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X-RAY INVESTIGATIONS ON MOLTEN Bi-Pb ALLOYS

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Using X-ray diffraction, structure factors and pair correlation functions of molten Bi-Pb alloys were determined. As well the calculated Debye temperatures as the partial pair correlation functions obtained with the concentration method indicate that alterations of the short range order due to a reduction of unlike atomic pairs with rising temperature take place. Moreover, the properties of the melt dependent on temperature can be explained if the existence of associates like the peritectically melting ϵ -phase is assumed.

KEY WORDS: X-ray diffraction, molten Bi-Pb alloys, short range order.

INTRODUCTION

The phase diagram of the binary system Bi-Pb given in Figure 1 shows a rather deep eutectic point in the neighbourhood of the equiatomic concentration. The eutectic is build up from bismuth with only a small part of soluted lead and the peritectically melting ϵ -phase. Because the peritectic reaction takes place 140 K below the melting point of lead the shape of the liquidus is hardly influenced by this phase. As can be seen from Figure 2 the system Bi-Pb has a nearly symmetric negative heat of mixing curve ΔH^M [2]. The deviation of the quantity $\Delta H^M/c_{\text{Bi}}c_{\text{Pb}}$ (c_i -atomic fraction of the species i) from the linear behaviour indicates that an arrangement of unlike atomic pairs is preferred in the melt. Structure induced pseudo gaps in the electronic density of states of liquid and amorphous Bi-Pb alloys [3] were studied by means of photoelectron spectroscopy. The pseudo gap near the Fermi energy gets less pronounced from the amorphous to the liquid state and disappears within the liquid state with rising temperature.

The specific excess volume of liquid Bi-Pb alloys at $T = 350^\circ\text{C}$ is positive and has a maximum in the range of the ϵ -phase [4]. In Figure 3 the density of the eutectic melt in dependence on temperature [5] is drawn. A remarkable density change occurs in the precrystallisation range above the eutectic line.

An explanation of this behaviour is based on the assumption of temperature depending association phenomena. With increasing temperature the part of associated atoms lowers and therefore the temperature dependent properties of the melt are

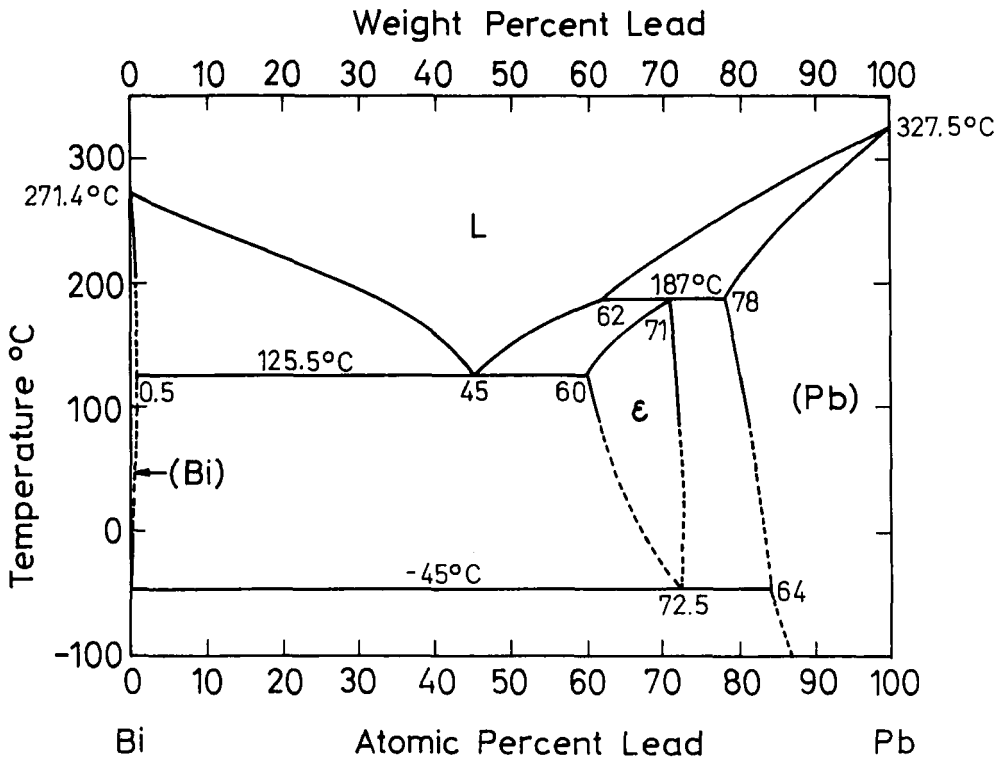


Figure 1 Phase diagram of the system Bi-Pb [1].

influenced. The question arises, what kind of associates are formed in molten Bi-Pb alloys, either atomic arrangement according the ϵ -phase or a specific equiatomic arrangement as could be concluded from the minimum of the $\Delta H^M/c_{\text{Bi}}c_{\text{Pb}}$ -curve near the equiatomic composition.

