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Structure of the equiatomic liquid alloys K–Sb, K–Bi, and Rb–Bi over a wide temperature range

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We report on neutron diffraction measurements on the equiatomic liquid alloys K–Sb, K–Bi, and Rb–Bi up to temperatures of T = 1800 K. The prepeaks in the resulting total structure factors S(Q) are indicative of intermediate range ordering. The shift of the prepeak positions towards smaller momentum transfer Q with increasing temperature suggests increasing distances between the structural polyanionic units. From reverse Monte Carlo (RMC) simulations the prepeak is assigned essentially to correlations between the polyvalent metal atoms (Sb or Bi), remaining even up to the highest temperatures measured. The simulations lead to models exhibiting Sb (or Bi) atoms clustered in short chains and dumbbells rather than in higher coordinated clusters or networklike structures. © 2000 American Institute of Physics. [S0021-9606(00)51717-6]

I. INTRODUCTION

Alloys of alkali metals M with group 13, 14, and 15 polyvalent metals PM are known to form compounds at different stoichiometric compositions in their solid state. Due to the large difference in electronegativity, an electron is transferred from the alkali metal to the polyvalent metal resulting in saltlike bonding and structure. On the one hand, if the composition is such that the number of electrons transferred is insufficient to complete the octet shell of the electronegative element, a saturated chemical bond can be formed only if valence electrons are shared among the electronegative atoms. This results in the formation of polyanionic clusters stabilized by strong covalent bonds which are immersed in a matrix of the electropositive species. In many cases the structure of these polyanions can be predicted according to the Zintl rule. On the other hand, so-called octet compounds are formed at compositions where each of the polyvalent metal atoms receives a sufficient number of electrons from the alkali metal atoms to obtain the desired octet shell. Due to sterical restrictions often only one of these compounds is found, with the light (and correspondingly small) alkali metals driving the alloys towards formation of the octet compound and the heavy ones towards the formation of Zintl compounds.

For most of the systems exhibiting extrema in the physical properties at one or both of these compositions in the solid phase, these extrema are found in the liquid phase as well.¹ Neutron diffraction studies validate the conclusion that polyanions survive the melting process.²

The phase diagram of KSb exhibits maxima at the equiatomic and at the K_3Sb composition, and in the liquid phase these compositions are characterized by maxima in the Darken excess stability function.^{3,4}

In contrast, the systems with heavy alkali metals and bismuth exhibit congruently melting compounds at the compositions M_3Bi and MBi_2^5 and not at the MBi composition. A maximum in the electrical resistivity is found for liquid M_3Bi (pronounced for Li, Na, and K, weak for Rb and Cs),

but no changes in the physical properties appear at the MBi_2 composition of the liquid phase. Instead, the resistivity peaks at about 40 at. % Bi (pronounced for Rb and Cs, weak for K and not visible for Li and Na), a composition where no congruently melting solid compound seems to exist.^{6,7} Moreover, measurements of the Darken stability function of liquid K–Bi⁸ and Rb–Bi⁹ indicate a compound at the equiatomic composition, which is inconsistent with the results from resistivity measurements.¹⁰

Due to these uncertainties we considered it worth while to perform neutron scattering experiments on the liquid alloys K–Bi and Rb–Bi to learn what structural features make up the peculiarities of the liquid. A further aim was to investigate structural changes of liquid K–Sb, K–Bi, and Rb–Bi over a large temperature range to explore the stability of polyanionic structural features in these systems.

II. EXPERIMENT

Antimony or bismuth (at least 99.999%) were added to molten potassium or rubidium (at least 99.95%) in small amounts because of exothermic reactions. The mixtures were heated to 950 K in an aluminum oxide crucible, and the resulting brittle alloys were ground and filled into a sample cell. Due to reactions with the air and moisture of both products and educts, all steps were carried out inside an argon-filled glove box (<2 ppm O₂, <2 ppm H₂O).

