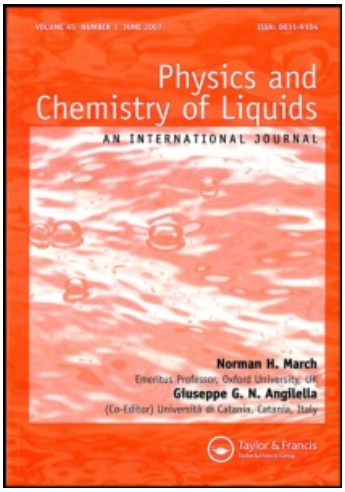


**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Structure of Liquid Cu-Pb Alloys

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**To cite this Article** Mudry, S.(1996) 'Structure of Liquid Cu-Pb Alloys', Physics and Chemistry of Liquids, 32: 4, 239 — 244
**To link to this Article: DOI:** 10.1080/00319109608030539
**URL:** http://dx.doi.org/10.1080/00319109608030539

*Phys. Chem. Liq.*, 1996, Vol. 32, pp. 239–244
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# STRUCTURE OF LIQUID Cu-Pb ALLOYS

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*(Received 5 March 1996)*



Liquid Cu-Pb alloys containing 14.7; 34.5; 40 and 67 at.% Pb were investigated by means of X-ray scattering method. Temperatures at which structure factors were measured are corresponding to one phase region on the phase diagram. Analysis of the structure factors and calculated pair correlation functions may possible to conclude that tendency to microsegregation is most pronounced at 34.5 and 40 at.% Pb.

*Keywords:* Structure factor; miscibility; short range order.

## INTRODUCTION

Considerable interest has been expressed recently in materials that exhibit liquid miscibility gap. This interest is based on the possibility to obtain the materials with valuable properties by changing the solidification conditions. For example, solidification under microgravity allows to avoid the gravity induced sedimentation of the more dence immiscible phase. System Cu-Pb belongs to such systems and due to its small miscibility gap and significant difference of the first peak positions of $S(k)$ is convenient subject for structural study. According that if the mixing of components yields solution of atoms, the $S(k)$ should be significantly transformed. If the solubility is not large, the structure factor of melt will exhibit the features of both components. Thus some interesting structures may appear when such elements as Cu and Pb are mixed together.

## EXPERIMENT

X-ray investigation of the structure was carried out by using of high temperature diffractometer with horizontal honiometer and graphite monochromator installed in the scattered beam. For the sufficient resolution of the intensity curve versus scattering angle and to reach the optimal values of $r_{max}$ needed in Fourier transformation, Cu-$K_\alpha$ radiation was used.

The samples were prepared by arc melting method in argon atmosphere. The measuring of intensity was done with accuracy better than 2%. The temperature was maintained with accuracy of 2 K in the high temperature chamber. The step width was between 0.25° and 0.5° in $k$-region $1.0 < k < 8\text{Å}^{-1}$. The measured values of intensities were corrected taking into account palaryzation, absorption factors and incoherent scattering [1].

The macroscopic densities needed for the evalution were not available and they have been calculated from the densities of pure components.



## RESULTS AND DISCUSSION

Figure 1 shows the structure factors obtained for liquid alloys containing 14.7; 34.5; 40 and 67 at.% Pb. The investigation of melts was done at

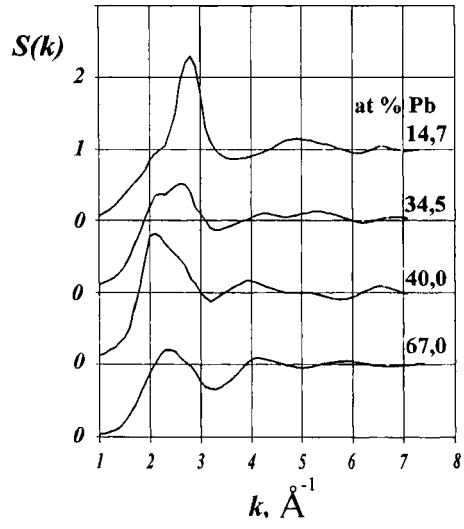


FIGURE 1 Structure factors for liquid Cu-Pb alloys.

