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Atomic dynamics in liquid $\text{K}_x\text{Sb}_{1-x}$ alloys

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Abstract

The atomic dynamics of liquid $\text{K}_x\text{Sb}_{1-x}$ alloys is studied using cold neutron inelastic scattering. Dynamical properties extracted from the experimental spectra, like the dispersions obtained from the maxima of the longitudinal current correlation function, $J_l(Q, \omega)$, and the vibrational spectra, show a strong dependence on concentration. With increasing content of Sb, higher frequency modes are observed in the vibrational spectrum. For the Sb-rich compositions the dispersion is split into two branches. This indicates the de-coupling of the dynamics of the two components, due to the difference in atomic mass, already around the position of the principal

peak of the static structure factor, $S(Q)$. The observations are consistent with results from earlier experiments on similar systems and from *ab initio* molecular dynamics simulations.

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1 Introduction

Binary *Zintl*-type liquids are model systems to study the influence of the interatomic potential on the atomic dynamics. Due to charge transfer the variation of the alloy composition allows a change of the dominant type of interaction from metallic to ionic and to partly covalent. This leads, e.g., to a strong concentration dependence of the thermodynamic, electronic and transport properties [1]. In alkali metal – post-transition group (semi-)metal alloys (M_xX_{1-x}), the physical properties often show extrema around two concentrations, the octet and the equiatomic compositions. In the *Zintl* picture [2], the former corresponds to an ionic system with formally closed shells ($nM^+ + X^{n-}$), whereas in the latter the anions are isoelectronic to the neighboring element in the periodic table ($M^+ + X^-$) and form similar structures. This leads to the formation of covalently bonded polyanions, e.g. chains of $[Sb]^-$ in the case of M-Sb alloys. The stability of these polyanions depends strongly on the cation size [3].

The atomic structure of these liquids has been subject to a number of experimental studies (e.g. [4, 5, 6] for M-Sb alloys). In the transition from the pure alkali metal to the octet composition, the structural changes are considerable due to the big differences in the electronic structure of a metal and an ionic system. At the octet composition, a prepeak as a signature of structural order on length scales larger than the nearest neighbor distance is observed in the total static structure factor, $S(Q)$, with Q being the modulus of the wavevector transfer. The prepeak persists up to the equiatomic composition, with only small changes in $S(Q)$. Reverse Monte-Carlo (RMC) simulations are often used for a qualitative discussion of experimental structure factors. However, for a quantitative understanding of the atomic structure the interatomic

potential plays an essential role. Therefore it is not surprising that the partial radial distribution functions $g_{ij}(r)$ of liquid KSb obtained by RMC [7] and *ab initio* molecular dynamics simulations [8] differ considerably on a quantitative level.

The conclusion of this disagreement is that the interatomic forces are not sufficiently represented in $S(Q)$ to allow a unique access to the structural properties. Measurements of partial structure factors would improve the situation, but these experiments are extremely difficult. Another approach to understand structural arrangements in these liquids and at the same time gain insight into the atomic interactions is to measure dynamic properties, e.g. the vibrational spectrum or the dispersion of the collective excitations, and combine this information with that obtained from $S(Q)$. In previous studies on the atomic dynamics of liquid Rb-Sb [9] and Na-Sn [10] alloys we have shown that these properties can be extracted from measurements of the total dynamic structure factor, $S(Q, \omega)$, which is the spectrum of the time-correlation function of density fluctuations, weighted by the concentration and scattering power of the individual species. $\hbar\omega$ is the energy transfer and ω the respective frequency. Here we present results from inelastic neutron scattering experiments on liquid $\text{K}_x\text{Sb}_{1-x}$. We will compare dynamic properties of this alloy to results obtained from the investigation of other members of this type of liquid alloy and study the mass effect of the alkali metal atom on the dynamics. Thus we will contribute to a more systematic and conclusive picture on the structure and dynamics in these liquid alloys.

2 Experiment and data treatment

The samples were prepared from the pure elements, weighed and mixed in a glove box under an Ar atmosphere. To avoid chemical reactions during the experiment the samples were synthesized in corundum ampullae at temperatures well above the melting point before they were filled into Nb containers with a wall thickness of 0.2 mm. Finally the containers were

sealed by electron beam welding. K_xSb_{1-x} -samples of the following concentrations were prepared: $x=0.90, 0.75, 0.50$ and 0.33 .

Inelastic neutron scattering experiments were performed at the cold neutron time-of-flight spectrometer IN6 at the High Flux Reactor of the Institut Laue-Langevin in Grenoble. We used an incident neutron energy of 4.75 meV. The detector bank covered scattering angles θ between 11° and 113° . The measurements were carried out at temperatures well above the melting temperatures, for all samples at $T=1120K$ and for the lower melting compositions ($x=0.90$ and 0.50) additionally at $T=920K$. We will present here only the results for $T=1120K$.