Details of the experimental setup and data treatment are published elsewhere.^{11,12} Briefly, the neutron diffraction experiments were carried out on the SLAD instrument of the Studsvik Neutron Research Laboratory, Sweden (λ = 1.1 Å). The *Q* range covered was 0.36 Å⁻¹<*Q* <10.47 Å⁻¹. The sample was contained in a specially designed molybdenum cell within a custom made hightemperature high-pressure autoclave. The differential scattering cross sections ($d\sigma/d\Omega$) have been determined up to temperatures of 1800 K, and the structure factors have been obtained according to



FIG. 1. Static structure factor S(Q) of liquid K–Sb. Dots are the experimental data points, the line is the equally spaced spline used for the RMC simulations. The column graph represents a calculated neutron diffraction pattern of the solid phase [LiAs type with lattice constants a=7.18 Å, b=6.97 Å, c=13.40 Å, $\beta=115.1^{\circ}$ (Ref. 13)].

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right) = \frac{\sigma_{\mathrm{coherent}}}{4\pi} (S(Q) - 1) + \frac{\sigma_{\mathrm{total}}}{4\pi},\tag{1}$$

where $\sigma_{\rm coherent}, \sigma_{\rm total}$ are the coherent and total scattering cross sections.

III. RESULTS AND DISCUSSION

Figures 1–3 show the structure factors of liquid K–Sb, K–Bi, and Rb–Bi over a wide temperature range up to 1800 K. The lowest temperatures were chosen little above the corresponding melting points (see Table I). For K–Sb (Fig. 1) we find a pronounced first sharp diffraction peak (so-called "prepeak") at Q = 1.06 Å⁻¹ which is indicative of chemical short-range order, and a main peak at Q = 2.1 Å⁻¹. The position of the prepeak corresponds well to an ensemble of intense diffraction peaks of the solid phase,¹³ suggesting the



FIG. 2. Static structure factor S(Q) of liquid K–Bi. Dots are the experimental data points, the line is the equally spaced spline used for the RMC simulations. The column graph represents a calculated neutron diffraction pattern of the solid compound KBi₂ [MgCu₂ type with lattice constant *a* = 9.60 Å (Ref. 15)].



FIG. 3. Static structure factor S(Q) of liquid Rb–Bi. Dots are the experimental data points, the line is the equally spaced spline used for the RMC simulations. The column graph represents a calculated neutron diffraction pattern of the solid compound RbBi₂ [MgCu₂ type with lattice constant *a* = 9.50 Å (Ref. 17)].

partial preservation of structural characteristics during the melting process. Compared to the structure factor of liquid Cs-Sb,¹⁴ the first peak is clearly more pronounced, whereas the second peak around 2 Å⁻¹ is of comparable height (1.61 for K–Sb at 650 K, 1.67 for Cs–Sb at 600 K). One could conclude from the different scattering cross sections of the alkali metals—assuming a similar structure of both alloys—that the first peak is essentially due to Sb correlations, as the weight of the partial structure factor $S_{SbSb}(Q)$ is larger in the case of K–Sb. Even for the lowest temperature measured we do not find distinct oscillations beyond the second peak of S(Q). Please note that the sample container broke during the 1773 K measurement. Because of the resulting poor statistics this S(Q) was not used as input for RMC simulations.

The structure factor of liquid K-Bi (Fig. 2) at 850 K exhibits a prepeak at about $Q = 1.17 \text{ Å}^{-1}$ and a main peak at about $Q = 2.05 \text{ Å}^{-1}$. According to the rough approximation Qd=7.7, a characteristic distance d=6.6 Å can be estimated from the position of the prepeak. Again we tend to assign it to the appearence of Bi polyanions. The phase diagram of KBi¹⁵ at the equiatomic composition exhibits an eutectic mixture of the compounds KBi₂ and K₄Bi₅. The stoichiometry of the latter is still not confirmed, and the crystal structure is unknown. The column graph in Fig. 2 (bottom) represents the neutron diffraction pattern of solid KBi2. The position of the prepeak corresponds approximately to the (111) diffraction peak, but there are no diffraction peaks corresponding to the main peak. However, x-ray diffraction patterns of the potassium-richer solid phases show a number of diffraction peaks in this region,¹⁶ so solving the crystal structures of these phases would be desireable to calculate the neutron diffraction patterns.

