Structure of liquid equiatomic KSn and CsSn

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The structure factors of liquid equiatomic KSn and CsSn alloys have been determined by neutron diffraction. A distinct peak at about 1 Å^{-1}, the first sharp diffraction peak (FSDP), occurs in all measured structure factors. The temperature dependence of the structure has been studied for KSn: apart from the FSDP, whose position shifts toward smaller wave vector and magnitude decreases with increasing temperature, the structure factor remains essentially unaltered. The radial distribution function clearly shows three maxima in the first coordination shell. The simultaneous presence of the FSDP and several maxima in the first coordination shell are indications of formation of polyatomic species in the liquid. Application of two simple structural models, taking into account the presence of structural units, yields reasonable agreement with the measured structure factors.

INTRODUCTION

Several properties of the alkali-metal–lead alloys in the liquid state have been experimentally determined, including the electrical resistivity,[1,2] the Darken excess stability,[3,4,5] the specific heat capacity,[6] and neutron diffraction.[7] These investigations have revealed anomalies at one or two compositions. At the octet composition of Li-Pb and Na-Pb, i.e., that corresponding to the ratio of the chemical valences of the constituent metals, the anomalies could be interpreted by a mechanism based on a charge transfer between the two constituents resulting from the relatively large electronegativity difference. At the equiatomic composition, the strong deviations from ideal behavior occurring in all the alkali-metal–lead alloys except Li-Pb cannot be resolved by this mechanism; Geertsma et al.[8] have advanced the formation of polyvalently charged anions, Pb_4^{4-} (referred to as Zintl ions), as the mechanism responsible for this behavior.[8] These Pb_4 tetrahedra are known to exist in the crystal structure of NaPb (Ref. 9) and have also been observed recently in the crystal structures of KPb, RbPb, and CsPb.[7] A distinct first sharp diffraction peak (FSDP) has been obtained at about 1 Å^{-1} in all the structure factors of equiatomic liquid NaPb, KPb, RbPb, and CsPb determined by neutron-diffraction experiments; this feature can be explained on the basis of the presence of polyatomic units.[6,10]

Relatively less work has been devoted to the alkali-metal–Sn alloys, even though the Sn_4^{4-} ions are expected to be more stable than the Pb_4^{4-} since the Sn atoms are smaller and more electronegative than the Pb atoms. The difference in stability between liquid NaPb and NaSn is displayed in the behavior of the electrical resistivity and to a lesser extent in that of the thermodynamic properties. However, from an experimental point of view, the alkali-metal–Sn alloys are less attractive because they are

difficult to handle due to their relatively high melting points combined with the extreme corrosivity of the tin. Recent calorimetric measurements revealed the presence of a dramatic maximum in the variation of the heat capacity of liquid equiatomic alkali-metal–tin alloys with temperature.[10] The resistivity and the Knight shift of both Li-Sn and Na-Sn alloys were measured by Van der Marel et al.[2,11] For Li-Sn, the resistivity attains a maximum value of 850 $\mu\Omega$ cm at 20 at. % Sn; for Na-Sn, two maxima are observed: one at 43 at. % Sn and another, although weaker, at 23 at. % Sn. At the same compositions, the Knight shift shows minima. Electromotive force (emf) measurements of Li-Sn and Na-Sn liquid alloys have been performed by several groups using the same techniques.[12,13] Tamaki et al. and Alqasmi and Egan[13] have investigated the whole composition range and reported minima in $S_{CC}(0)$ or, correspondingly, maxima in the excess stability, at about the equiatomic composition and at Na_3Sn. The structure factors of these alloys were determined by Alblas et al.[14] The structure factors of the Li-Sn alloys show a prepeak at about 1.6 Å, pointing to chemical short-range order.[15,16] The structure factors of the Na-Sn alloys show a small peak at 1.1 Å, which is absent for the Sn-rich alloys. The magnetic susceptibility for K-Sn has been measured by Takeda and Tamaki[17] and shows a minimum close to the equiatomic composition. Resistivity measurements on amorphous Na-Sn and Cs-Sn films at 20 K have been performed by Avci and Flynn.[18] The resistivity shows an extremely high peak (> 10 $\mu\Omega$ cm) at the equiatomic composition. Band-structure calculations of NaSn have been made by Springelkamp et al.[19] By comparing the density of states of a system containing Sn_4 tetrahedra with that of a CsCl-like structure, the authors have shown that the presence of Sn_4 tetrahedra is required to explain the large resistivity.