The measured spectra were corrected for background, empty container, self-absorption of the sample and detector efficiency. A vanadium spiral with the same geometry as the sample was used to normalize the data to the incoming flux. Multiple scattering has been subtracted using the Monte Carlo program MSCAT [11]. The input model for $S(Q, \omega)$ was derived by fitting the experimental data with a model and extrapolating the parameters to cover the required dynamical range. Finally, the obtained $S(\theta, \omega)$ were transformed into $S(Q, \omega)$ by spline fits of $S(Q, \omega = const.)$. A more detailed description of the data treatment procedure is given in [12].

3 Results

The total $S(Q, \omega)$ of a binary system contains contributions from the partial dynamic structure factors, $S^{ij}(Q, \omega)$ ($i, j=K, Sb$), which reflects the collective dynamics, and from the self-parts of the dynamic structure factors, $S_s^i(Q, \omega)$ ($i=K, Sb$), describing the single particle dynamics. For all concentrations, the latter have a very small weight due to the small incoherent scattering cross-sections of K ($\sigma_{inc}^K = 0.27barn$) and Sb ($\sigma_{inc}^{Sb} < 10^{-2}barn$), compared to the respective

coherent scattering cross-sections, $\sigma_{coh}^K = 1.69barn$ and $\sigma_{coh}^{Sb} = 3.90barn$. Thus, the measured spectra contain mainly contributions from $S^{ij}(Q, \omega)$ with a continuously changing, concentration-dependent relative weight.

With the present experiment, the dynamic region around Q_p , the position of the principal peak of $S(Q)$, is accessed. This region is already far away from the hydrodynamic limit. Theoretical models of $S(Q, \omega)$ for binary systems in this Q -range are not fully developed but would involve a larger number of parameters than acceptable for a fit to experimental data. Therefore it is appropriate to study the dispersion of dynamic modes in terms of the maxima of the longitudinal current correlation function $J_l(Q, \omega) = (\omega/Q)^2 S(Q, \omega)$. Cuts of $J_l(Q, \omega)$ at constant Q as a function of composition are shown in Fig. 1. While for $x=0.90$ there is one sharp maximum in each constant Q spectrum, the shape of the function becomes more complex with increasing content of Sb. For $x=0.50$ and $x=0.33$, some of the spectra exhibit two distinct maxima. The dispersion curves obtained by plotting the positions of the maxima of $J_l(Q, \omega)$ as a function of Q are shown in Fig. 2. The position of the minimum of $\omega_m(Q)$ is closely related to the shift of Q_p of $S(Q)$ with composition [5]. As mentioned above, the biggest change in $S(Q)$ is observed between the pure alkali metal and the octet composition. This is followed by a wide range of Sb richer compositions where the position of the main peak of $S(Q)$ is almost unchanged. Consequently, the minimum of the dispersion is shifted considerably on the alkali-rich side but only little for alloys with $x < 0.75$. However, on the Sb-rich side the dispersion is split, similar to observations made in liquid Na-Sn alloys [10].

The total vibrational spectrum $z(\omega)$, that is again a concentration and scattering cross-section weighted average of the corresponding partials $z^i(\omega)$ ($i=K, Sb$), can be obtained by using an extrapolation scheme proposed by Egelstaff and Schofield [13]

$$z(\omega) = \lim_{Q \rightarrow 0} \frac{\omega^2}{Q^2} S_s(Q, \omega) \quad (1)$$

In Ref. [9] we have discussed how to approximate $S_s(Q, \omega)$, that contains only single particle motion, by the experimental $S(Q, \omega)$, and technical aspects of the application of the extrapolation scheme. In summary, coherence effects in $S(Q, \omega)$ are small at large Q and ω . At intermediate Q and ω , as accessed in the experiment, the interference effects from coherent scattering are averaged out by fitting a regression line to $(\omega/Q)^2 S(Q, \omega)$ at constant ω over the full experimental Q range followed by an extrapolation of the regression line to $Q=0$. This approximation gives reasonable results at high frequencies, but fails at small ω (<5 meV) due to the strong coherence effects and the limited experimental Q range.

The application of the extrapolation scheme yields the vibrational spectra $z(\omega)$ for the K-Sb alloys (Fig. 3). There is a clear change of the spectral weight toward higher frequencies with increasing Sb concentration. Again, the biggest change is on the alkali-rich side.

4 Discussion

The unusual behavior of the dispersions $\omega_m(Q)$ (Fig. 2), compared to those of so called simple liquids, can be interpreted in analogy to studies of similar systems [14, 10]. If Sb is added to liquid K, charge transfer takes place. The transition from metallic to ionic regime is accompanied by a considerable volume contraction [15] due to shorter interatomic distances, which is reflected by the shift of the principal peak of $S(Q)$ and of the dispersion minimum to larger Q . Formation of strong K-Sb bonds [8] also causes a shift of the dispersion, still dominated by the K-K correlations, toward higher frequencies. Beyond the octet composition, the Sb-Sb correlations become more visible due to the larger weight of the corresponding partial

correlation function, $S^{SbSb}(Q, \omega)$. For these Sb-rich compositions, two dispersion branches are observed at Q around and larger than Q_p .