The structure factor S(Q) of Rb–Bi (Fig. 3) at 673 K displays several sharp peaks, indicating an incomplete melting of the sample at this temperature. The S(Q) did not change with time, suggesting the coexistence of a solid and a liquid phase. This is in reasonable agreement with the pub-

TABLE I. Liquid state number densities ${}^{1}\rho/\text{nm}^{-3}$ as determined by the RMC simulations of the scattering data at the corresponding experimental conditions (temperature *T*/K, pressure *p*/bar). In addition, the melting temperatures T_{m} are given.

K–Sb			K–Bi			Rb–Bi		
Т	р	$^{1} ho$	Т	р	$^{1} ho$	Т	р	$^{1} ho$
			673	2	21.0	673	4	-
923	14	19.5	850	3	19.5	850	4	19.5
1073	20	19.0	1073	8	18.5	1073	13	18.5
1273	22	18.0	1273	20	17.0	1273	26	17.5
1573	38	16.0	1573	44	14.0	1573	53	15.5
1773	50	14.5	1800	76	11.5	1800	96	13.0
	<i>T</i> _m =878 К		$T_{\rm m}$ = 628 K			$T_{\rm m} = 649 {\rm K}$		

lished phase diagram, showing that the melting point of the equiatomic composition is not far below the temperature here. Note that the components in the solid at this composition are still uncertain.¹⁷ The compounds under consideration are RbBi₂, RbBi, and Rb₄Bi₅. The existence of RbBi (proposed from EMF measurements⁹) is yet unconfirmed, as is the stoichiometry of Rb₄Bi₅. The structure of RbBi₂ is solved, and the column graph in Fig. 3 shows the calculated neutron diffraction pattern. The peak in the experimental S(Q) at about 2.2 Å⁻¹ and the shoulder at about 1.85 Å⁻¹ might correspond to those of the diffraction pattern, but not the peak at 2.0 Å⁻¹. The dashed line indicates the position of an experimental x-ray diffraction peak of the equiatomic solid, thus indicating the presence of a more rubidium-rich compound.

At 850 K a prepeak at about $Q = 1.08 \text{ Å}^{-1}$ and a main peak at about $Q = 2.05 \text{ Å}^{-1}$ are conspicuous, the prepeak being much less pronounced than that for liquid K-Bi. From the position of the prepeak a characteristic real-space distance of d = 7.1 Å can be calculated. It can be concluded that polyanions appear in liquid Rb-Bi as well and they are separated farther from each other due to the increasing size of the alkali metal compared to K-Bi. They are separated even more when going to Cs-Bi,¹⁸ where d = 7.3 Å was determined. Another hint of the presence of polyanions is the increase in the height of the prepeak in the order Rb-Bi, Cs-Bi, and K-Bi: The weight of the partial Bi-Bi structure factor $S_{\text{BiBi}}(Q)$ to the total S(Q) increases with decreasing scattering cross section of the alkali metals Rb-Cs-K. Thus, if the prepeak can be assigned to Bi-Bi correlations mainly, its pronounciation in S(Q) should follow the observed order.

Furthermore, a systematic trend towards larger Q values in the prepeak position (Table II) is evident for the alloys of alkali metals with polyvalent metals, when going to the right of the periodic table. That the Bi alloys are subject to this trend, again points towards the occurence of polyanions in the liquid Bi alloys.

We find that the structure factor of liquid K–Sb changes remarkably little with temperature, but the temperature range accessible to investigation with our equipment was limited to an interval of 650 K. For liquid K–Bi and Rb–Bi, we were able to measure S(Q) over a much larger temperature interval of 1127 K, enabling us to investigate systematic temperature effects. A clear shift of the prepeak maximum towards smaller Q values with increasing temperature can be observed for both alloys, indicating an increase in average distances between the polyanionic clusters. Furthermore, the heights of both prepeak and main peak decrease, indicating a gradual loss of structural order at high temperatures. Although less pronounced, the same temperature dependence of S(Q) is observed for liquid K–Sb.

