on interstitial places or belong to fcc microdomains. This effect is attributed to the lower packing density of the bcc lattice, since in fcc melts (for example, lead) r_0 does not change at the melting point and instead of interstitials atomic vacancies appear.

I. INTRODUCTION

Atoms in liquid metals are always interacting with a great many others; therefore, simplifications of the kinetic theory of gases are not available. The structure of liquids plays an important role in the theory. Bernal and King¹ have tried to describe liquid structure using random packing of hard spheres. The data on random close packing of spheres from Bernal *et al.* show quite clearly that such packing has an inherently lower density than an ordered one.

Kaplow *et al.*,² on the other hand, have attempted to describe the structure of molten lead as a distorted crystalline arrangement. Their results were compared with paracrystalline distortions described by Hosemann *et al.*³ Both studies are capable of reproducing the observed experimental results, but they have different physical interpretations for their different formulations.

The paracrystal is based on the idea that each atom in a liquid spends statistically much of its time confined by its neighbors to a comparatively restricted region. This means that the mean local atomic environment in a liquid in spite of its relative larger fluctuations is not very different from that in a solid. However, the paracrystal is described according to Ornstein and Zernike's idea⁴: Each atom has *a priori* the same distance distribution from its neighbors. Contrary to Ornstein and Zernike this distance distribution is not a spherically symmetric one. Mathematically it can be described in terms of a convolution polynomial so that long-range order is no longer present. This corresponds with the experimentally observed results. The theory of paracrystals has been applied to analyze the structure of various solids, for example, promoted ammonia catalysts⁵ and polymers.^{6–8} This theory has recently been employed for describing the radial distribution of molten metals.^{9,10} The synthesized radial distri-

bution functions (RDF) of Refs. 3 and 9 are based on the paracrystalline distorted fcc lattice, they can reproduce the observed experimental RDF of copper and lead.

In this work experimental RDF data of the alkali group are investigated because these are broadly studied and their crystalline structure is bcc instead of fcc. Ruppertsberg¹¹ has shown that a classification of liquid metals is possible with regard to their reduced density. Willmann and Hosemann¹⁰ found that the reduced pair distribution functions of liquid alkali metals are different from those of other liquid metals. Nevertheless, it is still doubtful whether one can fit the experimental RDF of any molten metal with only one lattice type or if there exists no unique solution. We will analyze the structure of liquid alkali, therefore, on the basis of different paracrystalline-distorted lattice types. Furthermore we will try systematically to fit the experimental RDF of the alkali group with the changing c axis of their unit cell. In other words, the paracrystalline-distorted bcc lattice will be transformed to the paracrystalline-distorted body-centered tetragonal (bct) which with increasing c/a at $c/a = \sqrt{2}$ becomes the fcc lattice.

II. PARACRYSTALLINE DISTORTIONS AND COORDINATION STATISTICS

The x-ray scattering pattern of a liquid is related to the radial distribution function $g(r)$ by the following equation:

$$s i(s) = 4\pi\rho_0 \int_0^\infty r [g(r) - 1] \sin(sr) dr, \quad (1)$$

where $i(s)$ is the intensity function. [$i(s) = I(s)/I_c(s) - 1$, $I(s)$ is the scattered intensity, and $I_c(s)$ represents the coherent part of the normalized independent scattering of the atoms.] This equation

was first given by Zernike and Prins.¹² The related quantity, $g(r) - 1$, is called the pair correlation function which tends to zero at larger r , corresponding to the fact that the correlation is then lost. $g(r)\rho_0 dv$ is the probability of finding an atom in the volume element dv at a distance r from a reference atom in the liquid. ρ_0 is the mean atomic number density.