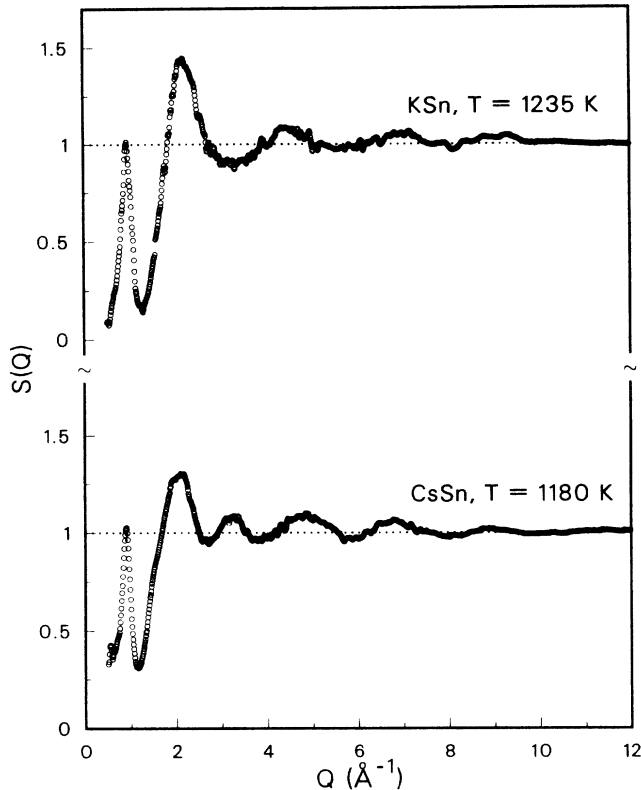As a further step in our study of polyanions in liquid

FIG. 1. Total structure factors, $S(Q)$, for liquid KSn and CsSn.

alloys, we decided to determine the structure of KSn and CsSn equiatomic alloys and compare the results with those of the alkali-metal–Pb alloys. We have performed neutron-diffraction experiments on liquid KSn at 1135, 1185, 1235, and 1285 K and on CsSn at 1180 K. The melting points of these alloys are 1124 K for KSn and 1161 K for CsSn as determined from recent high-temperature drop calorimetric experiments.[10] The crystal structures of KSn, RbSn, and CsSn are tetragonal

with space group D_{4h}^{20} ($I4_1/acd$) and, like those of KPb, RbPb, and CsPb, are isomorphous with the structure of NaPb.[9] The measurements were carried out on the Special Environment Powder Diffractometer (SEPD) of the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL).

EXPERIMENTS

Thin-walled vanadium crucibles (wall thickness about 0.02 cm) with an internal diameter of 0.64 cm and a height of 6.35 cm were used as containers. Details of the sample preparation can be found elsewhere.[7] The time-of-flight technique was used for carrying out the neutron-diffraction measurements. The samples were heated in a vanadium-foil vacuum furnace. The data were collected by five groups of ^{3}He-filled detectors, positioned at $\pm 90°$, $+60°$, $+30°$, and $-15°$ with respect to the incident beam. Measurements were made at 1200 K on an empty container identical to the ones loaded with the samples, and with the spectrometer empty. Thus, the contributions of the container, furnace, and spectrometer could be separated from the scattered intensity of the sample. Finally, a measurement using a vanadium standard of 0.64 cm diameter was made to calibrate the spectrometer and to normalize the data.