From S(Q) one obtains the total pair correlation function g(r) by Fourier transformation:

$$g(r) = 1 + \frac{1}{2\pi^{2}\rho} \int Q^{2}[S(Q) - 1] \frac{\sin(Qr)}{Qr} dQ.$$
 (2)

To avoid truncation problems reverse methods (MCGR)²⁰ have been applied but deviations in our case are small between direct and reverse methods of calculating g(r). For multicomponent systems the total structure factor is a linear combination of the pairwise contributions from different types of atoms, i.e., the partial structure factors $S_{ij}(Q)$:

$$S(Q) = \sum_{ij} w_{ij} S_{ij}(Q).$$
(3)

In the same way the total pair correlation function can be expressed as a combination of the partial pair correlation functions $g_{ij}(r)$:

$$g(r) = \sum_{ij} w_{ij} g_{ij}(r).$$
(4)

The weighting factors w_{ij} arise from the corresponding neutron coherent scattering lengths b_{ij} and concentrations (mole fractions) x_{ij} (see Table III):

$$w_{ij} = b_i b_j x_i x_j / (x_i b_i + x_j b_j)^2.$$
(5)

TABLE II. Position of the prepeak of S(Q) for the equiatomic liquid alloys at temperatures close to the melting point.

Alloy	Peak positions	References
Cs-Tl	$0.74/0.72$ Å $^{-1}$	18 and 19
K-Tl	0.80 Å^{-1}	18
Cs-Pb	0.92 Å^{-1}	18
K–Pb	0.96\AA^{-1}	18 and 2
Cs-Bi	1.06 Å^{-1}	18
K-Bi/Rb-Bi	1.17/1.08 Å ⁻¹	This work
K-Sb	1.06 Å^{-1}	This work

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TABLE III. Neutron coherent scattering lengths b of the components (Ref. 21) and weighting factors w_{ij} of the partial functions for the different alloys.

		K–Sb	K–Bi	Rb-Bi
b(Bi) = 8.53 fm b(Sb) = 5.57 fm b(K) = 3.67 fm b(Rb) = 7.09 fm	w _{mm} 2 · w _{mpm} w _{pmpm}	0.158 0.479 0.363	0.090 0.421 0.489	0.206 0.496 0.298

The covalent intracluster Sb-Sb or Bi-Bi distances cause a sharp first peak of g(r) for the alloys of Sb or Bi with Cs.^{14,18} When trying to analyze g(r) of K–Sb, K–Bi, and Rb-Bi^{11,22} in terms of their different pair contributions we face the problem that an assignment of peaks to particular pair contributions is not possible due to the small size of the alkali atoms. The first peak is probably composed of contributions from M-M-, M-Bi-, and Bi-Bi-correlations. Compared to K-Bi, for Rb-Bi a shift of the first peak towards larger r values is obvious. This might be partly due to increased distances of the first coordination sphere, but the effect is rather large considering the similar densities of both alloys. More important seems to be the increased scattering power of Rb compared to K which causes an increasing weight of the M-M-correlations. These correlations probably make up the right shoulder of the first peak of g(r).

We decided to perform RMC simulations²⁰ of the data to derive the various contributions to the total S(Q)'s and g(r)'s, to assess what kind of structural features are in agreement with the scattering data, and to refine the so far unknown densities of liquid K–Bi and Rb–Bi at the thermodynamic conditions chosen (Table I). The cutoff radius of the different atomic species has to be considered carefully, as it depends on the degree of charge transfer as well as on the kind of bonding present in the given alloy. Tegze and Hafner²³ showed in their *ab initio* molecular dynamics (MD) simulations that a transfer of valence electrons from M to PM orbitals occurs, but with still a high probability of localization close to the M atom. This leads us to the assumption, that the radius for the alkali metals is far greater than the ionic radius. However, to avoid an unjustified exclusion of



FIG. 5. Partial structure factors $S_{ij}(Q)$ of liquid K–Bi from the RMC simulation without nearest neighbor constraint.

closer distances, we applied rather soft cutoff constraints for the minimum distances between the atoms in the simulation. We used the ionic radii for the alkali metals and the covalent radii for the polyvalent metal atoms (for all atom pairs PMPM, MPM, MM: 2.5 Å for liquid K–Sb, 2.7 Å for liquid K–Bi, 2.8–2.9 Å for liquid Rb–Bi).