temperatures of about 5 K above the corresponding liquidus temperatures and at more higher temperatures. As it can be seen from Figure 1 the main peaks of the $S(k)$ shows the anomalous shape. For liquid alloy containing 14,7 at.% Pb position of first peak of $S(k)$ is closer to that of pure Cu than for Pb. Left hand side of $S(k)$ pronounces the shoulder whose position is similar to that of pure Pb. Second maximum is shifted to large $k$ side and is corresponding with one for pure Pb. Influence of Cu is pronounced in the broadened right hand side of the second maximum. When temperature is rising to 1368 K the principal peak decreases and shoulder on its is more smoothed. Right hand side of the second maximum is more broaded and has the same position that for previous melt.

Significantly different shape of the $S(k)$ is characteristic of molten alloy with 34.5 at.% Pb. First maximum is broaden and consists of two subpeaks, positions of which are differently shifted correspondingly to main peak positions of pure Cu and Pb. More pronounced is subpeak of Cu but its position is shifted to smalled $k$ and these facts can be interpeted as an evidence of existence of Cu-like groups of atoms soluted by atoms of Pb. Position of subpeak of Pb is the same that in pure lead and one can conclude that Pb-like short range order exist in microdomains, where like atoms tend to pair as a nearest neighbours. With arising of temperature the fraction of Pb-like groups of atoms decreases and structure is more similar to that of Pb and Cu solution. $S(k)$ for liquid alloy with concentration of 34.5 at.% Pb has some features on the second maximum, which is wide and also shows two subpeaks with positions corresponding to ones of pure Cu and Pb.

Adding of Pb to 40 at.% leads to reduction of the assymetry of the main peak of $S(k)$. Nevertheless small shoulder exists on the right hand side and its position is corresponding with principal peak for pure Cu. First maximum is significantly shifted to lower $k$ values. Second maximum is also splited but more pronounced peak has the same position that pure Pb. Slightly smeared subpeak is located at 5.3 $\mathring{A}^{-1}$ i.e. near the position of the second peak of Cu. Thus although the concentration of Pb is only 40 at.% and smaller than equiatomic composition its influence on the structure factor is more significant than Cu. When temperature is increased to 1373 K the first peak shows the same position and its height is less. Features of the second maximum in the spliting confirm the suggestion about unchanging of this structure out the miscibility gap.

With further adding of Pb up to 67 at.% Pb that is corresponding to boarder point of miscibility gap, structure factor show low height of the main maxima and large width. Assymetry is not so large as in previous melt, but significant width of the first peak may possible to consider this

structure factor as an additive sum of $S(k)$ for components. Position of the first peak maximum is equal 2,5 $\mathring{A}^{-1}$, that is close to corresponding value obtained in assumption of statistical distribution of atoms. Position of the second peak is also more similar to that of pure Pb than for Cu and its shape is not so asymmetrical. Slight shoulder on the right hand side is influenced by the main peak of copper. The temperature increasing to 1313 K does not significantly change the features of $S(k)$ and as result tendency to mixing of unlike atoms met with some difficulties to form molten alloy with statistical distribution of atoms.

Pair correlation functions $g(r)$ calculated by Fourier transformation of structure factors are presented in Figure 2. The coordination numbers were determined by taking twice the area of peak between the low $r$ side minimum and the maximum of the radial distribution function. The distance $r_1$ of nearest neighbours was determined from pair correlation functions. The values $r_{st}$ in assumption of statistical distribution of both kinds of atoms, which follows from

$$r_{st} = C_1 r_1 + C_2 r_2 \tag{1}$$

where $C_1$; $C_2$ are atomic fractions of Cu and Pb respectively, $r_1$ and $r_2$-their coordination radii.