In order to analyze the liquid structure we will describe some of the important properties of a paracrystalline lattice in terms of convolution polynomials which are connected to the radial distribution function. The idea of describing the pair correlation function in a liquid by means of paracrystalline lattice has been developed in a series of papers by Hosemann and co-workers,^{13,14} Lemm,¹⁵ Willmann, and Hosemann¹⁰ and Steffen and Hosemann.⁹ The essential point is that the distance statistics of any two atoms can be calculated by convolution products from a limited number of fundamental statistics which describe the distribution of nearest neighbors. Let us consider, for instance, three atoms a_0 , a_1 , and a_2 : Let us assume that $H_1(\vec{x}_1)$ is the distribution of a_0 and a_1 ($\vec{x}_1 = \vec{R}_{a_0 a_1}$), and $H_2(\vec{x}_2)$ is the distribution of $\vec{x}_2 = \vec{R}_{a_1 a_2}$ then under the condition that correlation between \vec{x}_1 and \vec{x}_2 may be neglected, the distribution of $\vec{x} = \vec{R}_{a_0 a_2} = \vec{x}_1 + \vec{x}_2$ is the convolution product of H_1 and H_2 :

$$\begin{aligned} H(\vec{x}) &= \int H_1(\vec{x}_1)H_2(\vec{x}_2)\delta(\vec{x} - \vec{x}_1 - \vec{x}_2)dv_1 dv_2 \\ &= \int H_1(\vec{x}_1)H_2(\vec{x} - \vec{x}_1)dv_1 = H_1 * H_2(\vec{x}), \end{aligned} \quad (2)$$

where $\delta(\vec{x} - \vec{x}_1 - \vec{x}_2)$ is the Dirac δ function. Accordingly, the coordination statistics of a three-dimensional lattice as represented by Hosemann and Bagchi¹⁶ is

$$Z(\vec{x}) = \sum_{hkl} H_{hkl}(\vec{x}), \quad (3)$$

where

$$\begin{aligned} H_{hkl}(\vec{x}) &= \delta(\vec{x}) * (*H_1 * H_1 * \dots) \\ &\quad * (*H_2 * H_2 * \dots) * (*H_3 * H_3 * \dots). \end{aligned} \quad (4)$$

H_1 , H_2 , and H_3 are the coordination statistics in the directions of the three edges of the unit cell. Each factor $(*H_i * H_i * \dots)$ represents a p_i folding of H_i where the p_i 's ($i=1, 2, 3$) are the minimum number of steps to reach the given atom at position (h, k, l) from the origin $(0, 0, 0)$.

The shape of the function $H_{hkl}(\vec{x})$ is characterized by the fluctuation tensor T_{ik} which is defined by second-rank moments of $H_{hkl}(\vec{x})$ (x_i and x_k are

orthogonal components of \vec{x});

$$T_{ik} = \Delta x_{ik}^2 = \int (x_i - \langle x_i \rangle)(x_k - \langle x_k \rangle)H_{hkl}(\vec{x})dv. \quad (5)$$

The mean square fluctuation in some direction \vec{s} (\vec{s} is a unit vector with components s_i) is given by the equation

$$\begin{aligned} \Delta_s^2 &= \int [\vec{s} \cdot (\vec{x} - \langle \vec{x} \rangle)]^2 H_{hkl}(\vec{x})dv \\ &= \sum T_{ik} s_i s_k, \end{aligned} \quad (6)$$

Since only the spherical average of $z(\vec{x})$ is observable, we have to integrate over a sphere of radius r and thus we can connect the RDF with the coordination statistics by the equation

$$4\pi r^2 g(r)\rho_0 = \int_{|\vec{x}|=r} z(\vec{x})df = \sum_{hkl} \bar{H}_{hkl}(r), \quad (7)$$

where $\bar{H}_{hkl}(r)$ is the spherical average of $H_{hkl}(\vec{x})$:

$$\bar{H}_{hkl}(r) = \int_{|\vec{x}|=r} H_{hkl}(\vec{x})df. \quad (8)$$

If the shape of the function $H_{hkl}(\vec{x})$ is close to the spherical form, we may use the following approximation for this function:

$$\bar{H}_{hkl}(r) = \frac{1}{\sqrt{2\pi}\Delta} \frac{r}{\bar{r}} \exp -\frac{(r - \bar{r})^2}{2\Delta^2}, \quad (9)$$

where

$$\bar{r} = \int \vec{x} H_{hkl}(\vec{x}) dv_x = |\langle \vec{x} \rangle_{hkl}| \quad (10)$$

is the distance of the centroid of the function $H_{hkl}(\vec{x})$ from the origin. The width Δ is defined by Eq. (6) with

$$\vec{s} = \vec{s}_{hkl} = \langle \vec{x} \rangle_{hkl} / |\langle \vec{x} \rangle_{hkl}|. \quad (11)$$

For the case of a bcc lattice, the unit vector is given by the equation

$$\vec{s}_{hkl} = (h\vec{e}_1 + k\vec{e}_2 + l\vec{e}_3)/(h^2 + k^2 + l^2)^{1/2}; \quad (12)$$

and for the case of the bct lattice, we have

$$\vec{s}_{hkl} = (h\vec{e}_1 + k\vec{e}_2 + l\kappa\vec{e}_3)/(h^2 + k^2 + \kappa^2 l^2)^{1/2}, \quad (13)$$

where \vec{e}_1 , \vec{e}_2 , and \vec{e}_3 are three orthogonal unit vectors and κ is the ratio of the lattice constants, c/a .

III. APPLICATION TO THE STRUCTURE OF MOLTEN ALKALI ELEMENTS

The results of the structure analysis of liquid lead carried out by Steffen and Hosemann, which we have mentioned above, indicate that the structure of the melt possesses some relationship with the structure of its crystalline state. That is to say the structure of liquid lead can be des-

cribed by means of a paracrystalline-distorted fcc lattice.

In order to find out whether such a relationship can also be found in the alkali elements which have a bcc lattice in the solid state, we have first transformed the structure factor of liquid lithium, sodium, potassium, rubidium, and cesium measured by Gingrich and Heaton.¹⁷ In the case of liquid sodium and potassium more recent experimental data from Greenfield *et al.*¹⁸ are available. These are considered to be more accurate than those of Gingrich *et al.* and are in good agreement with the work reported by Huijben *et al.*¹⁹ We have therefore analyzed also these data and compared the resulting RDF with that obtained from Gingrich's data.

The number of the fundamental statistics needed to describe some type of paracrystalline lattice depends on the degree of symmetry. In the case of the bcc lattice we can build up the whole RDF on the basis of one fundamental statistic $H_1(\vec{x})$ which describes the distance-vector distribution between an atom in the position 111 and the reference atom at 000. The statistics $H_2(\vec{x})$ and $H_3(\vec{x})$, referring to the atoms in the positions $1\bar{1}\bar{1}$ and $11\bar{1}$, are obtained from $H_1(\vec{x})$ by corresponding rotations (see Fig. 1). On account of symmetry, the tensor T_{ik} has two equal main axes orthogonal to the $[111]$ direction. From Eq. (4) we may then calculate the coordination statistics $H_{hkl}(\vec{x})$ of an atom in any position hkl of a $\frac{1}{48}$ part of the lattice defined by the conditions

$$h \geq k \geq l \geq 0. \quad (14)$$

We represent the vector (h, k, l) as a linear combination of the three basis vectors $(1, 1, 1)$,

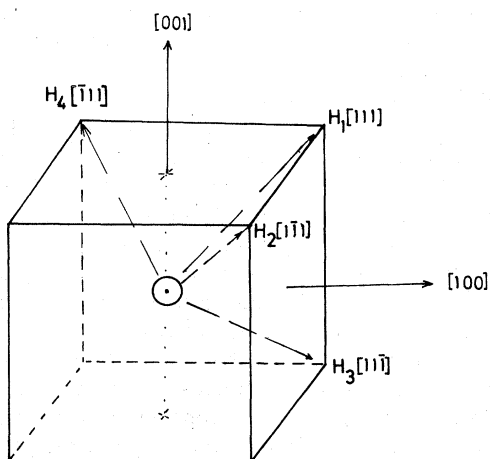


FIG. 1. Fundamental statistics for describing the paracrystalline bcc and bct lattice.