In order to get more informations about the nature of the associates in the eutectic region and about the influence of the temperature on the short range order X-ray investigations on molten Bi-Pb alloys have been done.

EXPERIMENT AND METHOD

The scattering intensities of liquid Bi-Pb alloys were measured with a θ - θ -diffractometer described in [6]. After the usual correction and normalization procedure the structure factor in the Faber-Ziman-form [7] was calculated from the coherent scattering intensity per atom I_a^{coh} :

$$S(Q) = \frac{I_a^{\text{coh}} - [\langle f^2 \rangle - \langle f \rangle^2]}{\langle f \rangle^2} \quad (1)$$

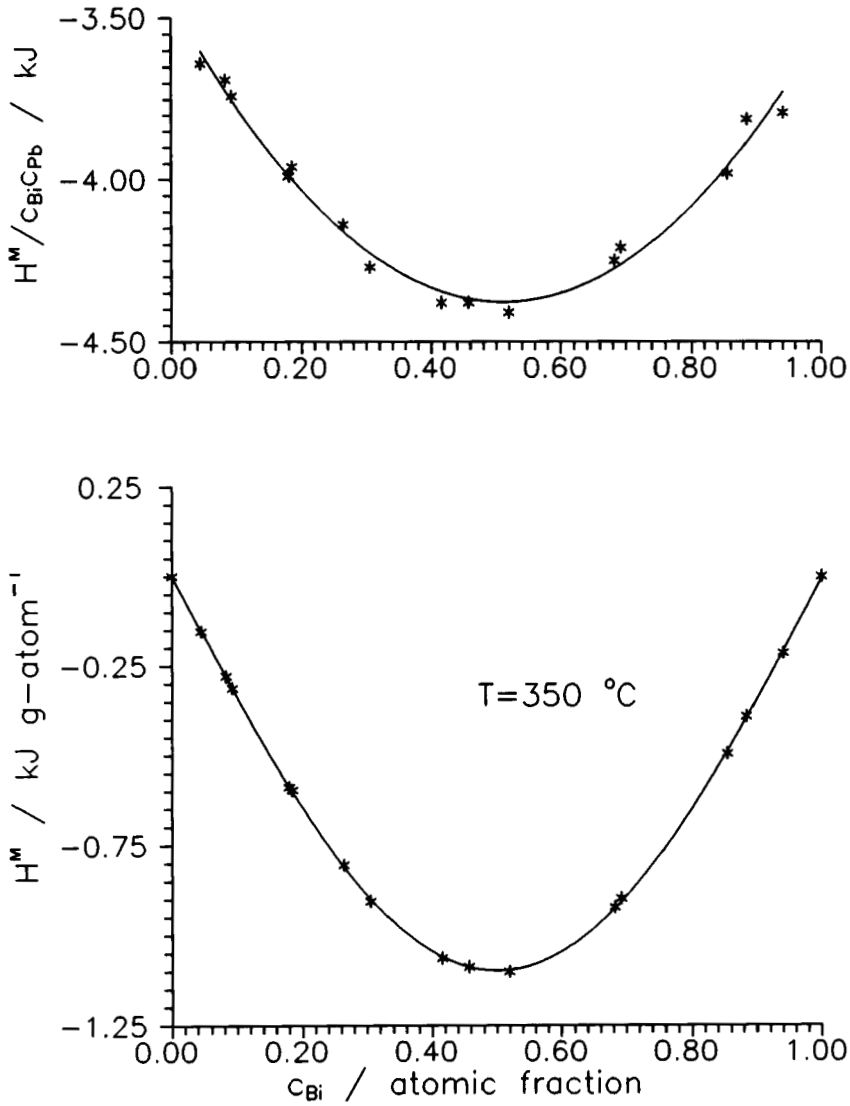


Figure 2 Heat of mixing of liquid Bi-Pb alloys [2].

$$\langle f^2 \rangle = c_1 f_1^2 + c_2 f_2^2$$

$$\langle f \rangle^2 = (c_1 f_1 + c_2 f_2)^2$$

Here $Q = (4\pi/\lambda) \sin\theta$ denotes the magnitude of the momentum transfer, while f_i and c_i refer to the atomic scattering factor and to the atomic fraction of the species i , respectively.