A series of programs developed at ANL (Ref. 20) was used to correct the data for absorption, multiple scattering, and inelasticity effects. From the calculated differential scattering cross section $d\sigma/d\Omega$, a total structure factor $S(Q)$ was derived, defined by

$$\frac{d\sigma}{d\Omega} = \langle \bar{b} \rangle^2 [S(Q) - 1] + \langle \overline{b^2} \rangle \ . \tag{1}$$

Here $\langle \ldots \rangle$ denotes an average over the concentrations of the components, and $\bar{b}$ and $\overline{b^2}$ are, respectively, the mean and mean-square scattering amplitudes averaged over nuclear isotopes and spins. The scattering lengths have been taken from a compilation by Sears[21] as $3.71f$, $5.42f$, and $6.23f$ for, respectively, K, Cs, and Sn. Fourier transformation of the structure factors yielded $D(r) = 4\pi r\rho_0[g(r) - 1]$ and the radial distribution

TABLE I. Positions and heights of the first and second peaks in the structure factors of KSn and CsSn. For comparison, the values for the corresponding Pb-based alloys are also shown, taken from Ref. 7.

		First peak		Second peak	
		Position ($\overset{\circ}{A}^{-1}$)	Height	Position ($\overset{\circ}{A}^{-1}$)	Height
KSn	1135 K	0.96	1.248	2.26	1.461
	1185 K	0.96	1.107	2.20	1.415
	1235 K	0.94	1.013	2.17	1.461
	1285 K	0.91	0.926	2.22	1.450
CsSn	1180 K	0.90	1.027	2.10	1.316
KPb	870 K	0.96	1.061	2.11	2.204
CsPb	930 K	0.92	1.122	2.01	1.184

$n(r)=4\pi r^2\rho_0 g(r)$, where $g(r)$ is the pair-distribution function and ρ_0 the total number density.

RESULTS AND DISCUSSION

Structure factors and coordination numbers

Figure 1 shows the structure factors of KSn at 1235 K and CsSn at 1180 K. Both structure factors show an FSDP at about 1 Å^{-1}. Interestingly, a slight asymmetry at the right side of the main peak in the $S(Q)$ of KSn can be distinguished. This asymmetry, also observed in the $S(Q)$ of several Na-Sn alloys of different compositions,[14] may be due to the presence of covalently bonded Sn_4 tetrahedra, as pointed out by Alblas et al.[14] The main peak of the $S(Q)$ of CsSn does not show an asymmetry, but a small peak appears at 3.3 Å. No peak is observed for KSn at this wave vector. It is likely that the shoulder on the main peak of KSn has developed into a separate peak for CsSn. This is interpreted as being due to a contraction of the Sn—Sn bonds within a tetrahedron. As Geertsma and co-workers[8] have explained, the covalent bonds in the tetrahedron are stabilized by the large size of the alkali atoms. The difference in electronegativity between K and Cs reinforces this effect. A similar satellite peak has also been reported in the $S(Q)$ of CsPb.[7] A recent molecular-dynamics study of the alkali-metal–Pb alloys[22] has shown that this peak is related to the presence of Pb_4 tetrahedra.
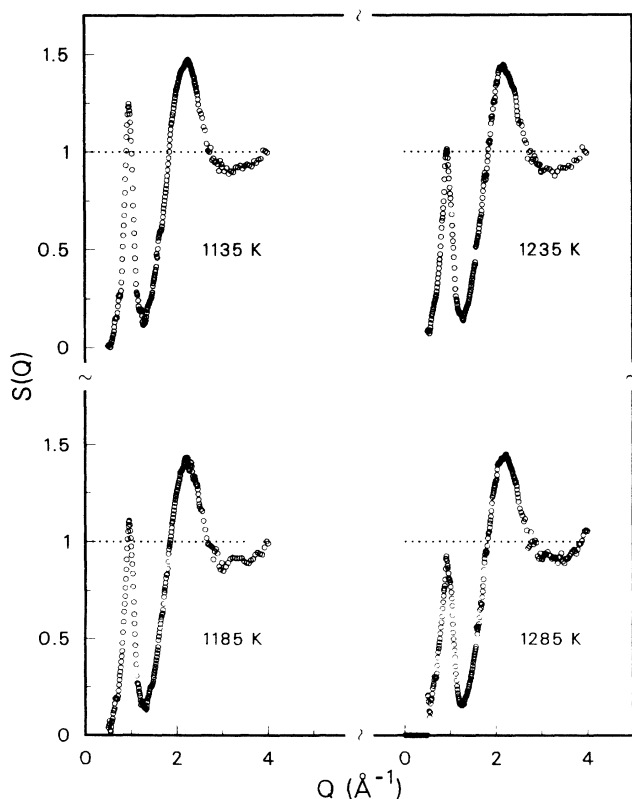
The positions and heights of the first and second peaks

FIG. 3. Radial distribution function, $n(r)$, defined as $4\pi r^2\rho_0 g(r)$, for KSn and CsSn.