$(1, \bar{1}, 1)$, and $(1, 1, \bar{1})$:

$$(h, k, l) = p_1(1, 1, 1) + p_2(1, \bar{1}, 1) + p_3(1, 1, \bar{1}). \quad (15)$$

The coefficients p_1 , p_2 , and p_3 are non-negative on account of condition (14) and define the folding powers occurring in Eq. (4) in this segment of the space. Due to symmetry, the spherical average of $z(\vec{x})$ can be calculated from the coordination statistics $H_{hkl}(\vec{x})$ restricted by condition (14) and the other parts of the lattice are taken into account by multiplication with the corresponding coordination numbers.

In the case of the bct lattice, because of its lower symmetry we need one more fundamental statistic [$H_4((\bar{1}, 1, 1))$] in addition to the three statistics H_1 , H_2 , and H_3 under the conditions $l \geq h \geq k \geq 0$ (see Fig. 1). Furthermore, it is convenient for the calculation of the convolution products to represent the coordination statistics by Gaussians [Eq. (9)] since these functions do not change their character after convolution operations. The square of the fluctuation at a given position hkl is just the sum of the squares of the fluctuations of the individual coordination statistics times their folding powers.

However, from an inspection of the experimental RDF (asymmetry of the first peak) we must conclude that the fundamental statistics cannot be symmetric so that it is necessary to use two Gaussians,

$$H_1(\vec{x}) = \alpha H_{I_1}(\vec{x}) + (1 - \alpha) H_{II}(\vec{x}) \quad (16)$$

whose centers do not coincide. Such a "bimodal statistic" has first been discussed by Hosemann, Vogel, and Weick²⁰ and its application to liquid lead and physical interpretation have been reported by Steffen and Hosemann.⁹ According to this interpretation, H_I describes the distances within the paracrystalline microdomains (intraparticle distances) and H_{II} the distances between neighboring atoms belonging to different clusters (interparticle distances).

Figure 2 shows three cuts of the bimodal fundamental statistic $H_1(\vec{x})$ of liquid lithium, sodium, and potassium at 180, 100, and 65 °C, respectively, along the $(1\bar{1}0)$ plane. With increasing atomic number they become more disklike and broader (Table I). The shape of the function $H_{hkl}(\vec{x})$ is almost spherical and therefore the use of equation (9) in the present work is justified. [We have checked the validity of Eq. (9) which is exact only in the case of spherical symmetry by performing the spherical average [Eq. (8)] numerically. In the present case no significant differences occurred.]