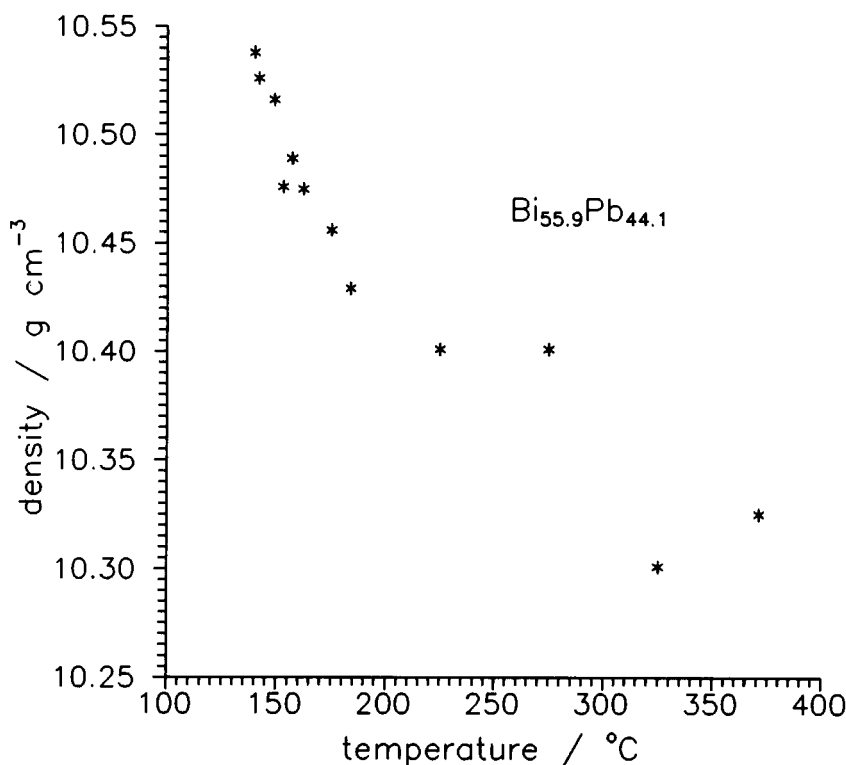


Figure 3 Density of the eutectic Bi-Pb melt as function of temperature [3].

The structure factor of a binary system is the weighted sum of the partial structure factors $S_{ij}(Q)$ according to the following equation:

$$S(Q) = \sum_{i=1}^2 \sum_{j=1}^2 w_{ij} S_{ij}(Q) \quad (2)$$

$$w_{ij} = \frac{c_i c_j f_i f_j}{\langle f \rangle^2}$$

If three independent experiments with different scattering lengths of the species i and j are not available, the concentration method is the only one to calculate partial structure factors. The use of the concentration method presupposes, that the partial structure factors are independent on the concentration of the alloys. This assumption is valid in melts with a nearly statistical distribution of the atoms, but not in a melt in which the preference of an associate-like atomic arrangement is expected. In these systems the calculated partial quantities are effected by the choice of the concentration of the investigated alloys. Nevertheless, the concentration method gives informations about the dependence of the short range order on temperature, if the composition of the alloys used for the calculation is unchanged.

The pair correlation function was calculated by the equation

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_o} \int_0^{Q_{\max}} Q[S(Q) - 1] \sin Qr dQ, \quad (3)$$

where ρ_o is the average number density and Q_{\max} the maximum momentum transfer reached in the scattering experiment. If $S(Q)$ is replaced by $S_{ij}(Q)$ the partial pair correlation function $g_{ij}(r)$ follows from Eqn. (3).

RESULTS

Structure Factors and Pair Correlation Functions

The structure factors of the liquid Bi-Pb alloys measured near the liquidus and at $T = 500^\circ\text{C}$ are shown in Figure 4. The shape of the structure factor is only weakly dependent on the concentration and agrees with earlier results of X-ray and neutron scattering investigations on molten Bi-Pb alloys [8]. Visible changes mainly take place on the right hand side of the first maximum, where a shoulder grows with rising fraction of bismuth. Because bismuth and lead have nearly the same atomic radius [9] the positions of the maxima of the structure factor are almost independent on concentration. In contrast, the structure factors undergo significant changes as function of temperature. The height of the maxima increases with decreasing temperature. In Figure 5 the height of the first maximum of the structure factors is drawn. Whereas at $T = 500^\circ\text{C}$ the height of the first maximum continuously changes about the whole concentration range, this function near the liquidus has both, a minimum in the range of the ϵ -phase and a maximum at the eutectic concentration. In order to check whether this feature at low temperature is a physical effect or will only be caused by the different liquidus temperatures the Debye-Waller factor will be considered. According to Sinha *et al.* [10] the structure factor $S_{T_2}(Q)$ at the temperature T_2 can be calculated from the structure factor $S_{T_1}(Q)$ at any temperature T_1 :

$$S_{T_2}(Q) = 1 + [S_{T_1}(Q) - 1] \exp\{-2[w_{T_2}(Q) - w_{T_1}(Q)]\} \quad (4)$$

where $w_T(Q)$ is the Debye-Waller factor:

$$w_T(Q) = \frac{3}{8\pi^2} \frac{h^2 Q^2 T^2}{m_a k_B \theta_D^3} \int_0^{\theta_D/T} \left[\frac{1}{2} + \{\exp(z) - 1\}^{-1} \right] z dz \quad (5)$$

h - Planck's constant
 k_B - Boltzmann's constant
 θ_D - Debye temperature

The only unknown quantity in the expression is the characteristic temperature θ_D which represents the character of the atomic motions in the liquid.