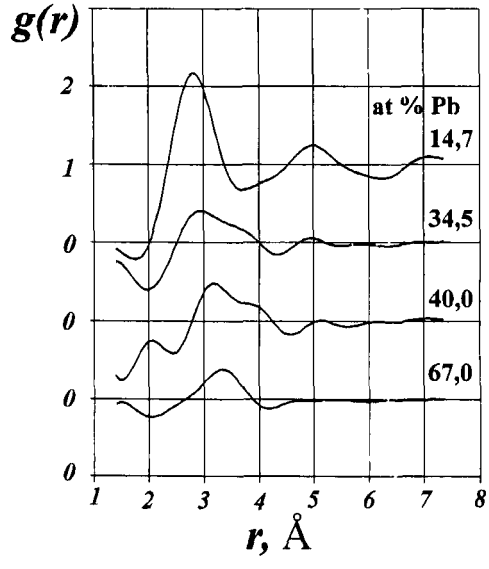


FIGURE 2 Pair correlation functions liquid Cu-Pb alloys.

For concentrations 14,7 and 67 at% Pb experimental values of $r$ are larger than corresponding calculated data. We must note there that difference $r_{exp} - r_{st}$ is significantly large (0.37 Å for melt containing 14,7 at.% Pb and 0,57 for liquid alloy with 67 at.% Pb). Hence the suggestion about preferred existence of like atom groups is confirmed by this comparision. Such comparing was not done for other concentrations because their principal peaks are wide and smeared showing two subpeaks. For liquid alloy containing 34,5 at.% Pb one can observe two subpeaks whose positions are larger than for liquid components. The similar features exist in the principal peak for melt with composition of 40 at.% Pb, but in this case resolution of subpeaks is better. The first peak corresponding to structure of Cu-enriched microdomains is displaced to large $k$ values. The second subpeak is shifted in the same direction and we may connect it with increasing of interatomic distances due to soluted atoms of Cu in Pb.

Liquid alloys containing 14,7; 40 and 67 at.% Pb were investigated also at 100 K above first temperature. The structure factor obtained at this temperature for liquid alloy with 14,7 at.% Pb shows the less pronounced shoulder on the left hand side and reduction of the principal peak height compared to the that near the liquidus curve. Position of the main peak is unchanged and show that structural disordering upon heating is not significant. On other hand for liquid alloy containing 40 at.% Pb increasing of the temperature lead beside broadening of the peak also to its shift to right hand side. This fact may possible to suggest that alloy, whose concentration is close to critical point of miscibility is more sensitive to temperature than other alloys. This suggestion is confirmed by small difference between main peaks of the structure factors at different temperatures for melt 67 at.% Pb. It is well known that main physical reason of miscibility in liquid state are large size factor and small electronegativity difference. According [2] they are equal 23,9 and 0.45 correspondingly. Thus so large size factor is responsible for the difficulties when atoms of different kind attempt to be soluted.

Liquid alloys of these system were investigated with using of neutron diffraction method [3, 4]. It was shown that tendency to microsegregation is most strong near the critical point /35 at.% Pb/. In [5] the copper-lead melts were investigated by measuring of electroresistivity and comparing it with one calculated from structure factors. The concentration dependence of the resistivity presented in this paper show the positive deviation from ideal behaviour.

Calculated resultes show the sharp increasing of resistivity when Pb is added to Cu in the range 0–20 at.%. Experimental results on

electroresistivity show also increasing of resistivity in the same region but its slope is not so large. It is clear that influence of Pb on the structure of Cu is more significant than vice versa. In the range coresponding to miscibility gap resistivity varies more slowly. Thus results on risistivity calculation are in accordance with presented in this paper structural data.

Interesting model, based on cluster of four atoms was used to describe the structure of Cu-Pb liquid alloys in [6]. It is shown that these alloys belong to self coordinated systems.

## CONCLUSION

The X-ray investigation of the short range order in liquid Cu-Pb alloys near two phase region show that they are characterised by prefering of like atoms pair. On the left edge of the miscibility gap in phase diagram Cu-Pb /14,7at.% Pb/ structure factor shows the influence of Pb-atoms on the atomic arrangement and as result structure of this melt may be described as a mixture of liquid solution Pb in Cu and Pb-like atom groups. With adding of Pb to 34,5 at.% like atom structure is most pronounced. In many respects the similar arrangement of atoms is characteristic of liquid melt with 40 at.% Pb. For these two alloys two interatomic distances, significantly larger than in pure liquid components determines the structure at all. Liquid alloys concentration of which is corresponding to right hand edge of miscibility gap has a Pb-like structure in which atoms of Cu are soluted in matrix of Pb.



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