FIG. 2. Total structure factors for liquid KSn at $T=1135$, 1185, 1235, and 1285 K.

are shown in Table I. For comparison, the peak positions of KPb and CsPb are also included. The positions of the FSDP of KSn at 1135 K and of CsSn at 1180 K hardly differ from those of the corresponding Pb alloys. On the other hand, the positions of the main peak of the Sn alloys have shifted to larger Q values compared with those of the corresponding Pb alloys. This implies that the average distance between the structural units is very little changed, but the average interatomic distance has decreased. Using a simple approximating formula,[23] we find that the average distance between the structural units amounts to 8.1 Å in KSn and 8.6 Å in CsSn. Note that the height of the FSDP is larger for KSn that for KPb despite the smaller scattering length of Sn, while it is only slightly less for CsSn than for CsPb. This is an indication that the effects of polyanion formation are stronger in the Sn alloys.

Figure 2 shows the FSDP and the main peak of the $S(Q)$ of KSn measured at four different temperatures. The q value and height of the FSDP decrease monotonically upon increasing temperature due to the combined effects of thermal expansion of the alloy and dissociation of the units. The position and height of the main peak do not vary systematically in the investigated temperature range.

The radial distribution functions for KSn at 1235 K and CsSn at 1180 K are plotted in Fig. 3. The first coordination shell, which extends from 2.5 to 5 Å in KSn and

TABLE II. Densities determined from $D(r)$ and positions of the three peaks observed between 2 and 5.5 Å in $T(r)$. The coordination numbers have been derived from the areas under these peaks after integration over r. The Sn-Sn and A-Sn coordination numbers have been estimated from, respectively, the first and second peaks. For comparison, the values for the corresponding Pb-based alloys are also shown, taken from Ref. 7.

| System | T (K) | ρ_0 (Å^{-3}) | Peak positions (Å) | | | Coordination numbers | |
			1st	2nd	3rd	Z(Sn-Sn)	$Z(A$-Sn)
KSn	1135	0.0237	2.97	3.69	4.74	1.8	7.2
	1185	0.0232	2.97	3.67	4.83	1.7	7.1
	1235	0.0229	2.98	3.51	4.60	1.6	4.3
	1285	0.0225	2.93	3.46	4.62	1.0	4.9
CsSn	1180	0.0182	3.02	4.00	5.17	2.5	3.8
KPb	870	0.0217	3.17	3.70	4.75	1.9	5.1
CsPb	930	0.0168	3.15	3.75	4.40	2.1	2.1

from 2.5 to 5.5 Å in CsSn, has three maxima, which we ascribe to peaks in the three partial pair-distribution functions. We have tried to deconvolute these peaks by fitting three Gaussian functions to the function $T(r)=4\pi r\rho_0 g(r)$. The results are summarized in Table II. By converting the fitted functions to $n(r)$ and integrating over r, we have estimated the coordination numbers, assuming the first peak to be a Sn-Sn correlation and the second peak an alkali-metal–Sn correlation. The Sn-Sn coordination number varies from 1.8 to 1.0 in KSn. The deviation from the value 3, which the coordination number would be for a tetrahedron, implies that tetrahedra, if present, are formed by only a fraction of the Sn atoms, which decreases with increasing temperature. The Sn-Sn coordination number of CsSn (2.5) is closer to 3, indicating more stable tetrahedra. This is to be expected because of the larger electronegativity difference and the larger size of the alkali-metal atoms in the Cs-Sn system compared with the K-Sn system. The Sn-Sn distance in KSn is hardly affected by temperature and is close to the value 2.98 Å measured by Hewaidy et al.,[9] who investigated the crystal structure of KSn in detail. The Sn-Sn distance determined for CsSn is slightly larger than this value and does not seem to follow the trend observed for the Pb-Pb distances in the alkali-metal–Pb alloys.[7] The estimated alkali-metal–Sn coordination numbers of KSn show a jump between 1185 and 1235 K; it is doubtful whether this is real. We have not attempted to calculate a coordination number from the third peak since at this distance different correlations become mixed up and cannot be resolved by a single diffraction experiment.