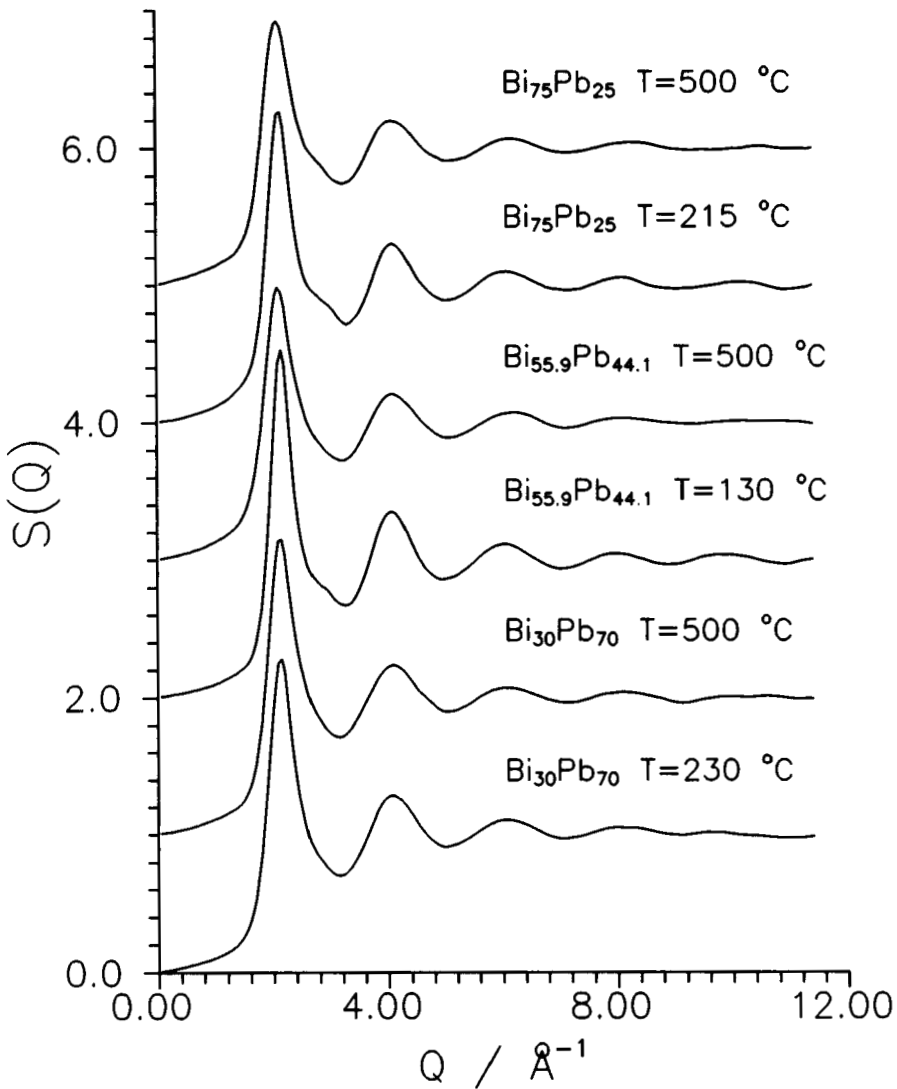


Figure 4 Structure factors of molten Bi-Pb alloys.

The high temperature approximation $\theta_D/T \ll 1$ leads to the equation:

$$S_{T_2}(Q) = 1 + [S_{T_1}(Q) - 1] \exp \left\{ -\frac{3}{4\pi^2} \frac{h^2 Q^2}{m_a k_B \theta_D^2} (T_2 - T_1) \right\} \quad (6)$$

Because the atomic form factor and the atomic mass m_a of bismuth and lead are nearly equal, Eqn. (6) is suitable for determining the Debye temperature of the investigated alloys from the first peak position (Table 1) and the first peak height at