The partial structure factors (see Fig. 4 for K-Sb, Fig. 5 for K-Bi, data for Rb-Bi are not shown) indeed confirm that the prepeak is mostly due to PM-PM correlations, with little contributions from PM-M correlations. This is obvious up to the highest temperatures measured, revealing the persistence of polyanions over the full temperature range. In the case of liquid K–Sb, only the $S_{ii}(Q)$'s of the lowest temperature are shown in Fig. 4 because of the small temperature range explored. The partial pair correlation functions for K-Sb and K-Bi are displayed in Figs. 4 and 6. The partial g(r)'s of the Bi alloys exhibit distinct peaks for the first coordination sphere, shifted towards larger distances with increasing atomic size. The first peak in $g_{BiBi}(r)$ remains rather sharp, even up to 1800 K for both alloys. In contrast, the peak in $g_{\rm RbRb}(r)$ flattens with increasing temperature, and the peak in $g_{KK}(r)$ vanishes completely. At 1800 K barely any hint for an ordered short-range structure can be drawn from $g_{\rm KK}(r)$. Whereas it is not possible for these alloys to resolve very sharp features in the partial g(r)'s, such as a clear splitting of the first peak of $g_{PMPM}(r)$ into an intracluster and



FIG. 4. Partial structure factors $S_{ij}(Q)$ (lower panel) and partial pair correlation functions $g_{ij}(r)$ (upper panel) of liquid K–Sb at 923 K from the RMC simulation without nearest neighbor constraint.



FIG. 6. Partial pair correlation functions $g_{ij}(r)$ of liquid K–Bi from RMC simulation without nearest neighbor constraint.

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FIG. 7. Fraction f(n) of Bi atoms in liquid K–Bi as a function of the number of Bi neighbors *n* within 3.4 Å over the complete temperature range. Inset: Quotient of the average coordination numbers $\langle n \rangle$ up to a distance *r* at 1800 K and 673 K (the horizontal line represents the quotient of the bulk densities). Results are from RMC simulation without nearest neighbor constraint.

intercluster peak, in $g_{SbSb}(r)$ of K–Sb there is an indication for such splitting into peaks at around 2.9 Å and 3.6 Å. We attribute the peak at 2.9 Å to Sb–Sb–correlations of covalently bonded Sb.

Furthermore, we analyzed the structural models obtained from the RMC simulations of S(Q) near the melting point with respect to the fraction f(n) of PM atoms with a fixed number n of neighboring atoms of the same kind within a maximum distance $d_{\rm PM}$. We have chosen $d_{\rm Bi} = 3.4$ Å (respectively $d_{\rm Sb}$ = 3.3 Å) to take into account predominantly neighbors that are able to form covalent bonds in the polyvalent metal atom clusters. f(n) displays a clear maximum for atoms with one neighbor only, a considerable amount of atoms with two neighbors, and very few higher coordinated atoms only. There is no significant difference between f(n)of liquid K-Bi, Rb-Bi, and K-Sb. These results indicate that these alloys contain only few networklike structural features or three-dimensional clusters, instead consist predominantly of short chains and dimers. For liquid K–Bi, f(n) is shown in Fig. 7 for all temperatures to demonstrate the small temperature dependence found for f(n). Only for the highest temperatures a slight increase in the number of zerofold coordinated Bi atoms is visible, stressing again the stability of covalent intracluster bonds up to 1800 K. The results obtained for liquid Rb-Bi are very similar and therefore not shown here. These findings correspond well to the increase in the relative height of the first peak of $g_{\text{PMPM}}(r)$ with increasing temperature. From the inset in Fig. 7 it can be deduced that this temperature stability of coordination is indeed short ranged. The average coordination number at 1800 K is smaller compared to the one at 673 K at distances exceeding significantly the covalent bond length, and finally scales with the bulk density for distances larger than 6.5 Å.

To distinguish between the formation of chains and dimers, we performed RMC simulations with two different nearest-neighbor constraints; (a) "dumbbell constraint:" configurations with PM atoms neighbored by one other PM atom being favored above configurations with a lower num-

TABLE IV. Fraction of onefold and twofold coordinated PM atoms resulting from the simulations with (a) "dumbbell constraint" and (b) "chain constraint."

