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The concentration dependences of molar volume, thermal expansion coefficient, and interdiffusion coefficient for liquid lead–magnesium system

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The coefficients of binary diffusion for liquid lead–magnesium alloys (19.11, 33.45, 52.46, and 83.06 at.% Pb) have been measured at 950 K by a γ-ray attenuation technique. Literature data on the thermal properties of Mg–Pb melts have been summarized. The composition dependences of molar volume, volumetric thermal expansion coefficient, and interdiffusion coefficient in the liquid state have been constructed and discussed.

1. Introduction

Molten eutectic $Pb_{83}Mg_{17}$, along with lead–bismuth eutectic and pure lead, is considered as a promising heat carrier for fast neutron reactors [1]. However, many thermodynamic and kinetic properties of liquid lead–magnesium system are still not sufficiently explored, which considerably hinders an examination of perspectives on the use of liquid eutectic as a coolant. In particular, there is practically no information on the density and mutual diffusion in the binary melts. Meanwhile, these data are essential for a prediction of the heat carrier behavior during the operation of the reactor. Moreover, data on the diffusion coefficients are required for an evaluation of the performance of the coolant circuit during its start-up as well as in an emergency accompanied by the segregation of the binary alloy. In the Institute of Thermophysics (Novosibirsk), the measurements of the density and thermal expansion of liquid lead, magnesium, and a number of Mg–Pb alloys have been made [2–4]. In present work, the results of these studies are generalized and analyzed. Besides, new experimental data on binary diffusion coefficients for the melts at 950 K are presented.

2. Experimental details

To study the mutual diffusion in Mg–Pb melts, the technique that has been used is based on direct investigation of the evolution of composition profile in inhomogeneous liquid sample with γ-rays. Recently, the γ method was applied for the measurement of the coefficients of mutual diffusion in liquid Pb–Sn, Al–Ge, and Bi–Ga alloys [5,6].

The experiments were performed with a γ densimeter, a scheme of which is shown in Fig. 1. A narrow beam (4-mm diameter) of γ quanta of 0.662 MeV energy from a Cs^{137} source with an activity of 50 GBq penetrates through a cylindrical crucible containing the two-component melt. The intensity of transmitted radiation is measured with scintillation counter. The electric furnace can move in vertical direction by means of the lifting gear. This makes it possible to measure the γ-ray attenuation in the liquid sample as a function of a distance between the beam axis and the crucible bottom. During the test, a mechanical stirrer is immersed into the melt and is withdrawn from it through a hole in the cup.

The electric furnace of the γ densimeter has an operating temperature range of 293–1100 K. The temperature of the sample was measured with chromel–alumel thermocouple immersed into the melt. The protective sleeve of the thermocouple abuts on the bottom of the crucible to provide a constancy of horizontal sectional area of the melt column through the height and to realize a one-dimensional process of mass transfer. Four additional thermocouples are placed in a copper thermostating block. They are intended for monitoring the temperature gradients. During the diffusion experiment, the temperature is held constant within 0.3 K by the control system. The calibration of the thermocouples was checked against the crystallization points of pure metals (tin, lead, antimony, and aluminium). The temperature uncertainty was ±1.5 K.

The radiation attenuation in a binary melt with components A and B may be written as [6]:

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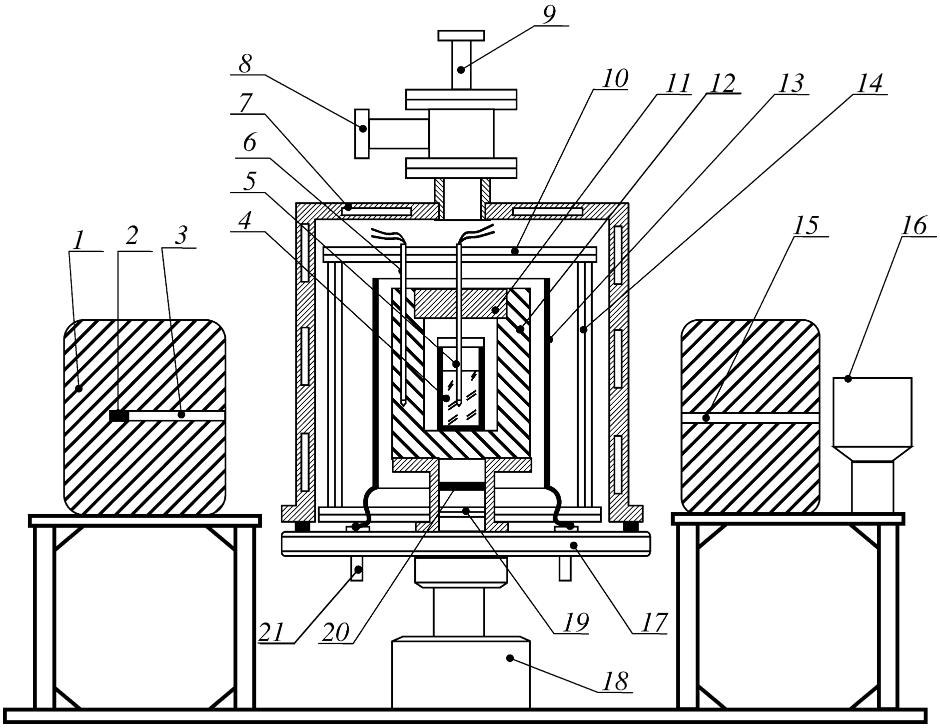

Fig. 1. Basic schematic of γ densimeter. 1 – radiation protection; 2 – γ-ray source; 3, 15 – collimators; 4 – crucible with liquid sample; 5, 6 – thermocouples; 7 – water-cooled body; 8 – flange for gas and vacuum lines; 9 – mechanical stirrer; 10, 14, 19 – heat radiation shields; 11 – cup of thermostating block, 12 – thermostating block (copper); 13 – main heater; 16 – scintillation counter; 17 – water-cooled base; 18 – lifting gear; 20 – additional heater; 21 – current leads.

$$\frac{S_A X(x) + S_B[(1 - X(x)]}{V[X(x)]} = \frac{1}{d} \ln\left[\frac{J_0}{J(x)}\right], \tag{1}$$

where x is the coordinate (height of the beam passage with respect to the crucible bottom), in m; J and J_0 are the intensities of the radiation after passage through the crucible with and without the sample, respectively, in s^{-1}; d is γ-ray attenuation length (the inner diameter of the crucible corrected for beam diameter), in m; $X(x)$ and $V[X(x)]$ are the molar concentration of component A, in mole fraction, and molar volume of the melt at the site of the beam passage, in m^3/mol; S_i (i = A, B) are attenuation sections of the components, in m^2/mol.

With knowledge of concentration dependence of the molar volume, $V(X)$, Eq. (1) enables the determination of the concentration at the site of the beam passage. By moving the crucible in a vertical direction, one can determine the distribution of the components through the height of the melt column [$X(x)$] and its variation with time. For construction of $V(X)$ for Mg–Pb liquid system, the results of studies [2–4] were used (see below).

The γ-ray attenuation sections of the components were measured on solid samples of lead (99.99 mass% pure) and magnesium (99.95 mass% pure) with accurately metered geometric dimensions. The density of the samples was determined by Archimedean method. The S_i uncertainty was no more than 0.15%. The crucibles, their caps, and protective sleeves for thermocouples were made from tantalum. The internal diameter of the crucibles (26–38 mm) was measured to better than 0.1%. The corrections were made for the thermal expansion of the crucible material.

Lead and magnesium used for the preparation of the alloys were first remelted under argon atmosphere. Thereafter, a surface of the ingots was cleaned from the oxides. The weights of the lead and magnesium samples (50–300 g) needed for calculation of mean compositions of the alloys were determined on an analytical balance with an accuracy of 0.01 g. The sample consisting of the two pure components was placed into the crucible so that lead was located in the bottom half of the cell. Before the experiments, the furnace of the γ densimeter was evacuated and was filled with pure argon up to 0.1 MPa. After diffusion test the alloy was reweighed.