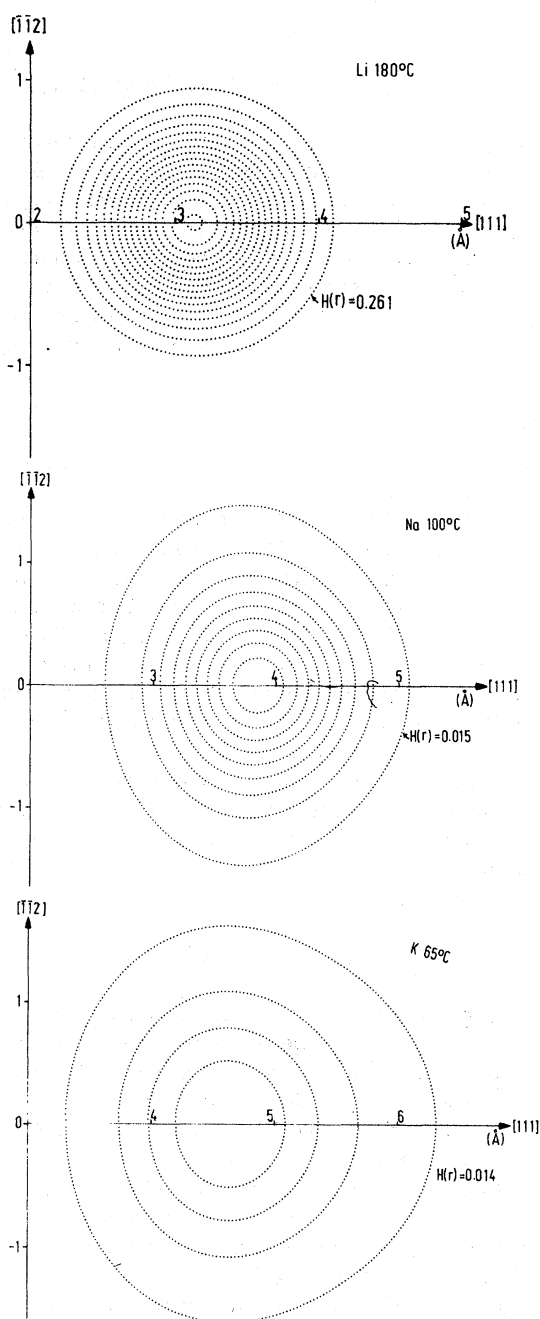


FIG. 2. Contour lines of the fundamental statistic in the $(1\bar{1}0)$ plane. The increment of the contour line is 0.05 \AA^{-3} .

IV. RESULTS AND DISCUSSION

The synthesized RDF curves based on the bcc lattice are shown in Fig. 3 in comparison with the experimental curves of molten lithium, sodium, and potassium obtained from Gingrich's experimental structure factor.¹⁷ The same was done

with the experimental data of liquid sodium and potassium measured by Greenfield *et al.* (see Fig. 4). The positions of the peaks and their profiles of these synthesized curves agree very well with the experimental data in both cases. However, the widths of the fundamental statistics are a little different, which results from the fact that the peaks in Fig. 4 are somewhat higher than in Fig. 3. Fittings have also been done for rubidium and cesium; except for the second maximum, the positions of the calculated RDF curves are in good agreement with experiments. Since we do not know whether the disagreement in the second maximum could result from unaccurate experimental data or from physical effects, we ignore the results on Rb and Cs in the present work. The parameters which give the best fit to the observed experimental RDF curves are shown in Table I. $r_0 = r_1 + \beta\Delta r$ is the position of the center of gravity of the coordination statistic H_1 , r_1 is the first-nearest-neighbor distance of the first statistic H_I and r_s is the first-nearest neighbor distance of the solid state at the melting point. Δr is the difference between interparticle and intraparticle distances. β is the percentage of the second statistic; g_{11} , g_{12} , and g_{13} are the fluctuations of the edge vector \bar{a}_1 in the [100], [010], and [001] directions respectively, related to its mean length \bar{a}_1 . a_I , b_I , and c_I are the corresponding widths of the fundamental statistic H_I [Eq. (13)] and a_{II} is the width of the second part of the fundamental statistic H_{II} . To reduce the number of parameters, we chose the spherical Gaussian for the second part of the fundamental statistic H_{II} . The mean densities ρ_x^I are calculated on the basis of the paracrystalline unit cell $[= 2/(2r_0/\sqrt{3})^3 (\text{\AA}^{-3})]$. These calculated mean densities are always smaller than the experimental densities ρ_0 , while for molten lead (fcc melt) the contrary is the case. The difference can be explained in the following way:

The bcc lattice is not the most dense packing. Atoms can penetrate into the interstices of the bcc lattice above the melting point. This causes statistically an increase of the local atomic density in the melt. Another cause could be that a small part of the paracrystalline microdomains exist in the form of a more ordered close packing (for example, fcc lattice). It is interesting to mention that in the case of lead,⁹ $r_0 = r_s$ at the melting temperature. The observed macroscopic density ρ_0 , however, changes at the melting point. This apparent discrepancy may be explained by an increase of vacancies during the phase transition. On the other hand, in the case of liquid Li, Na, and K r_0 is larger than r_s (see Table I). The same has also been observed in the

TABLE I. Statistical parameters of the synthesized RDF.