	K–Sb	K–Bi	Rb-Bi
(a) onefold	0.81	0.88	0.80
(a) twofold	0.00	0.01	0.00
(b) onefold	0.24	0.18	0.20
(b) twofold	0.43	0.41	0.39

ber of PM dimers—this constraint induces the maximum number of dumbbells in a model configuration with its structure factor being in agreement with the scattering data; and (b) "chain constraint:" configurations with PM atoms neighbored by two other PM atoms being favored, this constraint induces the maximum number of atoms in chain structures. Note that we found it impossible to model the data assuming a significant number of threefold coordinated PM atoms, thus proving the absence of significant three-dimensional structural features in these systems (in other liquid Zintl alloys, such as K–Pb, Cs–Pb, and Na–Sn, networklike structures are found at conditions close to their melting point). For these simulations we chose a maximum nearest neighbor distance of 3.0 Å for Sb atoms, respectively 3.2 Å for Bi atoms, for covalent bonding between the PM atoms.

The results obtained for all three alloys show remarkably similar fractions of PM atoms with a given coordination number (Table IV). For the simulation with the "dumbbell constraint," between 80% and 88% onefold coordinated atoms are found with barely any twofold coordinated ones. Applying the "chain constraint" 39%-43% of the polyvalent metal atoms are double coordinated. The tendency to form chains or dimers thus seems to be similar in these alloys regardless of whether the polyvalent metal is Sb or Bi. Figure 8 (left panel) shows the partial pair correlation functions of liquid K–Bi being derived from the different simulations. The first peak in $g_{\text{BiBi}}(r)$ is clearly split into an intracluster and an intercluster part due to the applied constraints. The striking feature is the following: Despite the difference in f(n) values of models originating from simu-



FIG. 8. Comparison of partial pair correlation functions $g_{ij}(r)$ of liquid K–Bi (left panel) and fractions f(n) of Bi atoms as a function of the number of Bi neighbors *n* (right panel) from RMC simulations with different nearest neighbor constraints.

lations with different constraints (right panel in Fig. 8), the $g_{ii}(r)$'s are practically indistinguishable. This result implies that the structure factor does not contain enough information to make a clear-cut decision whether an alloy prefers formation of short chains or dumbbells. Even the use of isotopic substitution experiments seems not to be very helpful here, as the advantage is the firm determination of the partials only. The problem for distinguishing between a set of rather similar structures remains-at least in this case. This problem could probably be solved using ab initio MD simulations. A study on solid alloys of alkali metals and both Sb and Bi23 explains the strong differences in the bonding behavior of the Sb and the Bi alloys by the more extended nature of the Bi 5p orbitals destabilizing chain structures compared to Sb. A recent ab initio MD study on liquid K-Sb²⁴ gives an average number of Sb atoms in chain fragments of about 5, which is in good agreement with the chainlength that can be calculated from the coordination numbers of the "chain constraint"-RMC simulation of our scattering data. They also compared experimental structure factors with structure factors resulting from their MD configurations, and found a good agreement. Therefore we consider it as essential to perform an ab initio MD simulation also for liquid Bi alloys to explore conformational differences between Sb and Bi alloys.

IV. CONCLUSIONS

The static structure factors of the liquid alloys K–Sb, K–Bi, and Rb–Bi display a distinct prepeak indicating a significant intermediate range order. Our experimental data and the RMC simulations performed indicate that the prepeak is dominated by correlations between atoms of the polyvalent metal. The simulations suggest a clustering of these atoms in short chains and dimers. A distinction between both structural models seems to be impossible from a scattering experiment because of the similar partial pair correlation functions of these structures. From the temperatureinduced shift of the prepeak in S(Q) of the Bi alloys, an increase of mean distances of their superstructures with increasing temperature is deduced. The Bi–Bi average coordination numbers at distances typical for covalent bonding are barely effected by the temperature increase up to 1800 K, showing the stability of the short-ranged structural features up to the highest temperatures measured. Whereas the Bi– Bi–correlations persist, the partial pair correlation functions of the alkali atoms reveal a loss of correlations at high temperatures, pointing to a structure made up of small Bi polyanions embedded in a randomly distributed alkali atom background.

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