A one-dimensional equation of nonstationary diffusion is as follows [7]:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial n}{\partial x}\right), \tag{2}$$

where t is time, in s; D is mutual diffusion factor, in m^2/s; $n = X/V$ is molar density of the component A (in our case, Pb) in the alloy, in mol/m^3. For diffusion over a length L (in our case L is the height of the binary melt column) with boundary conditions $(\partial n/\partial x)_{x=0,L} = 0$ (the sources and sinks at the ends of line segment L are absent), and for constant D, the general solution of Eq. (2) is of the form [8]:

$$n - n_\infty = \sum_{k=1}^{\infty} C_k \exp\left[-\frac{k^2\pi^2 Dt}{L^2}\right] \cos\frac{k\pi x}{L}. \tag{3}$$

Here $n_\infty = X_\infty/V(X_\infty)$; X_∞ is mean composition of the melt, or, in other words, the concentration of the sample at any point after its complete homogenization.

After a lapse of time, the t- and x-dependence of the molar density is described predominantly by the first term of the series expansion (3). Respectively, at long times, the t-dependences of $\ln|n - n_\infty|$ at any point of the melt take the same slope and become linear. The diffusion factor is derived from a slope angle φ of the rectilinear portion of this dependence by

$$D = (tg\varphi) \cdot (L/\pi)^2.$$

The diffusion experiment was done as follows: the compound sample was heated above the melting temperature of magnesium. The melt was stirred as long as the concentration difference through the height of the melt column decreased to 25–30 at.%. Thereafter, the sample was heated to 950 K and the height of the melt column L was determined from sharp jump in the x-dependence of the γ-ray attenuation coefficient on the upper border of the melt. Typical L value ranged from 35 to 50 mm and its uncertainty was ±0.4 mm. In the course of the experiment, the composition and molar density profiles were registered at intervals. In the intervening periods, the relaxation of the molar density was measured at individual points close to the upper and lower borders of the melt. The total time spent for the registration of one composition profile was about 1000 s. In this regard, the obtained profile might not be considered as instantaneous distribution, because during its measuring changes of the concentration and molar density with time proceeded. Besides, in view of the fact that the diameter of γ quanta beam was finite, the concentration was not measured at the points at distances less than 4 mm from the upper and lower melt borders. These features of the measurements needed to be taken into account in the subsequent data treatment. The diffusion test continued as long as the concentration difference through the height of the melt column decreased to 6–10 at.%. The total duration of one experiment was 4–5 h. By this time, the density profile became close to cosine function, and the slopes of the t-dependences of $\ln|n - n_\infty|$ registered at different heights became close to each other.

3. Results

Fig. 2 shows some primary data obtained in the experiments. The results of the treatment of the relaxation curves are given in Table 1. At the close of the diffusion test, the difference between the slopes of the relaxation curves (and hence between D values) obtained near the upper and lower borders of the melt was 2.5–10%. One reason for these discrepancies may be the concentration dependence of interdiffusion coefficient, which was ignored in derivation of Eq. (3). The second reason is related to the fact that actual density profile at the close of the test still slightly differs from cosine distribution (see Fig. 2(b)). The optimal estimate of $D(X_\infty)$ is the average of the experimental results (the last column in Table 1). An analysis made by the procedure [5] shows that the uncertainty of $D(X_\infty)$ is no more than 10%, and the main contribution to the error is connected with neglecting of the highest terms of the series expansion (3). Agreement between the D values (and thus between the relaxation rates) measured near the upper and the lower melt borders substantiates, among other things, the absence of pronounced buoyancy and thermocapillary convection in the layers close to the upper (free) sample surface.