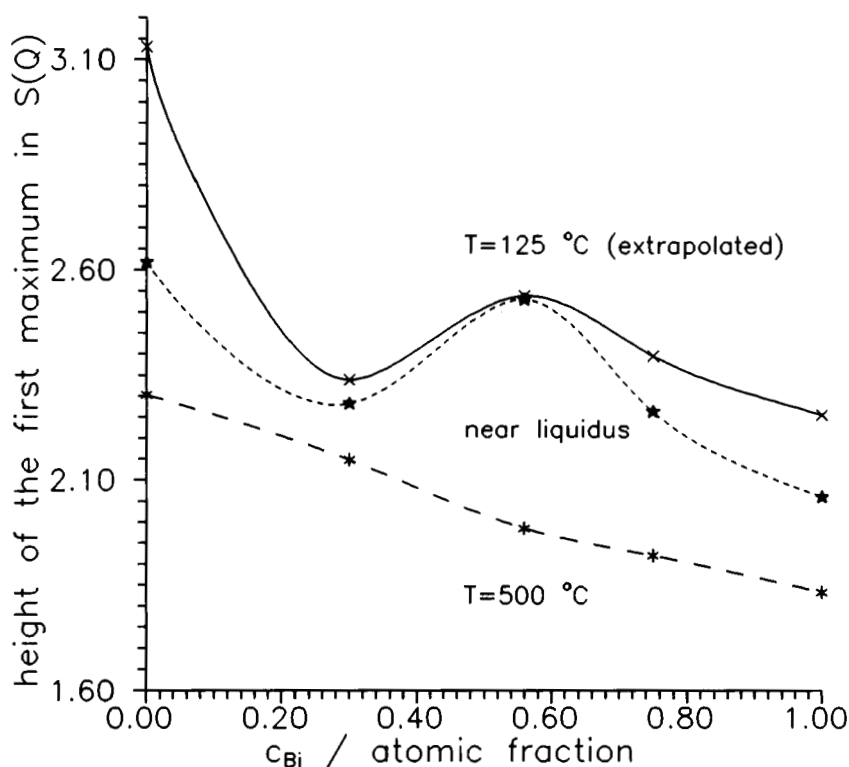


Figure 5 Height of the first peak of the Bi-Pb structure factors at different temperatures (the extrapolated values were calculated with equation (6)).

different temperature (Fig. 5). As can be seen from Table 1 the Debye temperature is constant about the whole concentration range except around the ϵ -phase. Moreover, the curve in Figure 5 obtained by the extrapolation to the eutectic temperature shows only a minimum at the ϵ -phase whereas the maximum at the eutectic concentration vanishes. This means, that the low melting ϵ -phase in any form influences the properties of the melt.

The pair correlation functions in Figure 6 are characterized by a shoulder on the right hand side of the first maximum, which is less-pronounced if the temperature increases. As follows from the variation of the upper integration limit in the Fourier

Table 1 Position of the first maximum in the structure factor and the Debye temperature calculated with Equation (6)

alloy	$Q_1/\text{\AA}^{-1}$	θ_D/K
Bi	2.10	53
Bi ₇₅ Pb ₂₅	2.10	52
Bi _{55.9} Pb _{44.1}	2.15	52
Bi ₃₀ Pb ₇₀	2.15	89
Pb	2.30	53