Element T (°C) Lattice type Reference	Li 180		Na 100				K 65			
	bcc	fcc	bcc	bcc	fcc	fcc	bcc	bcc	fcc	fcc
	17		17	18	17	18	17	18	17	18
r_1 (Å)	3.12	3.21	3.71	3.71	3.88	3.86	4.51	4.51	4.61	4.75
r_1 (Å)	0.17	0.17	0.28	0.28	0.04	0.15	0.46	0.46	0.25	0.47
r_0 (Å)	3.16	3.24	3.79	3.79	3.88	3.88	4.72	4.76	4.72	4.81
β (%)	20.5	18.7	29.8	29.8	10	10	45	55	33.7	13
r_s (Å)	3.067		3.737				4.530			
g_{11} (%)	13.2	15.1	12.3	9.3	13.6	11.5	11.5	7.0	13.6	11.3
a_I (Å)	0.41	0.53	0.45	0.35	0.53	0.44	0.52	0.32	0.63	0.54
$g_{12} = g_{13}$ (%)	13.2	16.6	16.7	15.5	14.6	14.1	15.5	13.3	13.6	13.6
$b_I = c_I$ (Å)	0.41	0.53	0.62	0.58	0.57	0.54	0.70	0.60	0.63	0.65
a_{II} (Å)	0.57	0.55	0.45	0.53	0.51	0.50	0.70	0.68	0.79	0.71
ρ_0 (Å ⁻³)	0.04373		0.0243				0.01276			

case of liquid gallium.²¹ Therefore the coordination numbers of Li, Na, and K in the melt are approximately 2%-5% larger than in the solid state, while that of Pb is 2%-4% smaller than in the solid state.

Steeb²² and Prokhorenko²³ have compared the ratios of the individual interatomic distances of the solid state with the positions of the peaks in the liquid state in order to check the correlation between them. The disagreement of the distance

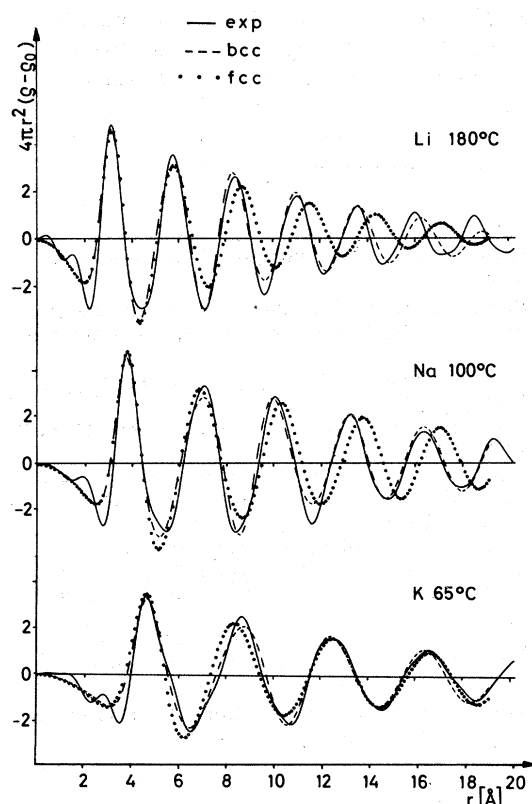


FIG. 3. Experimental RDF (—), Gingrich *et al.* (Ref. 17), in comparison with the synthesized RDF based the bcc (-----) and fcc (.....) lattice.