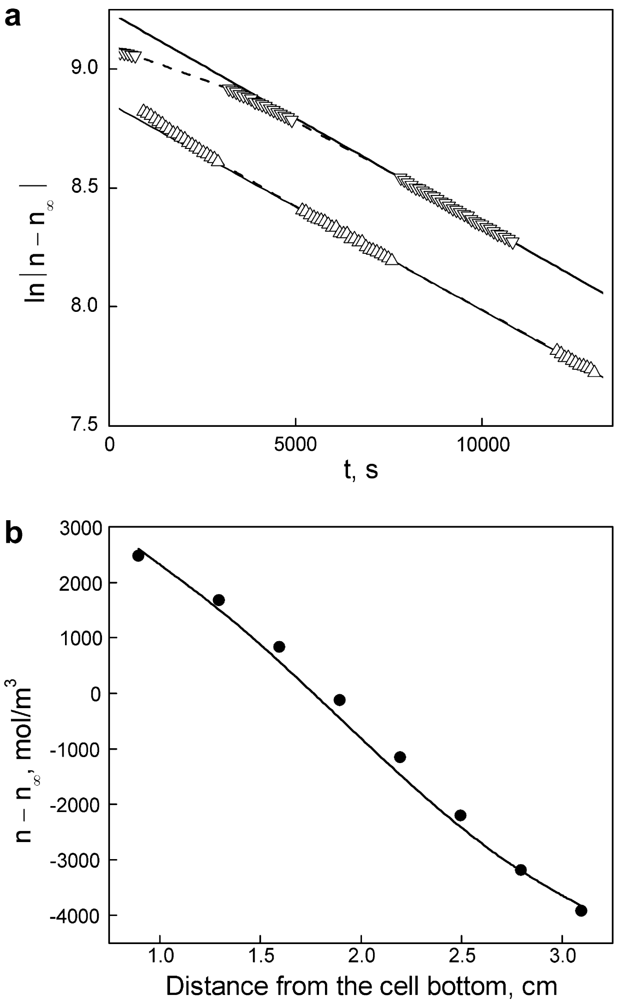

Fig. 2. Results of diffusion experiment with Mg–Pb melt (X_∞ = 19.11 at.% Pb, L = 35.3 mm, T = 950 K). (a) Relaxation of the molar density of lead (in semilog coordinates) at distances 9 mm (up triangles) and 31 mm (down triangles) from the crucible bottom. Solid straight lines are best fits of rectilinear portions of the dependences. (b) Distribution of lead through the height of the melt column at the end of diffusion experiment. The points are experimental data; the line is best fit by the first term of the series expansion (3).

4. Discussion

According to the survey [9], in the lead–magnesium system, there are crystallized two eutectics (19.1 and 83 at.% Pb) and intermediate compound Mg_2Pb (33.3 at.% Pb). In the past, a number of thermodynamic properties of Mg–Pb melts were experimentally investigated: enthalpy of mixing, Gibbs energy of mixing, and thermodynamic activity [10–13]. The concentration dependences of these properties exhibit strong deviations from the laws of ideal solution. The maximal deflections from ideality were observed at concentrations close to the stoichiometric composition Mg_2Pb. The concentration dependence of the resistivity of liquid alloys also peaks in the neighborhood of this composition, and temperature derivative of the resistivity becomes negative [14]. According to current concepts, such behavior of the system is a manifestation of a tendency for compound formation, or, in other words, for chemical short-range ordering (CSRO) in the liquid state [11,15,16]. In the simple chemical–physical theories, the liquid-metal solution with a tendency for CSRO is considered as a mixture of chemical complexes in dynamic equilibrium with the monomers, i.e., the atomic elements (in our case: $Mg_2Pb \leftrightarrow 2Mg + Pb$) [16]. It should be noted that concentration dependences of molar volume V and volumetric coefficient of thermal expansion β for compound-forming liquid systems also have special features [17]. Moreover, an analysis of these dependences provides one of the ways to detect (confirm) the presence of liquid compounds and to determine their stoichiometric compositions [18]. To our knowledge, the construction and examination of the dependences $V(X)$ and $\beta(X)$ was not performed previously for Mg–Pb system because of lack of experimental data.

In Table 2 are presented the summarized results of our previous measurements of density ρ of magnesium [3], lead [2], and their alloys [4] in the liquid state. In the temperature intervals under study, the dependences $\rho(T)$ have no peculiarities and, within the limits of experimental error, they are described by linear expressions (including the melts with concentrations close to the compositions of eutectics and intermediate compound):

$$\rho(T) = \rho(T_L) + (\partial\rho/\partial T)(T - T_L)$$

T_L is liquidus temperature. However, the X-dependences of molar volume and thermal expansion coefficient $\beta = -(\partial\rho/\partial T)/\rho$ for liquid Mg–Pb system constructed by the data of Table 2 show marked

Table 1
Results of diffusion experiments with Mg–Pb melts at 950 K[a]

X_∞, at.% Pb	L, mm	x_1, mm	D_1, 10^{-5} cm^2 s^{-1}	x_2, mm	D_2, 10^{-5} cm^2 s^{-1}	$\langle D \rangle$, 10^{-5} cm^2 s^{-1}
19.11	35.3	9.0	11.0	31.0	11.3	11.1
33.45	33.0	8.2	15.5	28.2	16.8	16.2
52.46	50.8	6.7	10.5	46.7	11.6	11.1
83.06	35.3	7.1	7.1	30.7	6.6	6.8

[a] x_1, x_2 are coordinates of the points, at which the relaxation curves were registered; D_1, D_2 are the interdiffusion factors derived from relaxation data measured at x_1 and x_2; $\langle D \rangle = (D_1 + D_2)/2$.