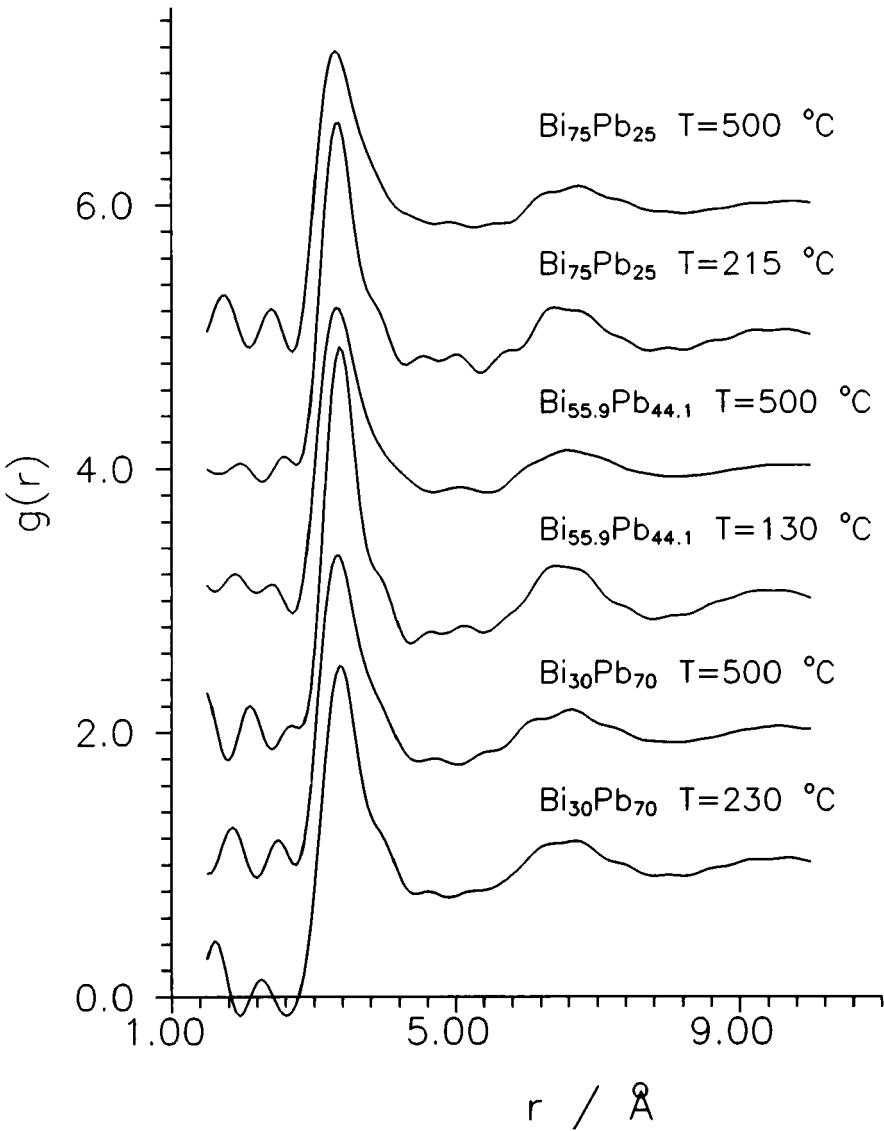


Figure 6 Pair correlation functions of molten Bi-Pb alloys.

integral in Eqn. (3) the shape of the shoulder is influenced by truncation errors whereas the position of the shoulder is nearly independent of them. Moreover, investigations with the energy dispersive X-ray diffraction method [11] have shown, that in the undercooled state just before the solidification a peak appears on this position. Therefore one can assume, that the shoulder on the main peak of $g(r)$ of the molten Bi-Pb alloys corresponds to a coordination sphere.

The dependence of the pair correlation function on the alloy composition is only weak. With increasing concentration of bismuth the height of the first maximum and

the number of nearest neighbours (Table 2) slightly decrease. The alterations as function of temperature mainly occur in the first coordination shell. The height of the first peak in $g(r)$ grows with decreasing temperature. Consequently, the number of nearest neighbours increases by cooling down the melt. All investigated Bi-Pb alloys show a slight decrease of the first distance (Table 2) if the temperature increases.

Concentration Method

Partial structure factors have been calculated using the concentration method. In Figure 7 the partial structure factors obtained from the total structure factors of the alloys $\text{Bi}_{30}\text{Pb}_{70}$, $\text{Bi}_{55.9}\text{Pb}_{44.1}$ and $\text{Bi}_{75}\text{Pb}_{25}$ at $T = 500^\circ\text{C}$ and of those at the temperature near the liquidus are drawn. Therefore the calculated partial functions are averaged quantities in the concentration range from 30 to 75 at-% Bi.

The comparison of corresponding functions shows that mainly the partial Bi-Pb structure factor undergoes alterations with changing temperature. The height of the maxima, especially of the main maximum decreases and the shoulder on the right hand side of the first peak vanishes with rising temperature. Whereas the partial Pb-Pb structure factor also changes as function of temperature the partial Bi-Bi structure factor is nearly independent on temperature in the observed temperature range.

Consequently, alterations with temperature also arise in the partial pair correlation functions drawn in Figure 8. The partial Bi-Pb correlation function near the liquidus has a high first maximum which strongly decreases with increasing temperature (Table 3). In contrast, the first peak of the partial Pb-Pb correlation function grows

Table 2 Distance of nearest neighbours, coordination number of the first shell (N_{\min} and N_{sym} are obtained from integration up to the first minimum and from the first shell assumed to be symmetrical) and the height of the first maximum of the pair correlation function

alloy	$T/^\circ\text{C}$	$r_1/\text{\AA}$	N_{sym}	N_{\min}	$g(r_1)$
$\text{Bi}_{75}\text{Pb}_{25}$	215	3.30	6.7	9.9	2.65
	500	3.30	5.5	8.7	2.17
$\text{Bi}_{55.9}\text{Pb}_{44.1}$	130	3.35	6.8	10.3	2.88
	500	3.30	6.4	9.5	2.17
$\text{Bi}_{30}\text{Pb}_{70}$	230	3.35	7.6	11.3	2.49
	500	3.30	6.6	10.2	2.34