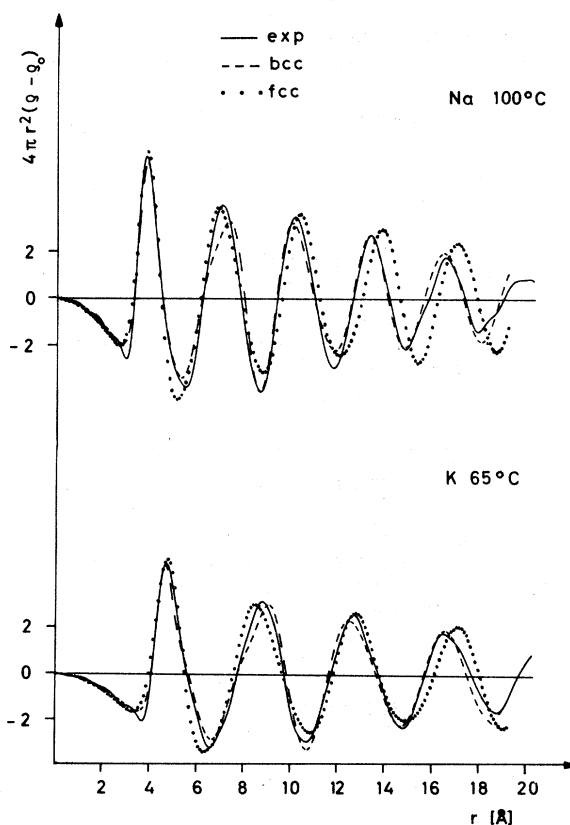


FIG. 4. Experimental RDF (—), Greenfield *et al.* (Ref. 18), in comparison with the synthesized RDF based on the bcc (-----) and fcc (.....) lattice.

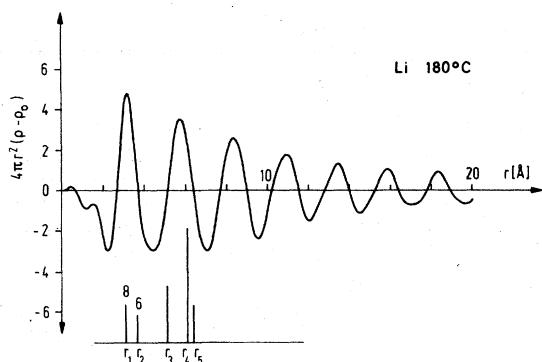


FIG. 5. Comparison between the positions of the maxima (I, II) of the experimental RDF and the interatomic distance of the bcc-paracrystal. The peaks are weighted by the corresponding coordination numbers.

ratio between the two states leads Prokhorenko to conclude that there is no relationship between the two states. The explanation of these discrepancies is obvious in the light of the paracrystalline state. Each RDF peak is composed of several different interatomic distances (Fig. 5) and its position shifts, if the coordination statistics become broader (Fig. 2). The results for the bcc lattice whose axial ratio c/a is ≥ 0.9 or ≤ 1.10 are in good agreement with the experimental RDF curves.

The synthesized RDF curves based on the fcc

lattice are shown in Figs. 3 and 4 by dotted lines in comparison with the experimental RDF curves of molten Li, Na, and K. In the case of sodium and potassium the second peak shifts to a smaller distance r . The third, fourth, fifth, and sixth peaks of lithium and sodium shift, on the other hand, to larger- r values and their amplitudes are more strongly damped. The nonrotational symmetrical statistics ($g_{12} \neq g_{13}$) have also been fitted, but no improvement can be obtained. It is obvious that the fcc synthesized RDF cannot correctly describe the observed experimental RDF curves of molten lithium, sodium, and potassium. However, this misfit decreases with increasing atomic radius in the alkali elements. On the other hand, the difference between the synthesized bcc and fcc curves tend to decrease. Obviously this can be due to the weaker cohesive forces in potassium²⁴ compared with lithium and sodium. Nevertheless, this can also depend on the electron configuration of the atoms.

ACKNOWLEDGMENTS

We wish to thank Dr. D. Weick for this helpful discussions and critical revision of the manuscript, and Dr. B. Steffen for his computer program of the fcc lattice and his stimulating discussions. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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