Table 2
Density data for liquid Mg–Pb alloys

Composition, at.% Pb	T_L, K	$\rho(T_L)$, kg m^{-3}	$-(\partial\rho/\partial T)$, kg m^{-3} K^{-1}	Temperature interval, K
0[a]	922	1557 ± 7	0.243 ± 0.014	922–1080
19.11	742	3773 ± 10	0.554 ± 0.022	742–1000
33.45	820	5256 ± 15	0.769 ± 0.042	820–950
52.46	727	7027 ± 17	0.905 ± 0.028	727–1000
83.06	524	9563 ± 27	1.120 ± 0.020	524–1000
100[b]	600.7	10651 ± 31	1.244 ± 0.037	600.7–1100

[a] Mg 99.95% pure.
[b] Pb 99.99% pure.

extremes at concentrations close to stoichiometric composition Mg_2Pb, see Figs. 3 and 4. Such behavior of the properties is typical of liquid metal systems with a tendency for CSRO [19]. In particular, the fact that maximal volume contraction is at about 33 at.% Pb confirms that just in this region noticeable charge transfer from Mg-ions to Pb-ions takes place (partially salt-like bonding appears), and local chemical order arises.

In Fig. 5 is shown the concentration dependence of interdiffusion coefficient for liquid lead–magnesium system, which is constructed by the data from Table 1. As is seen, this dependence also has pronounced peak near the stoichiometric composition. Experimental information about behavior of interdiffusion factor in liquid–metal systems with CSRO was not found in previous studies. However, the effect of mass-transfer acceleration is well known in heterogeneous liquid solutions with chemically reacting components [20]. It seems likely that in our experiments a similar phenomenon was observed: in inhomogeneous melt with mean concentration close to 33 at.% Pb, in parallel with usual 'physical' diffusion, there also proceeds noticeable 'chemical reaction' ($2Mg + Pb = Mg_2Pb$). This 'reaction' accelerates the rate of the melt homogenization, which appears as an increase in interdiffusion factor.

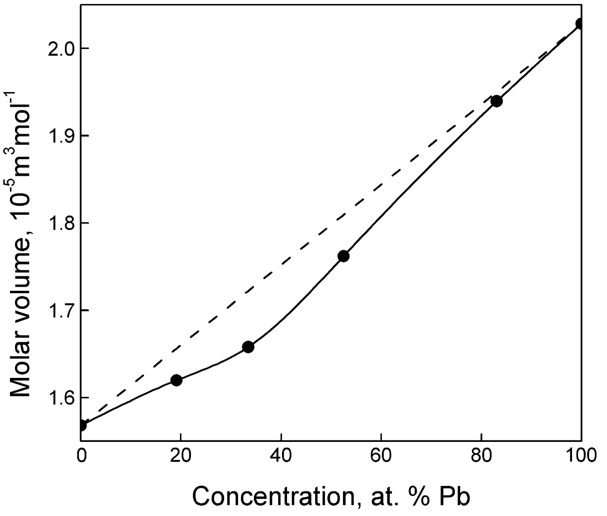

Fig. 3. Molar volume of liquid Mg–Pb system at 950 K as function of composition. The points are data from works [2–4]; solid line is cubic spline connection; dashed line represents the law for ideal solution.