Table 3 Partial distance and partial number of nearest neighbours of the first coordination shell calculated for the eutectic composition as well as the height of the first maximum of the partial pair correlation function

	$T/^\circ\text{C}$	$r_1/\text{\AA}$	N_{sym}	N_{\min}	$g(r_1)$
Bi-Bi	liquidus	3.25	2.9	5.0	2.26
	500	3.25	3.1	5.1	2.10
Bi-Pb	liquidus	3.40	3.3	3.8	3.59
	500	3.35	2.8	2.9	2.20
Pb-Bi	liquidus	3.40	4.1	4.8	3.59
	500	3.35	3.6	3.7	2.20
Pb-Pb	liquidus	3.35	2.9	4.9	2.18
	500	3.35	2.6	4.7	2.49

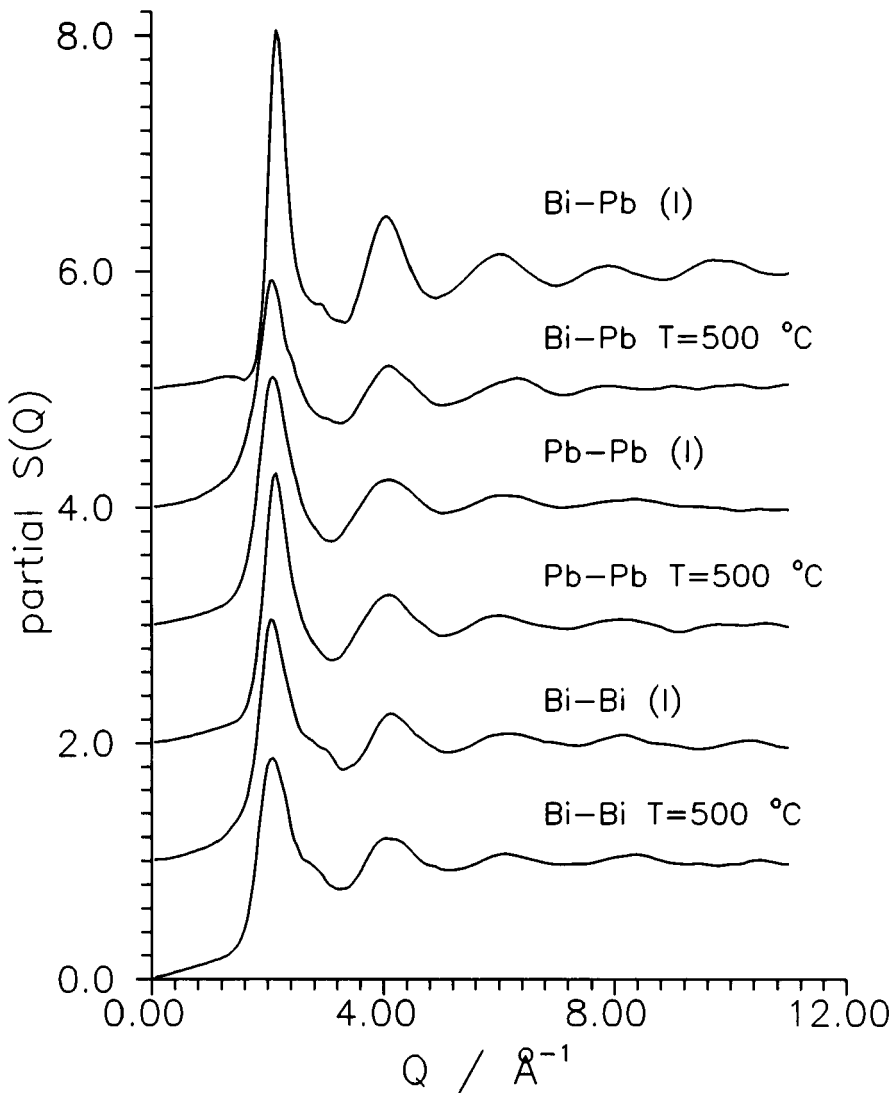


Figure 7 Partial structure factors in the system Bi-Pb calculated with the concentration method (the notation $T = 500\text{ }^{\circ}\text{C}$ and (l) means that the structure factors from Figure 4 at the temperature $T = 500\text{ }^{\circ}\text{C}$ and near the liquidus were used for the calculation).

with rising temperature. As can be seen from Table 3, the number of nearest neighbours of the Bi-Pb correlation significantly decreases with increasing temperature. The same tendency shows the first coordination number of the Pb-Pb correlation, whereas the first coordination number of the Bi-Bi correlation seems slightly to increase. With rising temperature the number of unlike atomic pairs reduces.