Model calculations

Two structural models have been used to generate structure factors. One is the random packing of structural units (RPSU) model, originally introduced by Egelstaff et al.[24] in their work on CCl$_4$ and generalized to systems consisting of polyatomic units by Moss and Price,[25] and the other is the reference interaction site model (RISM)

developed by Chandler and collaborators.[26] A description of these models applied to the alkali-metal–Pb alloys has been given in a previous publication.[7] By analogy with the calculations for the alkali-metal–Pb alloys, the structural unit used for both models was A_4Sn$_4$ (A=K,Cs), consisting of a Sn$_4$ tetrahedron surrounded by a larger A_4 tetrahedron oppositely directed. The Sn-Sn and the A-A distances in this unit have been derived from the crystal structure in which the Sn and A atoms form almost perfect tetrahedra. Since no crystallographic data are available for CsSn, we have determined the positions of the Cs and Sn atoms by rescaling the parameters of the crystal structure of KSn,[27] using the known crystal structures of KPb and CsPb.[7] The input parameters for RPSU and RISM are shown in Table III and were adjusted to give the best fits. The parameters needed for RPSU are the hard sphere diameter σ and the packing fraction ($\eta=\pi\sigma^3\rho_0/6n$, where ρ_0 is the number density of the atoms and n is the number of atoms in a unit). A Debye-Waller factor with mean-square displace-

TABLE III. Parameters used in RPSU and RISM models.

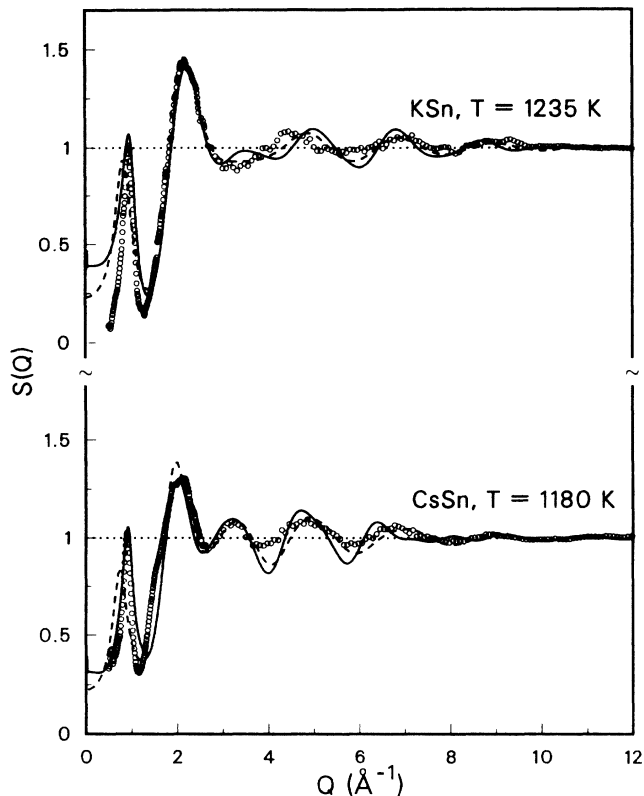|	KSn	CsSn
RPSU model		
σ (Å)	6.3	6.9
η	0.36	0.4
ρ_0 (Å^{-3})	0.022	0.019
$\langle u^2\rangle^{1/2}$ (Å)	0.2	0.2
RISM model		
σ_A (Å)	3.0	3.5
σ_{Sn} (Å)	3.5	3.5
ρ_0 (Å^{-3})	0.020	0.016
Δd_{AA} (Å)	0.35	0.35
Δd_{SnSn} (Å)	0.175	0.175
Δd_{ASn} (Å)	0.35	0.35