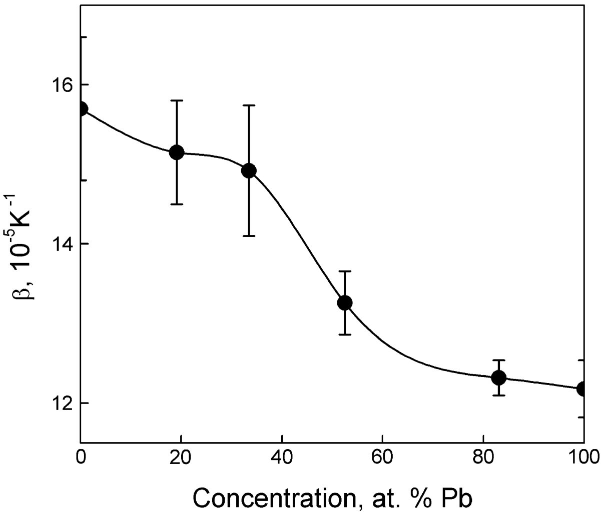

Fig. 4. Volumetric thermal expansion coefficient of liquid Mg–Pb system at 950 K as function of composition. The points are data from works [2–4]; the line is cubic spline connection.

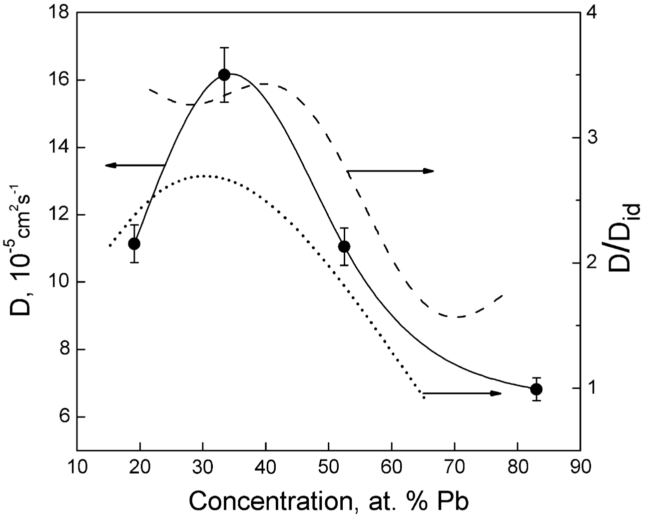

Fig. 5. Interdiffusion coefficient of liquid Mg–Pb system at 950 K as function of composition. The points are data from Table 1; solid line is cubic spline connection of experimental points; dashed line is evaluation of D/D_{id} at 1073 K by Eq. (4) and data [13] on Gibbs energy of mixing; dot line is evaluation of D/D_{id} at 833 K by Eq. (4) and data [21] on Gibbs energy of mixing.

Stronger analysis of $D(X)$ behavior may be performed using thermodynamic data for liquid lead–magnesium system. It is known that the coefficient of binary diffusion is connected with Gibbs energy of mixing by Darken's relation [15]:

$$(D/D_{id}) = (RT)^{-1}X(1-X)(\partial^2 G/\partial X^2)_{p,T}. \qquad (4)$$

Here R is gas constant, G is Gibbs energy of mixing, D_{id} is interdiffusion coefficient of hypothetic ideal solution with the same components:

$$D_{id} = XD_{Mg} + (1-X)D_{Pb},$$

where D_{Pb}, D_{Mg} are self-diffusion constants for the constituent atoms in the same system. Using dependences $G(X)$ from [13,21], we calculated the concentration dependences of D/D_{id}, see Fig. 5. Unfortunately, the validity of the results of works [13,21] is not very high and the value of $(\partial^2 G/\partial X^2)_{p,T}$ is found to be very sensitive to the procedure of their smoothing and approximation, especially at concentrations close to 0 and 100 at.%. In this case, to construct $G(X)$, cubic spline connection of the tabular data was used. As is seen, the concentration dependences of D/D_{id} based on different primary data have marked discrepancies, which are due to reason mentioned above. However, as a whole, they correlate with our experimental data and, in particular, confirm that D value near stoichiometric composition is more than twice as large as interdiffusion factor of ideal solution.

In conclusion, it should be noted that the CSRO phenomenon in the Mg–Pb liquid alloys may be of practical importance. According to experimental and theoretical studies made in Russian Research Center 'Kurchatov Institute' [22,23], analogous effect in K–Pb melts leads to the fact that the dissolving of stainless steels in this solutions is less than in pure lead. The authors of [22,23] believe that the compatibility of Mg–Pb liquid alloys with stainless steel structural materials also is better than that of Pb and Bi–Pb melts.

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