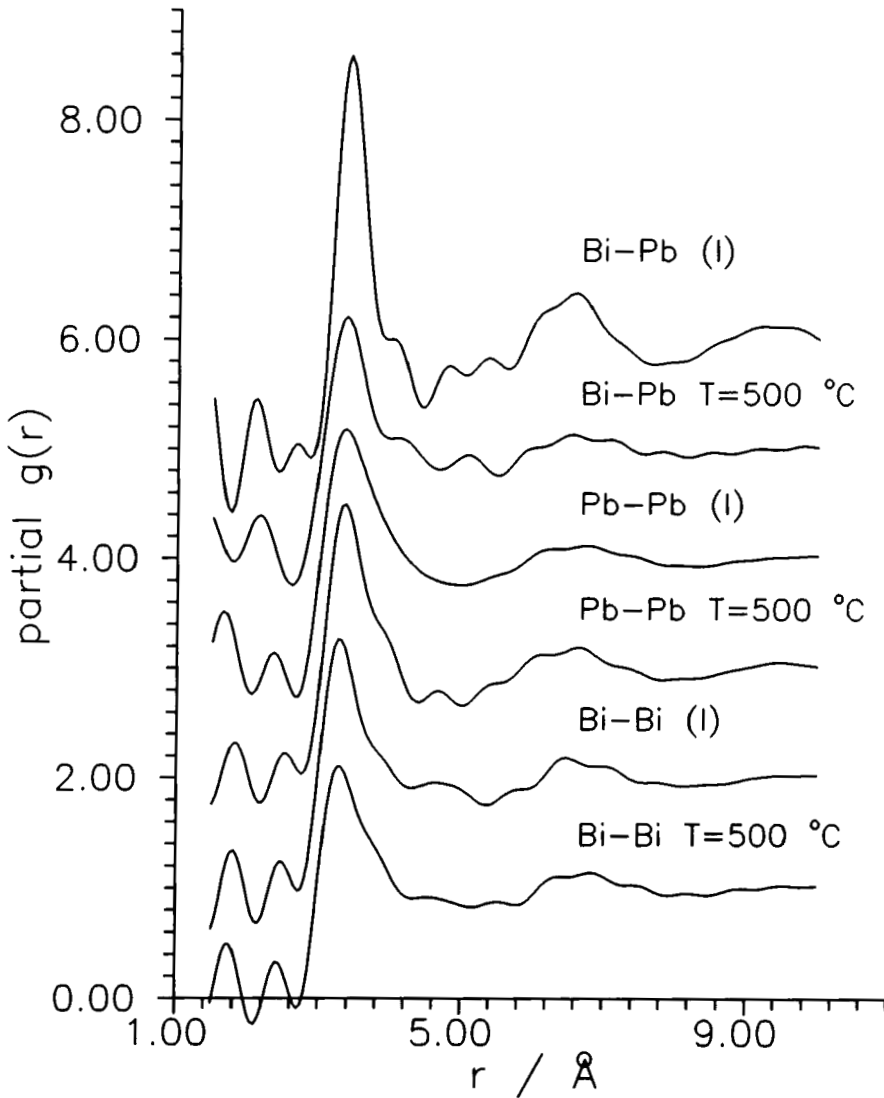


Figure 8 Partial pair correlation functions in the system Bi-Pb.

DISCUSSION

As well the presented results from the scattering investigations as the thermodynamical measurements [2] can be explained if the existence of atomic arrangements with a preference of unlike atomic pairs is assumed. Moreover, the conclusion is entitled that associates with a short range order like the ϵ -phase characterize the melt. With increasing temperature the probability of atomic association decreases with the consequence that the chemical short range order is destroyed and the arrangement of

the different types of atoms approaches a statistical distribution. Because associates like the ε -phase include more Pb-atoms than Bi-atoms a reduction of the fraction of associates mainly leads to an alteration of the partial Bi-Pb and Pb-Pb pair correlation function. In opposite to the decreasing number of Bi-Pb atomic pairs the number of Pb-atoms which contact each other increases with rising temperature. Consequently, a growth of the height of the first maximum of the Pb-Pb pair correlation function is observed. The change of density of the eutectic Bi-Pb melt (Figure 3) is probably caused by the reduction of the coordination number with rising temperature. The great coordination number in the associates leads to a great packing density of the melt at low temperature.

No indications were found that a special eutectic-like associate exists in Bi-Pb melts. On the contrary, the atomic arrangements according the peritectically melting ε -phase also influence the eutectic region. Because near the eutectic line the mean kinetical energy of the atoms is low the associates become especial great stability. Therefore, the atoms ordered in associates and the rest of atoms seem to built up an eutectic like structure which is compareable the solid eutectic. But it is not clear, why at so low temperatures as in the eutectic region an associate like the ε -phase is not the starting point of nucleation. The answer should be given in the dynamic of the melt.

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