FIG. 4. Model calculations (solid line, RPSU; dashed line, RISM) and experimental results (points) for the total structure factor $S(Q)$ of KSn and CsSn.
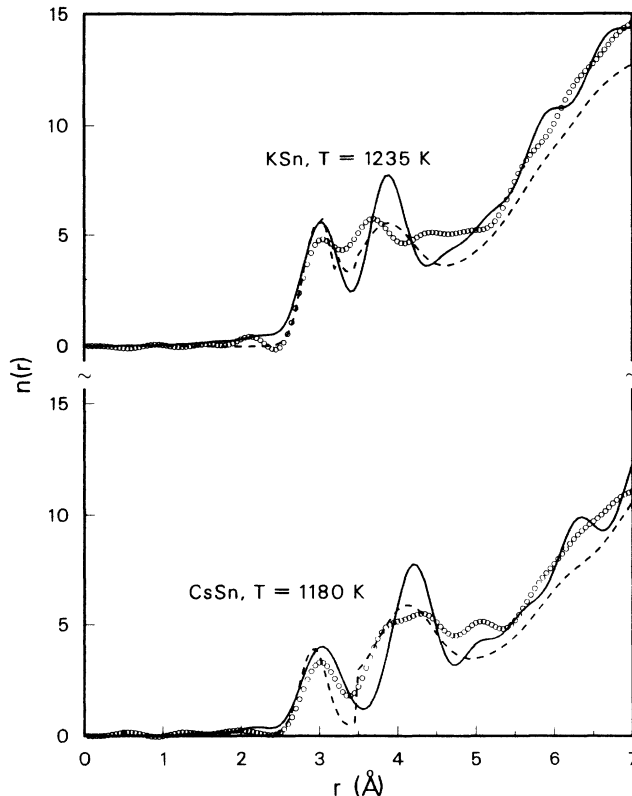

FIG. 5. Model calculations (solid line, RPSU; dashed line, RISM) and experimental results (points) for the radial distribution function $n(r)$ of KSn and CsSn.

ment $\langle u^2 \rangle$ allows for damping of the high-Q oscillations in $S(Q)$. In the case of RISM each atomic species has its own hard sphere diameter σ_i ($i = A$, Sn), and the internal vibrations are characterized by their root-mean-square deviations Δd_{ij}.

Comparing the RPSU and RISM results with the measured data (Figs. 4 and 5), we see that the position of the FSDP of both KSn and CsSn is correctly predicted by RPSU, while RISM has set the FSDP at lower Q. The main peak is satisfactorily described by RPSU and RISM, although both models fail to follow the leading edge of the main peak of CsSn. The higher-Q oscillations of RISM are better in phase with the measured structure factor than those of RPSU. The first peak in the coordination shell of the radial distribution function calculated by RPSU and RISM agrees well with the measured peak, although its height is slightly overemphasized by the models. This is because the Sn-Sn coordination number is exactly 3 in the A_4Sn_4 unit used in the models, while it is less than 3 according to the measurements. The calculated distribution functions show a strong peak around 4 Å that does not resolve into the two maxima observed in the measurements. Together with the measured Sn-Sn coordination number, this result suggests that a fraction of the alkali-metal and Sn atoms exists as clusters

different from the A_4Sn_4 units or as individual atoms, thereby giving rise to a more complex structure in the first coordination shell.

CONCLUSIONS

The structure factors of KSn and CsSn show a similar FSDP to that observed for KPb and CsPb. The main peak of the structure factor of KSn shows a slight asymmetry, while a satellite peak arises next to the main peak in the structure factor of CsSn. Three maxima can be distinguished in the first coordination shell of the radial distribution functions. Together, all these facts support the existence of polyatomic units in the liquid. Measurements on KSn at different temperatures show that the position of the FSDP shifts to lower Q and its height becomes smaller as the temperature increases. Satisfactory agreement with the measured structure factors is obtained with two models, RPSU and RISM, based on A_4Sn_4 units.

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