A similar splitting of the dispersion has been observed in liquid Na-Sn [10] but not in liquid Rb-Sb [14] alloys. As in the former system, the relative frequencies of the two branches observed here for $x=0.50$ and $x=0.33$ scale roughly with the square root of the inverse mass ratio ($\sqrt{M_{Sb}/M_K} = 1.5$) if the high frequency branch is assigned to motions of the lighter K ion and the lower branch to the heavier Sb ion. Also, it seems that at large Q the frequencies of the two components are decoupled and largely independent of the K - Sb interaction. Note that for $Q > 2.5 \text{ \AA}^{-1}$ the high frequency branches are very similar for the different alloys and that they are much less dispersive than at lower Q . Regarding the Rb-Sb system, it seems plausible that this splitting of the dispersion is not observed due to the rather small mass difference.

Another interesting feature is the presence of a broad second maximum in $J_l(Q, \omega)$ of the sample with highest Sb concentration ($x=0.33$) already at $Q=2 \text{ \AA}^{-1}$, which indicates the presence of an optic-like mode. This mode could be caused by vibrations of K ions out of phase with those of Sb ions, which would follow the discussion in [10]. However, in the frequency range around 15 meV there is another mode that could have some influence, the vibrations between covalently bonded Sb ions. In Fig. 4, the partial frequency spectra $z^i(\omega)$ obtained from *ab initio* simulations [8] are compared to the total $z(\omega)$ from the present experimental data. Fig. 4 clearly shows that both peaks contribute to the frequency range around 15 meV : the peak of $z^K(\omega)$ and the high frequency peak of $z^{Sb}(\omega)$, that is assigned to vibrations within the polyanionic chains [8]. In the total $z(\omega)$ the two contributions cannot be distinguished. From Fig. 3, there is only weak evidence for the high frequency band in $z(\omega)$ indicated by the increase of spectral weight around $\omega = 17 \text{ meV}$ with increasing Sb content. A more convincing

experimental evidence for the high frequency mode has been given for Rb-Sb alloys [9] where due to the higher mass of the alkali ion the frequency band of Rb does not overlap considerably with the high frequency band of Sb and the latter appears as a clear shoulder in $z(\omega)$.

The low frequency band of $z^{Sb}(\omega)$ around 5 meV cannot be extracted using the extrapolation scheme since the coherence effects are too strong in the small ω range. However, the presence of this band is indicated by the lower dispersion branch of $\omega_m(Q)$ for $x=0.50$ (Fig. 2) that has been assigned to the motions of Sb ions and has its minimum in the right frequency range. The respective high frequency branch is observed around 15 meV which is consistent with peak in $z^K(\omega)$.

5 Conclusion

With the present study we have extended a systematic investigation of the atomic dynamics of *Zintl*-type binary liquids. By comparison of the three systems studied so far it is concluded that if the mass difference of the components is large enough a splitting in the dispersion is observed. The high frequency branch is assigned to optic-like out-of-phase motion of the lighter cation against the anions, whereas the lower lying branch has its origin in the slower motions of the heavier anions. The vibrational spectra of the Sb-rich alloys show weak evidence of a high frequency mode, that was observed in computer simulations and in liquid RbSb, and that indicates the presence of covalent bonds between the anions. There is a reasonable agreement with simulation results. Finally, the combination of static and dynamic measurements supported by *ab initio* simulations allow us to understand the fundamental mechanisms that lead to the unusual properties of these highly interesting liquids.

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Figure captions

Figure 1: Longitudinal current correlation function $J_l(Q, \omega)$ of liquid K_xSb_{1-x} at $Q=2.0 \text{ \AA}^{-1}$ and $Q=2.5 \text{ \AA}^{-1}$, $T=1120K$, as a function of concentration.

Figure 2: Dispersion $\omega_m(Q)$ from the maxima of the current correlation function $J_l(Q, \omega)$.

The error bars depend on the width of the peaks and are generally larger towards higher frequencies, where the peaks become broader and noisier.

Figure 3: Vibrational frequency spectrum $z(\omega)$ of liquid K_xSb_{1-x} at $T=1120K$ as a function of concentration. Typical error bars are indicated for $x=0.33$.

Figure 4: Comparison of the vibrational frequency spectra $z(\omega)$ for (a) $x=0.75$ and (b) $x=0.50$ with the respective partial spectra obtained from computer simulations [8]. All spectra are normalized to unit area.